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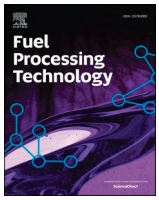

Supercritical water liquefaction of mixed plastic waste 'contaminated' with PET (polyethylene terephthalate): Influence on yields and product composition

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ABSTRACT

Supercritical water liquefaction of mixed plastic waste produces a hydrocarbon oil for the production of fuels or chemicals. However, a major processing challenge is the presence of polyethylene terephthalate (PET), which behaves as a process contaminant by generating solid terephthalic acid (TPA) and oxygenated intermediates that disrupt product quality and cause operational fouling. This study systematically evaluates the influence of PET content (10–50 wt%) and process operating severity on product yields and composition during supercritical water liquefaction of representative mixed plastics (polyethylene, polypropylene, and polystyrene). Increasing PET concentration consistently reduced oil yields and enhanced gas production, particularly CO_2 and CH_4. Oil-phase composition remained dominated by monoaromatic hydrocarbons derived from polystyrene, with additional aromatic species formed via decarboxylation of PET-derived intermediates. Higher PET levels also resulted in substantial accumulation of isophthalic and benzoic acids in the aqueous phase. Increased severity of the process conditions revealed that PET contents above 30 wt% progressively divert carbon from the oil to the aqueous phase, increasing oxygenate formation and imposing greater downstream treatment requirements. These results demonstrate that PET levels above 30 wt% compromise both process operability and product quality, establishing a practical upper limit for PET in supercritical water liquefaction of mixed plastics.

1. Introduction

Plastics have become indispensable to modern life due to their stability, durability, low cost, and lightweight properties, supporting widespread applications across packaging, automotive, textiles, and electronics industries [1]. However, these same properties that make plastics valuable also render them environmentally persistent, with degradation times extending to centuries [2]. Global plastic production and consumption have escalated substantially over recent decades, presenting significant environmental and resource management challenges. Worldwide plastic consumption is estimated at approximately 460 million tonnes (Mt), with projections indicating a rise to over 800 Mt. by 2050. Despite increased awareness, recycling rates remain low, for example, only about 9–10% of plastic waste is recycled globally, while roughly 22% is mismanaged which leads to leakage into terrestrial and marine ecosystems. Mismanaged plastics can fragment into microplastics, contributing to ecological harm, bioaccumulation, and adverse health effects including endocrine disruption and cancer [3,4]. Furthermore, plastic waste management processes contribute significantly to greenhouse gas emissions, releasing an estimated 1.8 gigatonnes of CO_2-equivalents annually from end-of-life activities alone [5].

Mechanical recycling, despite dominating global efforts, is constrained by material degradation, contamination sensitivity, and incompatibility with mixed waste streams [6]. Chemical recycling, particularly the thermochemical processes, pyrolysis, gasification, and hydrothermal liquefaction, offers greater flexibility for processing heterogeneous feedstocks [7,8]. Hydrothermal liquefaction has been promoted as a thermochemical recycling technology capable of processing heterogeneous plastic waste streams, without the need for pre-drying or extensive sorting. Supercritical hydrothermal liquefaction utilizes water at high temperature and pressure (typically above 374 °C and 22.1 MPa), functioning both as a solvent and reactant to facilitate depolymerization and degradation of polymers [9]. The use of supercritical water significantly enhances reaction rates, solubilizes organic intermediates, and reduces the residual char formation without requiring external catalysts [10,11].

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Even though the potential of hydrothermal liquefaction process is widely recognized, tackling the mixed plastic feedstock remains a challenge. Real-world plastic waste streams typically comprise polyolefins such as polyethylene, polypropylene, and also polystyrene, along with significant quantities of polyethylene terephthalate (PET). The distinct chemical structures of these polymers result in fundamentally different degradation behaviours under supercritical water liquefaction conditions. PET, an oxygenated polyester, undergoes hydrolytic depolymerization yielding aromatic acids such as terephthalic acid and benzoic acid. In contrast, polyolefins degrade predominantly via random chain scission, producing hydrocarbon-rich oils and gases [12–14]. Therefore, PET inclusion within polyolefin-rich feedstocks can substantially alter reaction pathways and influence the distribution and quality of final products.

In mixed plastic waste, PET is widely recognized as a problematic "contaminant" due to its fundamentally different chemical structure and decomposition behaviour compared to polyolefins. Recent studies show that increasing PET content in mixed plastic feeds consistently leads to higher yields of oxygenated intermediates and gaseous products, while suppressing hydrocarbon oil formation under thermochemical conditions [15]. This behaviour arises from the hydrolysis of PET into terephthalic acid (TPA), isophthalic acid, and benzoic acid, which are oxygen-rich, highly acidic compounds that significantly influence reaction pathways. [16,17]. The presence of these intermediates not only shifts carbon away from the oil phase but also inhibits secondary cracking, hydrogen transfer, and aromatisation reactions that normally convert polyolefin-derived radicals into stable hydrocarbons [18,19]. A particular problematic issue of the presence of PET in mixed plastics is that hydrothermal liquefaction of PET produces terephthalic acid, a solid product that leads to process operational issues of blockages in downstream pipelines, valves and filters. Therefore, the PET acts as a 'contaminant' in typical mixed municipal solid waste plastic feedstocks, comprised on mainly, polypropylene, polyethylene and polystyrene.

Despite this critical importance, current literature largely overlooks systematic analysis of the role of PET in influencing product yields and compositions during supercritical water liquefaction of mixed plastic wastes. This represents a significant research gap, given that post-consumer plastic waste streams inherently contain variable concentrations of PET. Understanding the impact of PET on the hydrothermal liquefaction process is essential for optimizing product recovery, improving process efficiency, and developing hydrothermal liquefaction systems capable of handling real-world waste inputs. Therefore, this study focuses on quantifying the effects of PET contamination and processing parameters on the phase distribution and chemical composition of products (oil, gas, solid and aqueous phase) during the supercritical hydrothermal liquefaction of mixed plastic waste.

2. Materials and methods

2.1. Plastics

The plastics used for the investigation, polyethylene terephthalate (PET), polystyrene, low-density polyethylene (LDPE), and polypropylene (PP) were selected to represent commonly encountered mixed plastic waste derived from municipal solid waste. PET was obtained as virgin granules (3–5 mm) from Goodfellow Cambridge Ltd. (Huntingdon, UK), while LDPE was purchased in pellet form from Sigma-Aldrich Company Ltd. (UK). Recycled PS and PP were acquired as 2 mm pellets from Regain Polymers Ltd. (Castleford, UK) to reflect the compositional variability typical of municipal solid waste. High-density polyethylene (HDPE), also sourced from Regain Polymers, was used exclusively for thermogravimetric analysis.

The PET concentrations of 10, 30, and 50 wt% were selected to evaluate the mechanistic influence of PET on hydrothermal conversion pathways rather than to mimic the exact composition of municipal waste streams. Real-world mixed plastic waste exhibits wide variability in PET content depending on collection methods, region, and sorting efficiency, and reported PET levels span from <10 wt% in mechanically pre-sorted streams to >50 wt% in packaging-rich or poorly sorted fractions. Therefore, instead of using a single composition that may not be broadly representative, three controlled PET loadings (10, 30, 50 wt%) were chosen to systematically isolate the effect of increasing PET concentration on product distributions, PET–polyolefin interactions, and aqueous-phase aromatic accumulation. The remaining portion of each blend was held constant as a representative mixture of PS and polyolefins to ensure that only the PET fraction varied, allowing clear interpretation of PET-dependent behaviour under supercritical water conditions. This design enables direct comparison of depolymerisation behaviour across a practical range of PET contamination levels that industries encounter when feedstocks are inconsistently sorted.

The elemental (ultimate) composition of each plastic was determined using a Thermos EA-2000 elemental analyzer, providing measurements of C,H,O,N and S content. Proximate analysis, including volatile matter, fixed carbon, and ash content, was conducted using a Shimadzu TGA-50 thermogravimetric analyzer under nitrogen flow at a heating rate of 10 °C min^{-1}. The results are shown in Table 1. PET exhibited the highest oxygen content (35.43 wt%) and fixed carbon (14.85 wt%), consistent with its aromatic, oxygenated polymer structure [20].

2.2. Experimental hydrothermal liquefaction reactor system

Supercritical water liquefaction (SWL) experiments were carried out in a 75 mL Hastelloy-C batch autoclave reactor (Parr Instrument Co., Illinois, USA), rated to a maximum pressure of 55 MPa. The reactor was equipped with a thermowell for internal temperature monitoring using a thermocouple, and heating was provided by an external electrical furnace. Internal pressure was self-generated by heating water in the closed reactor and monitored with a pressure gauge. A gas outlet and sampling valve were included for gas collection. For the experiment with 30 wt% PET at 460 °C and 210 min residence time, the total feedstock mass was reduced to 16 g (3.2 g plastic, 12.8 g water) to avoid exceeding the reactor's safe pressure threshold. All sample masses and water volumes were adjusted proportionally in this case. Deionised water was employed as the reaction medium. The plastic blends included varying proportions of polyethylene terephthalate, polystyrene, low-density polyethylene, and polypropylene. PET content was varied across 10 wt %, 30 wt%, and 50 wt%, with corresponding adjustments to the ratios of the other plastics. Each blend was subjected to different temperature and residence time conditions to assess the influence of feed composition and process severity on product distribution.

For each experiment, the feedstock and water were weighed into the reactor. After sealing, the system was purged with nitrogen gas for approximately 15 min to eliminate residual oxygen. The reactor was then securely bolted and placed inside the furnace. Thermocouples monitored the external and internal temperatures. Heating was continued until the internal pressure reached approximately 22.1 MPa, typically after 25 min, and the system was then held at the desired reaction temperature for the specified residence time. Upon completion, the reactor was rapidly cooled using compressed air and final pressure and temperature recorded.

To investigate the role of PET in supercritical water liquefaction,

Table 1
Ultimate and proximate analyses of individual plastics (wt%, dry basis).

Plastic Types	Ultimate analysis (wt%)					Proximate analysis (wt%)		
	C	H	O	N	S	Volatile	Fixed carbon	Ash
LDPE	83.2	16.0	0.1	0.37	NA	95.93	0.10	5.52
PP	84.0	14.0	1.0	0.02	0.08	95.30	0.03	6.04
PS	86.09	7.9	1.1	0.36	NA	95.43	0.15	5.52
PET	77.0	13.0	5.0	0.20	NA	81.92	14.85	4.51

plastic mixtures were prepared with PET concentrations of 10, 30, and 50 wt%. The 10 wt% PET blend comprised 45% PS, 27.5% LDPE, and 17.5% PP. Two variations were used at 30 wt% PET: one with 35% PS, 17.5% LDPE, and 17.5% PP, and another with 35% PS, 21% LDPE, and 14% PP. The 50 wt% PET mixed plastic blend consisted of 25% PS, 12.5% LDPE, and 12.5% PP. All blends were hand-mixed and stored at ambient conditions prior to use.

Gaseous products were sampled via a gas-tight syringe from the outlet valve for further analysis. The remaining solid and liquid phases were separated by filtration. Any residual oil was recovered by rinsing the reactor chamber with dichloromethane (DCM), and the extract was collected for subsequent characterisation.

2.3. Gas analysis

Gaseous products generated from the hydrothermal liquefaction reactions were collected immediately after venting, using gas-tight syringes. The collected samples were analysed using gas chromatography (GC) to determine both the qualitative and quantitative composition of the product gases. A Varian CP-3380 gas chromatograph was employed for the analysis, equipped with two different detectors: a thermal conductivity detector (TCD) for permanent gases and a flame ionization detector (FID) for hydrocarbon gases. Each sample was injected three times, and the average of the three replicates was used for all subsequent calculations. The identification and quantification of permanent gases, including hydrogen (H_2), oxygen (O_2), nitrogen (N_2), carbon monoxide (CO), and carbon dioxide (CO_2), were carried out using a Varian CP-3380 gas chromatograph fitted with a thermal conductivity detector (TCD). The instrument was equipped with a packed column measuring 2 m in length and 2 mm in internal diameter, filled with a 60–80 mesh molecular sieve. Argon was employed as the carrier gas. The operating conditions were as follows: the column oven was maintained at 40 °C, the injector was held at 120 °C, while the detector block and filament temperatures were set at 120 °C and 160 °C, respectively. For CO_2, a separate column packed (Hysep 80–100 mesh) was used under identical GC-TCD conditions. Calibration of the system was performed using a certified gas mixture containing 1 vol% of each target gas (H_2, O_2, CO, and CO_2), with the remainder comprising nitrogen (96 vol%). The analysis of hydrocarbon gases was conducted using a 2nd Varian CP-3380 GC equipped with a FID. A packed column measuring 2 m in length and 2 mm in internal diameter, filled with Haysep (80–100 mesh), was used for the separation of hydrocarbon species. Nitrogen served as the carrier gas throughout the analysis. The injector and detector were operated at 150 °C and 200 °C, respectively. The GC temperature was initially held at 60 °C for 3 min, then raised to 100 °C at 10 °C per minute. After an isothermal hold of 3 min, the temperature was further increased to 120 °C at 20 °C per minute. Calibration was conducted using a mixture of 1 vol% alkane and alkene standard gases.

Peak areas obtained from the GC chromatograms were used to calculate the volume percentages of each gas species. Response factors (RF) were first established using the known concentration (1 vol%) of each compound in the calibration standard. Moles of individual gas components were calculated from the molar fractions, and final gas yields were expressed as millimoles of gas per gram of plastic feedstock. Each experiment used 4 g of feedstock, except for the experiment containing 30 wt% PET, for which 3.2 g of feedstock was used.

2.4. Oil analysis

Following completion of the reaction and gas removal, dichloromethane (DCM) was then used to extract the oil phase from the solid–liquid mixture and to clean residual material from the reactor walls. The oil phase was analysed using a Varian 430 gas chromatograph equipped with a FID (GC-FID). A Zebron ZB-5MS capillary column (30 m long x 0.25 mm i.d., 0.25 μm thick internal coating) was used for separation of oil components. The oven was programmed to hold at 40 °C for 5 min, then heated to 70 °C at 2 °C per minute, and subsequently to 280 °C at 5 °C per minute. Oil samples were dissolved in DCM to obtain 5000 ppm solutions prior to injection. Identification of compounds was supported by comparison with analytical standards and GC–MS characterisation using a Varian 3800-GC instrument coupled with a Varian Saturn 2200 ITD-Tandem MS (GC–MS/MS) system as reported previously [8]. GC–FID was used for quantification of hydrocarbon products; however, as GC–MS was not available in the present study, minor oxygenated species could not be fully resolved or identified using FID detection alone.

2.5. Aqueous phase analysis

After oil extraction and filtration, the remaining aqueous phase was analysed using high-performance liquid chromatography (HPLC) to detect and quantify water-soluble aromatic acids (e.g. terephthalic acid, isophthalic acid and benzoic acid). Analysis used an Agilent HPLC with an Eclipse Plus C18 column (100 mm long x 4.6 mm i.d., 3.5 μm size). The mobile phase was 0.1% (*v*/v) trifluoroacetic acid/water/methanol. Detection was performed using a UV detector at 250 nm. Samples were filtered through a 0.45 μm membrane prior to injection. A gradient elution method was employed with methanol and trifluoroacetic acid (0.1 wt%) concentrations varying with time. Calibration curves for quantification were prepared using standard solutions of terephthalic acid, isophthalic acid and benzoic acid.

2.6. Solid product analysis

The solid terephthalic acid remaining after aqueous separation was further recovered following the procedure described by Colnik et al. [21]. A sodium hydroxide solution was used to convert the precipitated terephthalic acid into its water-soluble sodium salt. This solution was filtered to remove undissolved solids, and hydrochloric acid was added to the filtrate to reprecipitate terephthalic acid. The resulting solid was washed with distilled water, dried, and weighed. Visual comparison between raw PET feedstock and recovered terephthalic acid was documented to support mass balance and recovery analysis. FTIR spectroscopy was conducted to verify the functional groups and molecular structure of the recovered terephthalic acid. The measurements were performed with a PerkinElmer Spectrum Two FTIR spectrometer in attenuated total reflectance (ATR) mode. Approximately 1–2 mg of finely powdered terephthalic acid was placed directly onto the ATR crystal. A uniform pressure was applied using the integrated pressure arm to ensure adequate contact between the sample and the crystal surface. Infrared spectra were recorded (wavenumber range 4000–400 cm^{-1}, spectral resolution 4 cm^{-1}). Sixteen scans were accumulated for each spectrum to improve the quality of the signal and reduce background noise. The obtained spectra were examined to identify functional group vibrations characteristic of terephthalic acid. A broad absorption in the range of 2500 to 3300 cm^{-1} indicated the presence of hydroxyl stretching vibrations associated with carboxylic acid groups. A strong band observed near 1685 cm^{-1} was attributed to the carbonyl (C=O) stretching vibration. Additional peaks located between 1500 and 1600 cm^{-1} corresponded to aromatic ring C=C stretching, while bands observed between 700 and 900 cm^{-1} were assigned to out-of-plane bending vibrations of aromatic C—H bonds. These spectral features confirmed the aromatic and dicarboxylic nature of the recovered compound, consistent with the structure of terephthalic acid.

2.7. Product yield and mass balance calculations

The yields of individual product fractions were calculated based on the assumption that supercritical water functions not only as a reaction medium but also actively participates as a reactant. We have previously reported [8], that including water in the mass balance improves the representation of overall product yields and provides a more accurate

reflection of the reaction mechanisms occurring during hydrothermal liquefaction. Accordingly, product yields were calculated using the total organic input, consisting of 20 g of feedstock that included both the plastic material and water.

Gas yields were quantified based on the calculated mass of gaseous products (Eq.1, Eq.2). The mass was obtained by determining the number of moles of each gas species, using the ideal gas equation, and multiplying by the respective molar masses. This approach enabled accurate estimation of gas yields from the overall product distribution.

$$Total\ available\ weight\ of\ gases\ (g) = \frac{moles\ of\ gas\ (mol)}{Molecular\ mass\ \left(\frac{g}{mol}\right)} \quad (1)$$

$$Gas\ yields\ (\%) = \frac{Total\ available\ weight\ of\ gas\ (g)}{Total\ organic\ content\ of\ feedstock\ (g)} \times 100 \quad (2)$$

Solid and liquid products yields were also calculated (Eq.3, Eq.4):

$$Solid\ product\ yield\ (\%) = \frac{Total\ weight\ of\ solid(g)}{Total\ organic\ content\ of\ feedstock\ (g)} \times 100 \quad (3)$$

$$Liquid\ product\ yield\ (\%) = \frac{Total\ weight\ of\ liquid\ product(g)}{Total\ organic\ content\ of\ feedstock\ (g)} \times 100 \quad (4)$$

Oil product yields were quantified with Eq. 5.

$$Oil\ product\ yield\ (\%) = \frac{Weight\ of\ oil\ recovered\ (g)}{Weight\ of\ plastic\ of\ feedstock\ (g)} \times 100 \quad (5)$$

The total yield of gas, aqueous, oil, and solid products does not always sum to 100 wt% because a small fraction of the products could not be fully recovered or quantified during sampling and analytical work-up. This unaccounted fraction is primarily attributed to (i) minor experimental losses of volatile compounds during depressurisation, venting, solvent removal, and phase transfer steps, and (ii) partial analytical coverage of light hydrocarbons. Specifically, gas analysis quantified the permanent gases and light hydrocarbons up to C_4 (C_1–C_4), while heavier volatile hydrocarbons ($\geq C_5$) and semi-volatiles were mainly captured in the condensed liquid/oil fraction and analysed separately. A minor proportion of intermediate volatiles (particularly C_5-range compounds) may partition between gas and liquid phases and therefore not be fully accounted for by either method, resulting in a small mass balance gap. Experimental repeatability was determined with replicate experiments undertaken several times at the same conditions and same plastic mixture ratio. The results showed excellent repeatability.

3. Results and discussion

3.1. Hydrothermal liquefaction of plastics: product yield

Table 2 summarizes the product yield distribution from the hydrothermal liquefaction of the plastics under various reaction times (30–120 min) and temperatures (400–460 °C). In the present study, PET loading, temperature, and residence time were varied using a structured experimental matrix in order to evaluate both individual and combined effects. Importantly, several experiments at different PET contents were conducted under identical or comparable operating conditions (e.g., 400–460 °C and 30–120 min), enabling direct comparison of oil yields as a function of PET loading at constant severity. PET-rich feedstocks redistributed carbon toward the solid and aqueous phases, suppressing oil yields. Liquid product yields remained high (>75 wt%) in all cases, reflecting the role of water as a reactant and solvent during the hydrothermal liquefaction process [8,11]. A maximum oil yield of 64.25 wt% was obtained from the 10% PET plus plastic mixture at a temperature of 460 °C for 120 min reaction time. The high polystyrene content (50 wt %) in the 10 wt% PET blend further contributed to oil production, as PS decomposes readily via depolymerisation to styrene monomers followed by aromatisation and cyclisation reactions, yielding monoaromatic hydrocarbons [10].

Table 2
Product yields (gas, liquid, oil, and solid) obtained from supercritical hydrothermal liquefaction of the mixed plastics (LDPE, PP and PS) with different amounts of PET.

Plastic feedstock (%)	Conditions	Gas (wt%)	Aqueous (wt%)	Oil (wt %)	Solid (wt%)
10 wt% PET	430 °C 30 min	3.12	34.35	59.00	1.90
50 wt% PS	400°C 120 min	2.95	32.30	62.25	1.75
20 wt% LDPE	460 °C 120 min	4.29	22.10	64.25	1.55
20 wt% PP	430 °C 210 min	5.13	44.30	49.00	1.20
30 wt% PET	400°C 30 min	2.15	44.25	48.25	5.55
35 wt% PS	460 °C 30 min	3.73	44.65	44.50	4.95
17.5 wt% LDPE	430 °C 120 min	4.44	30.24	58.63	4.95
17.5 wt% PP	400°C 210 min	4.51	44.00	46.25	4.55
30 wt% PET	460 °C 210 min	6.43	42.19	41.25	5.06
35 wt% PS					
21 wt% LDPE					
14 wt% PP					
50 wt% PET	430 °C 30 min	3.64	42.15	44.75	8.95
25 wt% PS	400°C 120 min	3.95	47.45	37.25	10.10
12.5 wt% LDPE	460 °C 120 min	4.35	52.50	24.50	8.80
12.5 wt% PP	430 °C 210 min	4.73	48.40	37.00	9.35

In contrast, the highest solid yield of 10.10 wt% was recorded for the 50 wt% PET feedstock at a temperature of 400 °C for 120 min reaction time. Increasing PET content consistently resulted in higher solid residues. This observation correlates with literature reports indicating that PET predominantly decomposes via hydrolysis to produce TPA [21,22]. The tendency of PET-derived terephthalic acid to form solid residues limits its contribution to oil yields and redirects the carbon balance toward the solid phase, explaining the observed trend. Agostini et al. [13], similarly reported that feedstocks containing high PET content yield predominantly solid terephthalic acid under hydrothermal processing conditions.

Gas yields remained relatively low throughout the experiments, generally ranging between 2 and 6 wt%. Nevertheless, higher reaction temperatures and longer residence times were found to promote gas formation. The highest gas yield of 6.43 wt%, was obtained from the 30 wt% PET-plastic mixture blends processed at 460 °C for 210 min. This trend can be attributed to the progressive cracking of volatile intermediates and thermal decomposition of organics at prolonged reaction times, leading to the formation of light gases such as CO_2, methane, and C_2-C_4 hydrocarbons [23,24].

The aqueous phase constituted a significant but complex product stream across all experimental conditions. As water acted both as solvent and reactant under supercritical conditions, numerous water-soluble degradation products partitioned into the aqueous phase. HPLC analyses confirmed the presence of terephthalic acid, isophthalic acid, and benzoic acid in the aqueous phase following PET-rich experiments. The accumulation of these polar oxygenates not only contributed to the overall liquid yield but also impacted phase separation between aqueous and solid phases depending on their solubility at reaction conditions. The presence of these intermediates in the aqueous phase corroborates

literature findings that PET degradation predominantly generates water-soluble products when processed under hydrothermal conditions [13,21,22].

Overall, the product distribution results show that reaction severity mainly affects gas formation rather than increasing oil production. Higher temperatures and longer residence times promoted secondary cracking and decarboxylation, which increased the formation of carbon dioxide, methane, and light hydrocarbons, but caused only small changes in the oil yield. In contrast, the oil fraction was controlled largely by the feedstock composition, with the amount of PET having the strongest influence on how carbon was divided among the oil, aqueous, and solid phases. These findings indicate that improving the performance of supercritical water liquefaction for oil recovery is achieved primarily by managing the composition of the feedstock, especially by limiting the amount of PET, rather than by increasing reaction severity, which tends to favour gas formation without providing a clear benefit to liquid hydrocarbon production.

3.2. Hydrothermal liquefaction of plastics: gas composition

Fig. 1 shows that the gaseous product yield produced from the plastic feedstocks via supercritical hydrothermal liquefaction experiments produced yields that ranged between 2.15 wt% to 6.43 wt% depending on the PET content, temperature and residence time. These values are

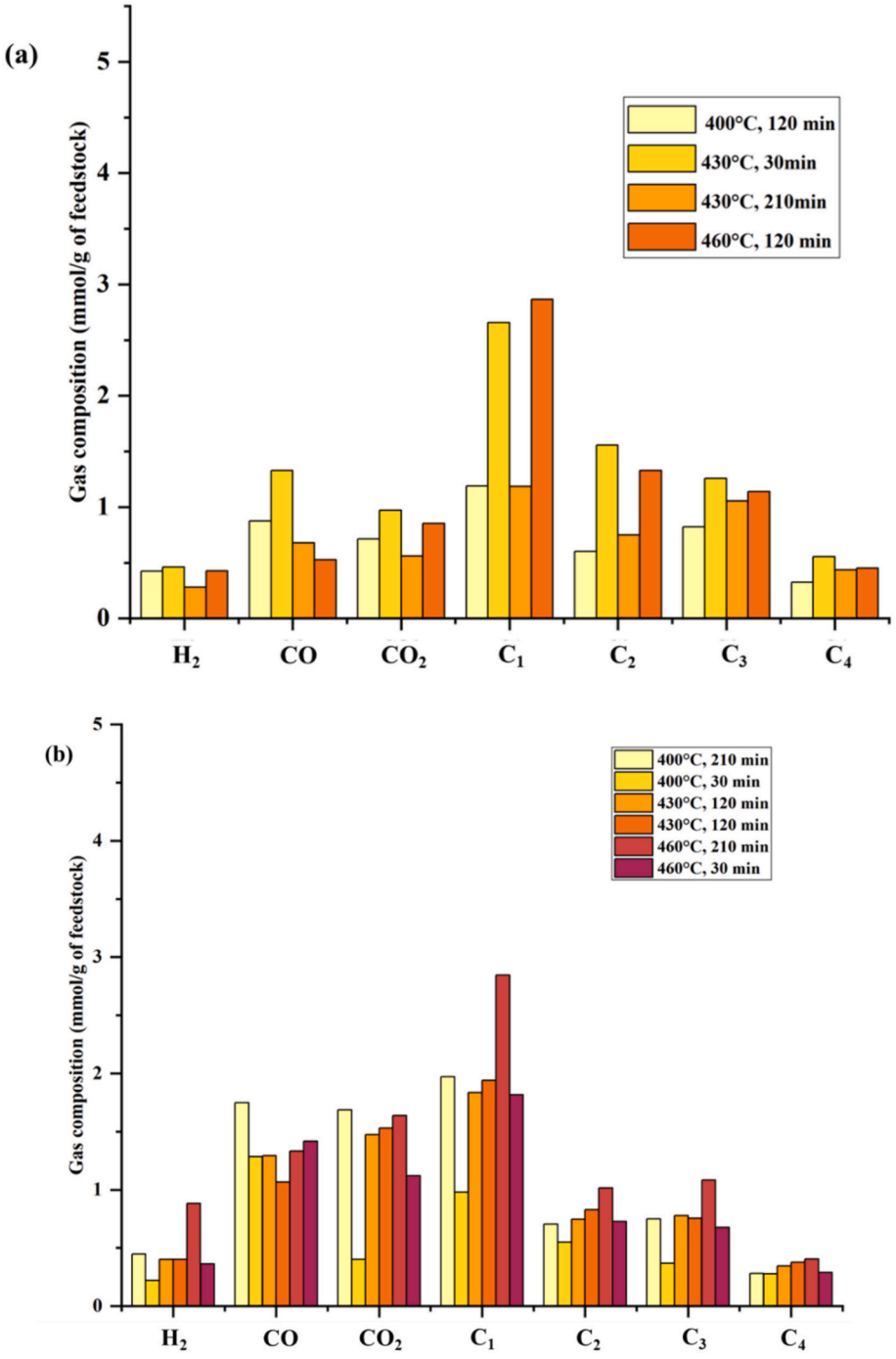


Fig. 1. Composition of gaseous products generated from supercritical hydrothermal liquefaction of plastic mixtures (LDPE, PP and PS) containing (a) 10 wt% PET, (b) 30 wt% PET, and (c) 50 wt% PET.

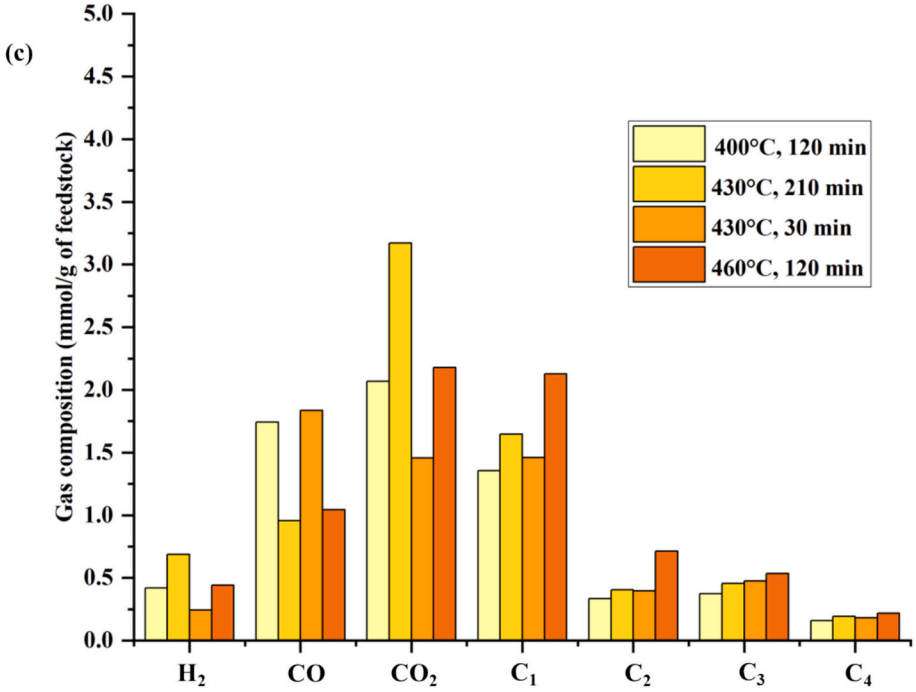


Fig. 1. (*continued*).

consistent with expectations for mixed polymer systems, especially under supercritical conditions. For instance, Mathew et al. [8], reported gas yields between 1.9 and 2.3 wt% for binary and tertiary mixtures of PP, PS, and LDPE at 450 °C for 60 min using the same 75 mL reactor system. The slightly higher gas yields in this study are likely attributable to the use of higher temperatures (up to 460 °C) and extended residence times (up to 210 min), which promote thermal cracking and secondary reactions that favour gaseous formation. Zhao et al. [25], observed gas yields ranging from 9.05 to 12.58 wt% for PE and PP under supercritical water liquefaction at 400 °C for 60 min, using a slightly larger 100 mL reactor. The higher yields reported in their study may result from differences in plastic feedstock composition and their use of a magnetic stirrer, which improves mass transfer and heat distribution, enhancing secondary decomposition reactions [25]. Similarly, Lu et al. [26], found gas yields ranging from 4 to 19 wt% during supercritical water liquefaction of HDPE, noting that higher temperatures (425–475 °C) and residence times (up to 4 h) contributed to increased gas formation. Their use of a smaller reactor (33–37 mL) likely increased heating rates and thermal efficiency, which also contributes to gas production [26].

Gas chromatography analysis of the product gases from the hydrothermal liquefaction of the plastics under supercritical water conditions showed a mixture of hydrogen, carbon monoxide, carbon dioxide, and hydrocarbon gases—methane, ethane/ethene, propane/propene, and butane/butene. Methane consistently dominated the gas fraction in all feedstock combinations, followed by CO_2, CO and C_3 hydrocarbon species. Hydrogen and methane predominantly originate from hydrogen donation and reforming reactions mediated by supercritical water [23]. For instance, Mathew et al. [8] and Seshasayee and Savage [27], identified H_2 and CH_4 as key supercritical water derived gases, attributable to the extreme reaction conditions of supercritical water, facilitating water–gas shift and hydrogenation of radical fragments formed during polymer breakdown [8,27]. The presence of CO and CO_2, typically in smaller quantities, is tied to decarboxylation of oxygenated polymer fragments and formate/formyl intermediates [28].

The experiment with the plastic mixture and 10 wt% PET (Fig. 1(a)) showed a typical gas composition of C1 > C3 > C2 > CO > CO_2 > C4 > H_2. Methane was clearly the dominant gas, supporting literature evidence that supercritical water processing promotes hydrocarbon cracking and hydrogenation reactions. The production of C_3 hydrocarbons, particularly propene and propane, is explained by the high polypropylene content. Polypropylene is composed of propene monomers, and at elevated temperatures, it degrades into C_3 compounds through β-scission and end-chain unzipping mechanisms [21,29]. Short-chain alkanes (C1–C4) are produced through a combination of β-scission and hydrogen abstraction mechanisms, as supported by the reaction pathways described by Liu et al. [30] and Pek and Ghosh [31]. Interestingly, CO_2 and CO levels were moderate despite PET inclusion, suggesting limited decarboxylation at the lower PET content and milder reaction conditions. The similar gas compositions observed at 430 °C for 30 min reaction time and 400 °C for 120 min reaction time suggest that both temperature and time independently influence yield, rather than acting synergistically. This finding supports the conclusions of Vaishnavi et al. [24] who proposed that secondary reactions responsible for gas formation are driven primarily by the energy input (temperature) and the extent of polymer degradation (residence time).

At 30 wt% PET (Fig. 1(b)), gas composition shifted to C1 > CO > CO_2 > C3 > C2 > H_2 > C4. The 460 °C, 210 min reaction time experiment exhibited particularly high CO_2 and CO levels, which can be attributed to decarboxylation of PET-derived terephthalic acid, as reported by Čolnik, et al. [21]. The degradation of PET under supercritical water liquefaction conditions releases carboxyl-rich intermediates, particularly terephthalic acid, which decomposes via decarboxylation to yield CO_2. At higher temperatures, this decomposition continues and produces CO, H_2, and light hydrocarbons. This mechanistic interpretation aligns with the present findings, where PET-rich mixtures consistently yielded more CO_2 and CO compared to those with lower PET content [11,32]. The experiment at 460 °C for 210 min reaction time produced the highest total gas yield in the 30% PET group. This confirms the combined influence of prolonged residence time and high temperature on complete polymer breakdown and secondary gas-forming reactions. The high C_1 levels also suggest intensified methanation activity under severe conditions.

In the experiments using 50 wt% PET (Fig. 1(c)), the gas composition prominently featured CO_2 > C1 > CO > C2 > C3 > H_2 > C4. The significantly higher CO_2 levels confirm the trend that PET-rich feedstocks favour oxidative decomposition and decarboxylation, in

agreement with Čolnik, et al. [21] and Fu et al. [33]. As PET concentration was increased, the proportion of polystyrene and polypropylene decreases, reducing the generation of C3 hydrocarbons. This explains the lower propane and propene levels observed at 50 wt% PET addition to the mixed plastics. Increased CO formation may also stem from partial oxidation of PET intermediates or reforming of volatile organics derived from PET and polystyrene. The overall results suggest that PET not only shifts the gaseous profile toward oxidised products but also suppresses the formation of hydrocarbon-rich gases commonly associated with polyolefins. The water–gas shift and methane reforming reactions (Eq. 1 and 2) impact the gas yields and composition in the supercritical hydrothermal liquefaction reaction.

$$CO + H_2O \rightarrow CO_2 + H_2 \text{ (hydrogen shift reaction)} \quad (6)$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \text{ (Methane reforming)} \quad (7)$$

These reactions explain the presence of CO_2 and H_2 even in experiments where polyolefin plastics dominate. Su et al. [34] also observed this effect in supercritical water systems. Additionally, hydrogen atoms from supercritical water have been shown to contribute to methane formation, explaining why CH_4 appears consistently across all conditions and feedstocks [35].

The composition of the plastic feedstock has a strong influence on the distribution of gases. Polypropylene-rich mixtures favour the formation of C_3 gases, while higher PET content promotes CO_2 and CO through oxidation and decarboxylation. The presence of polyethylene contributes to lighter hydrocarbons like C_2 and C_4, often through β-scission and random chain cleavage reactions [36]. C_2 and C_4 products—ethane, ethene, butene, and butane—were observed in all experiments, albeit at lower levels than C_1 or CO_2. These compounds result from both primary cracking and secondary reactions and are common in thermal degradation of polyolefin plastics [23]. Overall, increasing PET concentration progressively shifted the gaseous product distribution from hydrocarbon-dominant species (CH_4, C_2–C_4) to oxygenated products (CO_2 and CO), reflecting enhanced oxidative and decarboxylation pathways derived from PET decomposition. This transition highlights the strong influence of PET-derived oxygenates on gas-phase chemistry under supercritical water conditions, promoting the evolution of CO_2 through carboxyl group decarboxylation and water–gas-shift reactions, while simultaneously suppressing hydrocarbon gas formation typically associated with polyolefin degradation.

3.3. Hydrothermal liquefaction of plastics: Oil composition

Influence of PET concentration on oil yield: The effect of polyethylene terephthalate (PET) content in the plastic feedstock for the hydrothermal liquefaction of mixed plastics was evaluated using plastic blends containing 10, 30 and 50 wt% PET alongside LDPE, PP and PS. The results demonstrated a clear negative correlation between PET content and oil yield, attributed to the distinct hydrolytic decomposition pathway of PET [11]. For the 10 wt% PET feedstock, plastic mixture experiments, the oil yields ranged between 49.0 and 64.3 wt%, depending on the temperature and reaction time. The highest yield was observed at 460 °C for 120 min reaction time, conditions favoring rapid β-scission, radical generation, and subsequent cyclization of LDPE and PP chains into stable aromatic hydrocarbons. These findings are consistent with earlier studies that demonstrated that polyolefin-based plastics readily convert into high oil yields in supercritical water due to their hydrogen-rich, oxygen-free polymer backbone structure [8,37]. The presence of 50 wt% PS in the 10 wt% PET mixture likely contributed additional aromatic precursors, further promoting oil-phase formation.

Increasing PET content to 30 wt% resulted in a decline in maximum oil yield to 58.6 wt%, achieved at 430 °C for 120 min reaction time. This reduction is attributed to a shift in dominant decomposition mechanisms. PET, unlike polyolefin type plastic, decomposes via hydrolysis rather than radical cracking. The ester linkages of PET are cleaved in supercritical water, producing terephthalic acid and ethylene glycol as primary products. These polar intermediates are preferentially retained in the aqueous phase or precipitate as solids, reducing their contribution to the oil phase. As observed by Čolnik et al. [21], solid exhibits poor solubility in subcritical and near-critical water and readily precipitates under certain conditions. Consequently, oil yield is reduced as more carbon is diverted into non-oil phases. The suppression of oil yield at 30 wt% PET is consistent with trends reported by Seshasayee and Savage [27], who observed oil yields of 30.29–38.21 wt% for equal mass mixtures of PET, PP, PS, and PC in subcritical and near-critical water.

The 50 wt% PET blended with the mixed plastics exhibited the lowest oil yield, ranging from 24.5 to 44.8 wt%. Despite high-severity conditions (460 °C, 120 min), the oil phase remained limited, highlighting the low oil-forming propensity for PET. As reported by Căta et a [38], PET decomposes primarily via hydrolysis under supercritical water, rarely yielding significant amounts of volatile hydrocarbons. Instead, the solid phase becomes enriched in terephthalic acid, while ethylene glycol and other oxygenates partition into the aqueous phase. Interestingly, within each PET content group, there was no consistent correlation between oil yield and reaction time or temperature, suggesting that feedstock composition has a more pronounced influence than reaction severity. This implies that energy-efficient processing conditions (e.g., shorter times or lower temperatures) could achieve comparable yields, providing a potential avenue for optimizing supercritical water liquefaction from a sustainability standpoint.

Chemical composition of the oil phase: The chemical composition of the oil fractions generated from the supercritical water liquefaction of the PET with mixed plastic feedstocks (LDPE, PP, PS) was analysed using gas chromatography with flame ionization detection (GC-FID). In all experiments, the oil phase was predominantly composed of aromatic hydrocarbons, with lesser contributions from saturated and unsaturated aliphatic hydrocarbons and minor amounts of alicyclic compounds. Aromatic hydrocarbons constituted the major product chemical class in the oil derived from the plastics, regardless of the added PET concentration. The primary compounds identified included benzene, toluene, ethylbenzene, xylene isomers, cumene, and naphthalene. The abundance of monoaromatic hydrocarbons is attributed primarily to the presence of polystyrene in the feedstock, which depolymerizes readily under hydrothermal conditions [8]. Polystyrene degrades via random scission to yield styrene monomers, which subsequently undergo secondary cyclization, dehydrogenation, and aromatization reactions to form stable monoaromatic hydrocarbons [10,39]. role of PS in promoting aromatic formation has been highlighted in prior studies investigating both supercritical water and catalytic liquefaction processes. Similar alicyclic formation has been previously reported and attributed to polypropylene derived intermediates under hydrothermal conditions [8,23,40].

The majority of identified oil-phase products were characterized by short retention times (<20 min), indicative of low molecular weight, volatile hydrocarbons. This observation suggests that supercritical water liquefaction of mixed plastics preferentially produces gasoline-range hydrocarbons, consistent with previous studies [25,41,42]. The high aromatic content coupled with the presence of short chain aliphatic compounds underscores the suitability of supercritical water liquefaction for producing low molecular weight liquid fuels from plastic waste.

Increasing PET content in the feedstock influenced the chemical profile of the oil phase. The 10 wt% PET experiments yielded oils with a balanced mixture of monoaromatic hydrocarbons and measurable aliphatic and alicyclic fractions (Fig. 2(a)). Increasing PET content to 30 wt% (Fig. 2(b)) resulted in a relative increase in aromatic hydrocarbons and a reduction in aliphatic content. Oils obtained from 50 wt% PET feedstocks (Fig. 2(c)) exhibited near-complete aromatic dominance, with aliphatic and alicyclic compounds reduced to trace levels. This shift toward increased aromaticity with rising PET content was also evident in the GC-FID analysis, where ethyl benzene and toluene peaks became more prominent at higher PET loadings. The trend is attributed to the

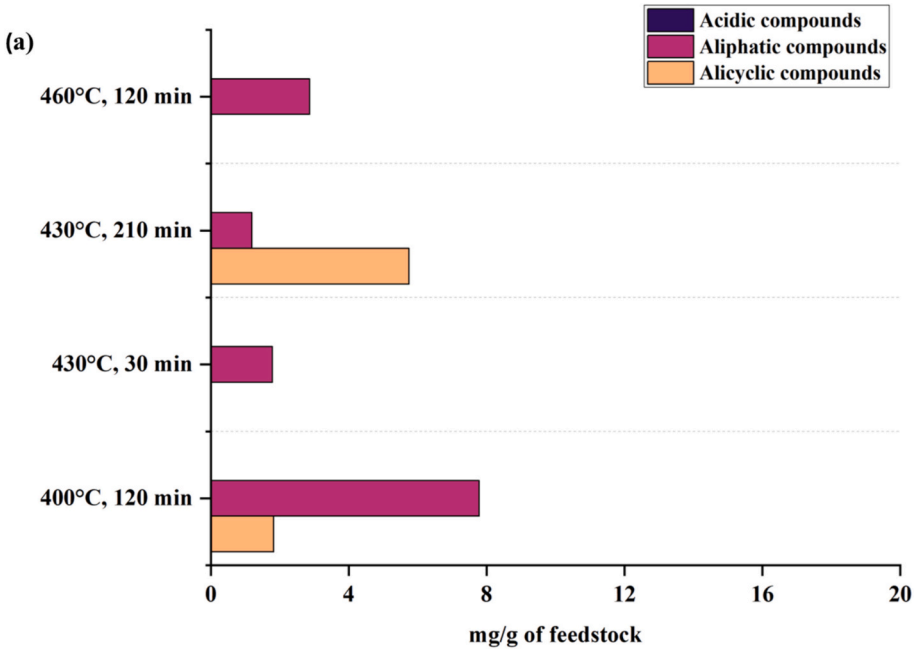


Fig. 2. Distribution of acidic, aliphatic, and alicyclic compounds in oil from the supercritical water liquefaction of plastic mixtures (LDPE, PP and PS) with (a) 10 wt % PET, (b) 30 wt% PET, and (c) 50 wt% PET.

hydrothermal decomposition of PET into aromatic oxygenates, such as benzoic acid and hydroxybenzoic acid, which may subsequently decarboxylate under supercritical water conditions to produce benzene [21,27,43]. This reaction mechanism aligns with earlier findings [16,43], that reported benzene formation from PET-derived benzoic acid during catalytic liquefaction. The observed increase in benzene concentration correlates with PET loading, suggesting that PET contributes indirectly to the aromatic hydrocarbon content of the oil phase.

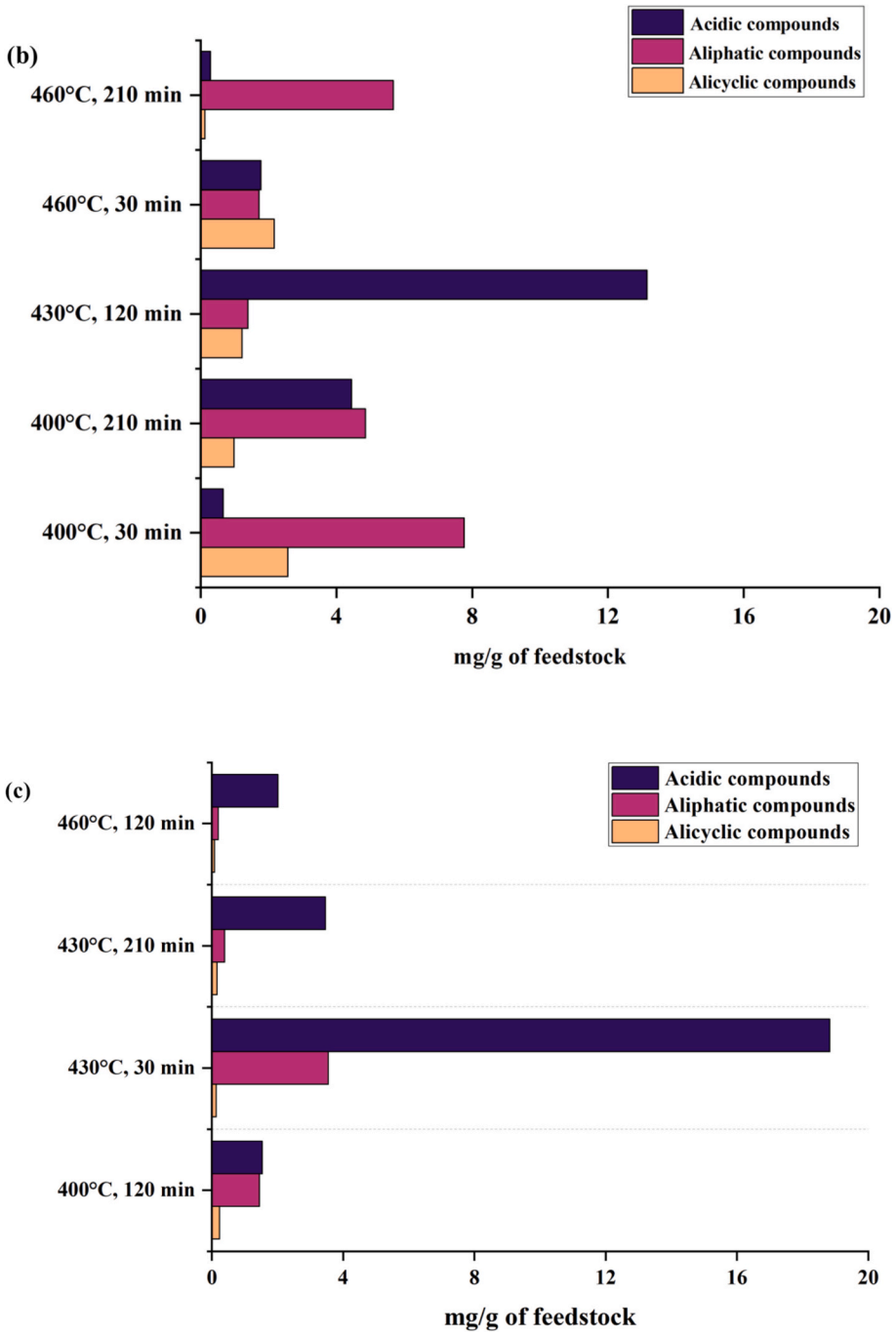
The decarboxylation pathways of PET-derived oxygenates contribute not only to benzene formation but also to the generation of reactive intermediates, such as phenol and hydroxybenzene, via ketonic rearrangements or partial hydrodeoxygenation. These phenolic species are known radical scavengers, which can inhibit the β-scission and hydrogen abstraction steps required for aliphatic chain fragmentation and radical-driven cyclization of LDPE and PP [14,25]. This radical suppression likely explains the diminished aliphatic and alicyclic signals in GC-FID chromatograms at higher PET content, despite comparable or higher reaction conditions. Although thorough detection of polar oxygenate compounds by GC-FID analysis was limited, the evidence of their presence was supported by increased benzene and monoaromatic signals and reduced hydrocarbon chain length distribution. Agostini et al. [13] and Seshasayee and Savage [27], also reported significant formation of monoaromatic acids and esters from PET hydrolysis under hydrothermal conditions, even when *co*-liquefied with polyolefin plastics.

The yield of aromatic compounds from the supercritical water liquefaction of the plastic blends with (a) 10 wt% PET, (b) 30 wt% PET (c) 50% PET under various conditions is shown in Fig. 3. For mixtures containing 10 wt% PET, the highest aromatic yield was observed at 460 °C for 120 min, with a production of approximately 650 mg/g of feedstock (Fig. 3(a)). This was followed closely by the conditions of 400 °C for 120 min and 430 °C for 30 min, yielding 615 mg/g and 590 mg/g, respectively. The lowest yield for this group, 510 mg/g, was recorded at 430 °C for 210 min. At this low PET loading, the presence of PET did not inhibit oil-phase aromatisation; instead, PET-derived intermediates such as ethylene glycol and subsequent formate formed species may enhance hydrogen availability indirectly through reforming and water–gas-shift reactions, which promote the stabilization of aromatic radicals formed from PS and PP decomposition. [44]. In contrast, 30 wt% PET mixtures exhibited a more variable aromatic yield profile (Fig. 3(b)). The highest value, 580 mg/g, was achieved at 430 °C for 120 min, while the lowest yield of 300 mg/g was observed at 460 °C for 30 min. Intermediate values such as 470 mg/g and 410 mg/g were obtained at 400 °C for 30 min and 460 °C for 210 min, respectively. The drop in yield at harsher conditions may be attributed to the excessive formation of oxygenated PET-derived compounds, such as benzoic and terephthalic acids, which could suppress secondary aromatization reactions due to their increased polarity and stability [11]. Aromatic yields were notably lower for 50 wt% PET mixtures under all tested conditions (Fig. 3(c)). The maximum yield of 360 mg/g was recorded both at 400 °C for 120 min and 430 °C for 30 min, whereas the lowest yields of 260 mg/g were observed at 430 °C for 210 min and 460 °C for 120 min. The trend indicates that at higher PET concentrations, the dominance of oxygenated monomers and intermediates from PET depolymerization leads to reduced formation of volatile aromatics, as these intermediates tend to favour solid-phase terephthalic acid formation rather than oil-phase aromatics [21].

The study shows that the PET has substantial influence on both the yield and composition of the oil, and it is necessary to maintain the PET content below 30 wt% in order to maximize oil phase hydrocarbon recovery while limiting the oxygenate content in the oil. This threshold minimizes oxygenate incorporation into the oil phase, preserves aliphatic hydrocarbon production from polyolefin plastics, and enhances overall oil yield and quality. Restricting PET content will significantly reduce downstream upgrading requirements, lower hydrogen consumption in hydrotreating processes, and improve the process energy efficiency. Also, improving the terephthalic acid recovery techniques would also improve the circular economy prospect of this process.

3.4. Hydrothermal liquefaction of plastics: FTIR analysis of the solid residue

To confirm the presence and purity of terephthalic acid in the solid fraction obtained from the supercritical hydrothermal co-liquefaction



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reaction of plastic feedstocks including PET, FTIR spectroscopy was performed and was compared to commercial standard terephthalic acid FTIR spectra reported by Čolnik et al. [21]. As shown in Fig. 4, the experimentally produced terephthalic acid spectrum demonstrates close spectral alignment with the standard, providing strong evidence of successful PET depolymerization and selective recovery of terephthalic acid with high purity, despite the complexity of the feedstock.

The FTIR spectra of the terephthalic acid obtained from the experiments closely match with that of the commercial standard as shown in Fig. 4 demonstrating the successful recovery of high purity terephthalic acid despite the presence of mixed plastic feedstock. A broad absorption band at 3063.29 cm^{-1} corresponds to the O—H stretching vibration of the carboxylic acid group, consistent with the typical range of 2500–3300 cm^{-1} reported in literature [21,45]. A distinct C═O stretching at 1679.29 cm^{-1} matches with the carbonyl group of carboxylic acid around 1683 cm^{-1}. This confirms the structural integrity of the carboxylic acid moiety in the recovered compound.

The most prominent peak at 1679.29 cm^{-1} corresponds to the C═O stretching vibration of the carboxyl group, aligning well with the expected carbonyl absorption near 1683 cm^{-1}. This confirms the structural integrity of the carboxylic acid moiety in the recovered compound. Additional bands at 1575.48 cm^{-1} and 1509.70 cm^{-1} can be assigned to C═C and C—C stretching vibrations within the aromatic ring system, both of which are characteristic features of the terephthalate structure. The peak at 1423.21 cm^{-1} corresponds to aromatic ring deformation or skeletal vibrations, while the absorption at 1283.36 cm^{-1} is indicative of C—O stretching within the carboxylic acid group [38]. Notably, a sharp peak at 880.10 cm^{-1} is attributed to out-of-plane C—H bending in a 1,4-

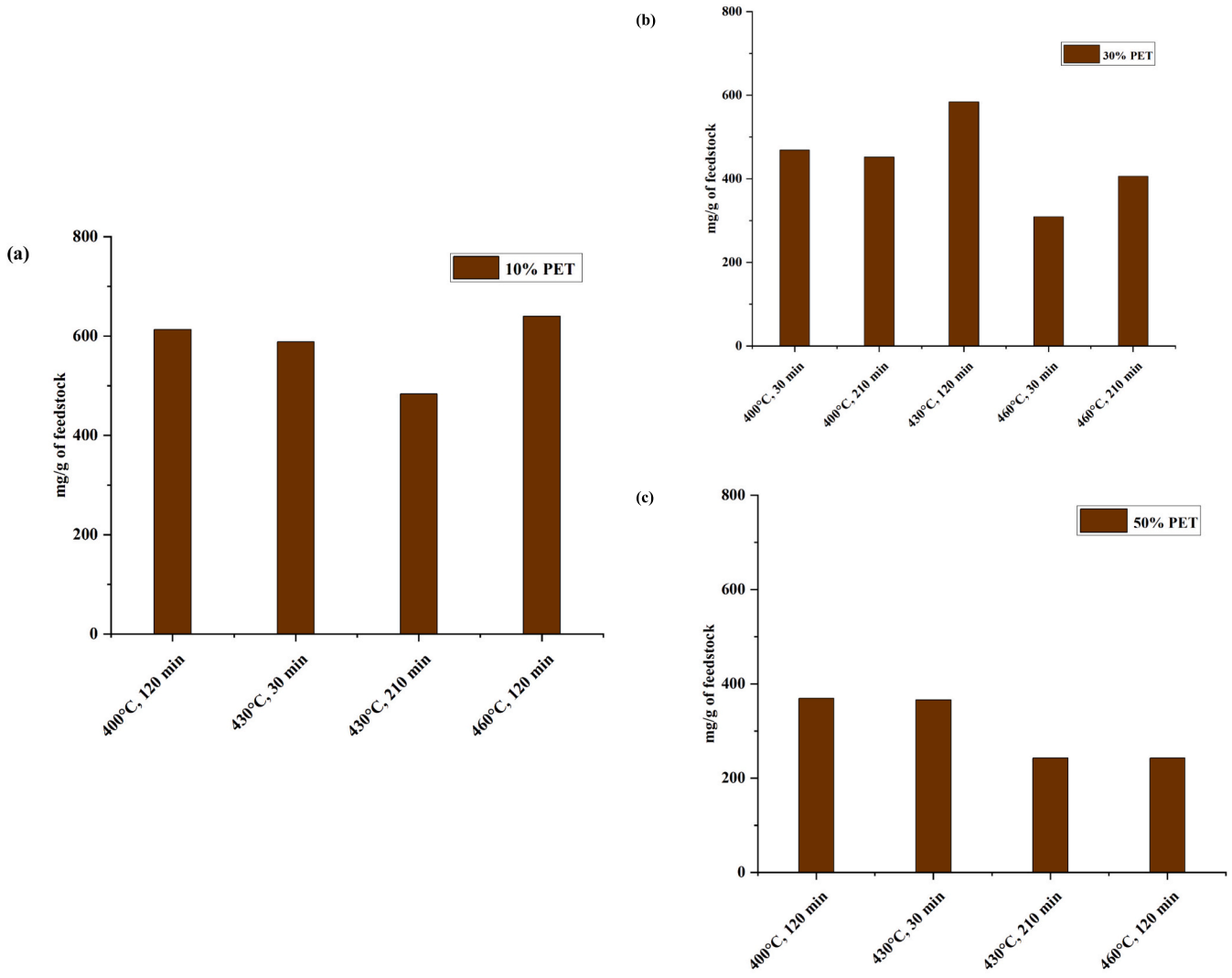


Fig. 3. Yield of aromatic compounds from the supercritical water liquefaction of plastic blends with (a) 10 wt% PET (b) 30 wt% PET (c) 50% PET under various conditions.

disubstituted benzene ring. This region is highly diagnostic of para-substituted aromatic compounds, which matches the substitution pattern of terephthalic acid derived from PET. The presence of this peak strongly reinforces the structural assignment of the recovered product as terephthalic acid. Overall, FTIR analysis confirms the successful depolymerization of PET and selective formation of high-purity terephthalic acid under supercritical water conditions. The close match with the commercial terephthalic acid standard demonstrates the process's efficiency and suitability for plastic waste valorization applications, even in the presence of complex feedstock mixtures.

3.5. Hydrothermal liquefaction of plastics: HPLC analysis of the aqueous phase

HPLC was used to characterise the oxygenated aromatic compounds formed in the aqueous phase during the supercritical hydrothermal liquefaction of plastic blends containing 10 wt% PET, 30 wt% PET, and 50 wt% PET. Fig. 5 shows the aqueous-phase concentrations of terephthalic acid (TPA), isophthalic acid (IPA), and benzoic acid (BA) at the different loadings of PET in the plastic mixture. Although PET depolymerization initially produces terephthalic acid, its low solubility in water under cooling conditions promotes precipitation into the solid phase, explaining its dominance there. In contrast, isophthalic acid is more water-soluble and can form via secondary rearrangement and partial oxidation of PET-derived aromatic intermediates under supercritical conditions. As a result, IPA preferentially remains dissolved in the aqueous phase and accumulates, while TPA is removed from solution through precipitation. Additionally, TPA can undergo partial decarboxylation to benzoic acid or structural isomerisation at elevated temperature, further reducing its aqueous concentration. This combined effect leads to apparent dominance of IPA in the aqueous fraction. A range of different process conditions showing different severities of process conditions, with various sub-critical and supercritical water conditions of temperature and hence different auto-generated pressures and different residence times are also shown. At 10 wt% PET, TPA (Fig. 5 (a)) is the most prominent PET-derived acid in the aqueous phase, exhibiting a distinct peak at moderate severity. This blend produced the highest TPA concentrations of all PET loadings, indicating that at low PET contents more of the hydrolysed monomer remains soluble in the aqueous phase rather than progressing rapidly to secondary reactions. IPA and BA were also present but at lower levels: IPA remained $\leq$5–6 mg mL^{-1} and BA typically ranged from 3 to 10 mg mL^{-1}. TPA decreased to nearly zero at high process severity, suggesting almost complete hydrolysis followed by further decarboxylation and transformation into smaller aromatic species. These findings are consistent with prior studies showing that under supercritical conditions, water-soluble aromatic

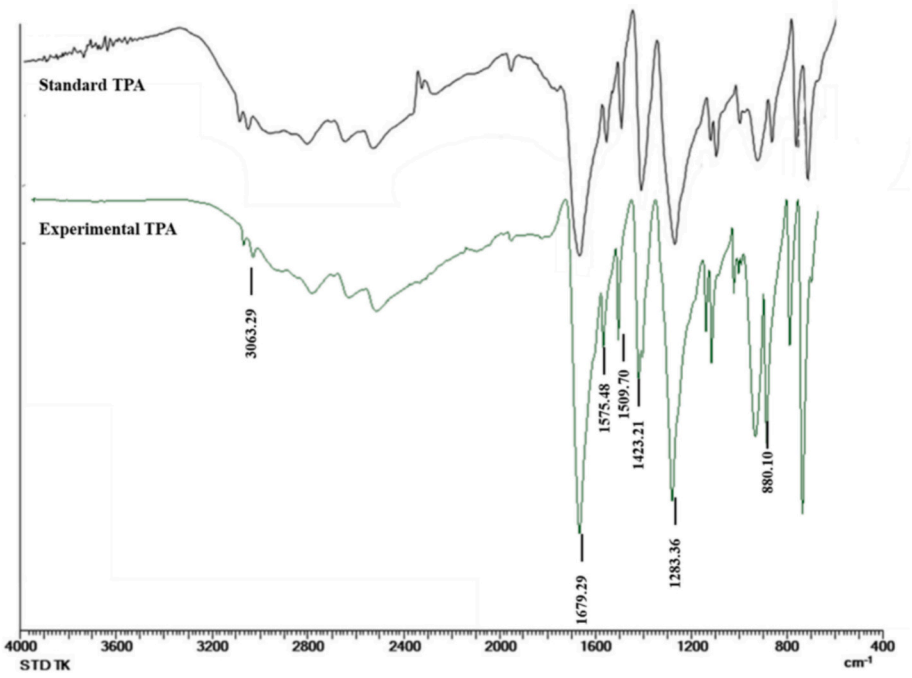


Fig. 4. FTIR spectra of experimentally recovered terephthalic acid (TPA) compared with standard TPA.

intermediates form transiently before undergoing further degradation or partitioning into the oil phase [46].

At 30 wt% PET (Fig. 5(b)), the aqueous-phase composition was dominated by IPA, which displayed a sharp maximum at the lowest severities studied, reaching concentrations >30 mg mL^{-1}. This represents the highest IPA concentration observed among all PET loadings. TPA remained extremely low or undetectable across most severities, confirming rapid conversion of the monomer at this PET content. BA concentrations also remained high (≈ 14–16 mg mL^{-1}) across the severity range, but unlike IPA they did not exhibit a strong severity-driven peak. The maximum concentration of isophthalic acid aligns with similar trends observed by Čolnik et al. [21] who found isophthalic acid concentrations peaking at 30 min of reaction time, followed by a decrease as reaction conditions intensified. They attributed this decline to thermal decomposition of isophthalic acid into smaller degradation products, a behaviour shared with structurally similar terephthalic acid. The relatively high isophthalic acid concentration found in this study, however, significantly exceeds the 0.496 mg mL^{-1} reported by Čolnik et al. [47]. This substantial difference can be attributed to variations in reactor configuration, including the absence of stirring, differing heat-up profiles, and the fixed 1:4 plastic-to-water ratio used here, all of which influence mass transfer, PET hydrolysis kinetics, and aromatic solubilization. Boel et al. [11], reported that the water-to-feedstock ratio can also shift degradation pathways by influencing radical versus ionic mechanisms. A lower water concentration often promotes radical-based reactions, which can suppress aqueous-phase intermediate accumulation. In the present study, a consistent plastic-to-water ratio of 1:4 was maintained, potentially favoring ionic mechanisms conducive to the formation and solubilization of isophthalic acid and benzoic.

In the 50 wt% PET blend (Fig. 5(c)), the aqueous phase was dominated by benzoic acid, which showed consistently high concentrations (10–18 mg mL^{-1}) across the entire process severity severity range. IPA also formed in significant quantities, reaching ~10–18 mg mL^{-1} at moderate severity process conditions. TPA concentrations were low but not negligible; a small TPA peak (~0.21 mg mL^{-1}) appeared at moderate severity process conditions before declining. The resilience of benzoic acid under supercritical conditions is further supported by studies that show that benzoic acid is primarily generated from terephthalic acid via decarboxylation and persists even as other degradation products decline [47]. These observations suggest that benzoic acid acts as a terminal degradation product in PET liquefaction, resisting further decomposition within the studied reaction envelope [21].

Isophthalic acid has emerged in literature as a relatively stable intermediate formed during PET degradation in both subcritical and supercritical water environments. Due to its structural similarity to terephthalic acid but higher solubility in water, isophthalic acid often accumulates in the aqueous phase under moderate reaction conditions before degrading into smaller molecules at elevated temperatures or prolonged residence times [21,48]. The stability and accumulation pattern of isophthalic acid observed in this study agree with this degradation model. Isophthalic acid was consistently detected at moderate temperatures (400–430 °C) and short residence times (30 min), whereas its concentration decreased with longer durations or higher temperatures. This further reinforces the role of isophthalic acid as a transitional degradation product enroute to smaller compounds [21]. A crucial finding was that increasing PET content led to a disproportionate increase in isophthalic acid and benzoic acid concentrations, while terephthalic acid levels remained low or undetectable at higher reaction severities. This shift indicates more complete hydrolysis and subsequent degradation of terephthalic acid, with isophthalic acid and benzoic emerging as stable aqueous intermediates. The persistence of isophthalic acid and benzoic acid even at 50 wt% PET highlights the complex interplay between PET concentration, thermal severity, and aromatic product profiles. Furthermore, these findings suggest that isophthalic acid and benzoic acid accumulation in the aqueous phase might serve as indicators of incomplete conversion or excessive PET input, especially when aiming to maximize oil yield and minimize downstream aqueous-phase processing.

Benzoic acid exhibited a somewhat contrasting trend. While isophthalic acid levels clearly declined with increasing temperature and time, benzoic acid concentrations remained relatively stable across conditions and feed compositions. This stability supports prior observations that benzoic acid is more thermally resilient and may persist even as other intermediates degrade. It has been reported that benzoic acid could further degrade into benzene via CO_2 loss under severe hydrothermal conditions [29,49]. However, this transformation may

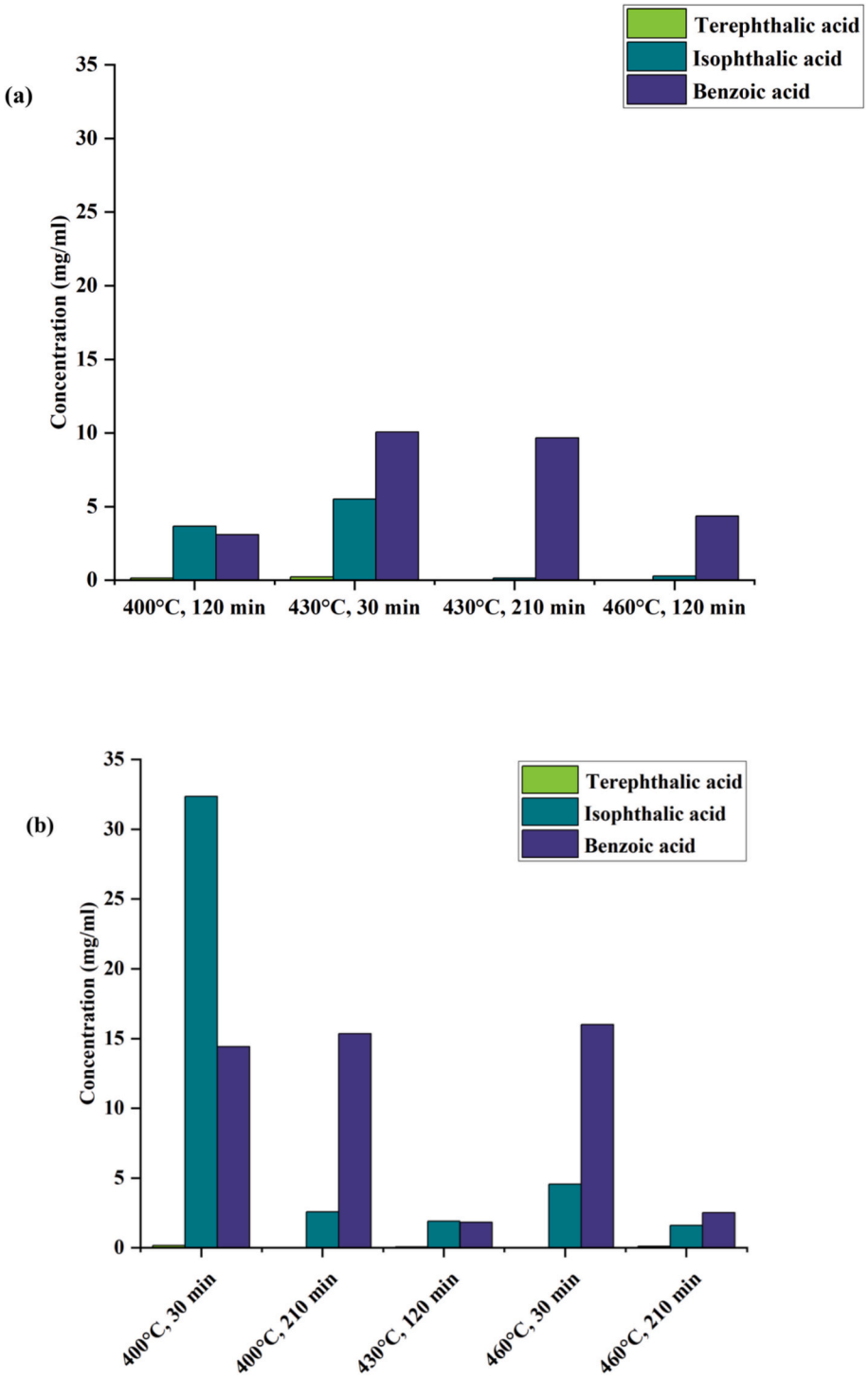
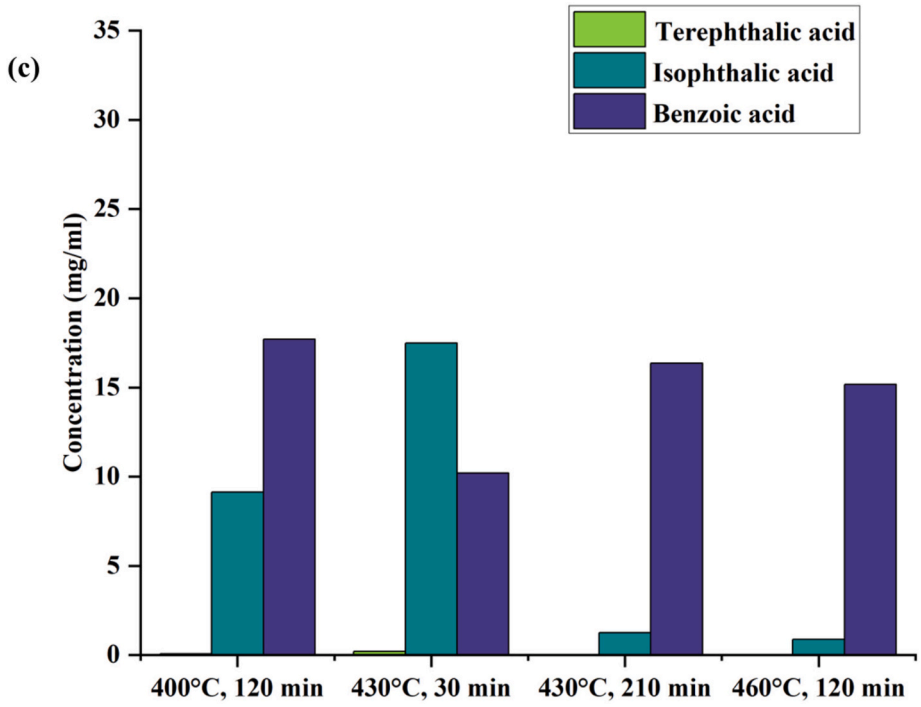


Fig. 5. Concentrations of isophthalic acid, benzoic acid, and terephthalic acid in the aqueous phase from supercritical water liquefaction of plastic blends with (a) 10 wt% PET, (b) 30 wt% PET, and (c) 50 wt% PET.

require more extreme conditions than those explored in the present study. An additional explanation for the stable benzoic acid levels could be its potential partitioning behaviour between phases. Harisankar et al. [50], reported benzoic acid as a major compound in the oil phase extracted using dichloromethane, rather than in the aqueous fraction. This suggests that the distribution of benzoic acid between aqueous and oil phases is solvent-dependent and may also be influenced by the specific feedstock and reaction parameters. Nonetheless, its high concentration in the aqueous residue of the current study affirms its importance as a key product of PET hydrothermal degradation.

Increasing PET concentration correlated with significantly higher isophthalic acid and benzoic acid in the aqueous phase. While 10% PET maintained a balance between oil quality and aqueous load, feedstocks with 30% and 50% PET skewed strongly toward water-soluble aromatic accumulation. Across all PET loadings, isophthalic acid and benzoic acid are the dominant aromatic species detected in the aqueous phase, indicating that PET degradation in supercritical water proceeds mainly through formation of water-soluble aromatic acids rather than



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accumulation of terephthalic acid. For 10 wt% PET, both IPA and BA increase markedly at 430 °C for 30 min, reaching approximately 5.5 mg mL^{-1} and 10 mg mL^{-1}, respectively, suggesting that moderate supercritical conditions favour their formation and accumulation. At 30 wt% PET, IPA shows a pronounced maximum (≈32 mg mL^{-1}) at 400 °C for 30 min, demonstrating that IPA is a key intermediate formed rapidly from PET-derived aromatic structures. As temperature and residence time increase, IPA concentrations decrease sharply, consistent with its secondary decomposition. In contrast, BA remains relatively high across most conditions (≈10–18 mg mL^{-1} for 30 and 50 wt% PET), indicating greater thermal stability and supporting its role as a terminal degradation product. These trends show that PET loading primarily governs the magnitude of IPA and BA formation, while reaction severity controls their persistence in the aqueous phase. These results indicate that PET levels exceeding 30 wt% shift carbon into the aqueous phase as TPA, IPA, and BA, lowering oil yield and increasing the need for aqueous-phase treatment, thereby identifying 30 wt% PET as a practical upper limit for efficient supercritical water processing.

3.6. Hydrothermal liquefaction of plastics: Reaction pathways of PET decomposition

The degradation of PET under supercritical water liquefaction conditions involves a complex interaction of hydrolysis, decarboxylation, and radical-mediated pathways, which collectively influence the distribution of products across the aqueous, gaseous, oil, and solid phases. The distinct decline in oil yield and concurrent increase in aqueous-phase aromatics and gaseous CO_2 observed at higher PET loadings can be attributed to these sequential transformation mechanisms [16].

Fig. 6 shows the suggested reaction mechanism for the supercritical hydrothermal liquefaction of PET [16]. Initially, PET undergoes hydrolytic cleavage of its ester bonds, forming terephthalic acid and ethylene glycol. Terephthalic acid exhibits poor solubility in water at elevated temperatures and readily precipitates, explaining both the significant solid residues in PET-rich mixtures and the detection of terephthalic acid in the aqueous phase under milder conditions. With increasing temperature and residence time, terephthalic acid undergoes decarboxylation, producing benzoic acid and releasing CO_2. This process, known to initiate around 300–350 °C, intensifies at higher temperatures and longer exposure times, as reflected in the substantial benzoic acid concentrations detected during HPLC analysis of the aqueous phase as well as the oil phase in the present study [13,21].

Benzoic acid itself is unstable under supercritical water liquefaction conditions, particularly above 350 °C, and undergoes further decarboxylation to form benzene, alongside additional CO_2. The progressive accumulation of CO_2 with rising PET content and reaction severity observed in the gas analysis aligns with these sequential decarboxylation steps. This conversion pathway also explains the moderate benzene levels detected in the oil phase, especially under high-severity conditions where thermal decarboxylation dominates. Given benzene's thermal resilience, its decomposition is slower; however, under the extreme conditions such as up to 460 °C and 210 min reaction time, as applied in this study, partial degradation via radical-mediated ring opening likely occurred, contributing to the formation of methane, CO, and hydrogen [43].

Ethylene glycol, a primary product of PET hydrolysis under supercritical water conditions, is itself reactive rather than stable in the aqueous phase. Under SCW, ethylene glycol undergoes dehydration and rearrangement to intermediates such as 1,4-dioxane and acetaldehyde (Sepini et al., 2024). Acetaldehyde can oxidise to acetic acid or decompose via decarbonylation and decarboxylation reactions, generating CO, CO_2, and light hydrocarbons such as CH_4 under more severe conditions (Fig. 6). These pathways explain the low accumulation of ethylene glycol in the aqueous phase and support its progressive transformation into smaller oxygenated compounds and permanent gases, consistent with previous hydrothermal studies of glycol systems. The formation of these oxygenates may also promote ionic and water–gas shift type reactions that indirectly enhance secondary cracking and gas formation from other polymer-derived species.

Beyond hydrolysis and decarboxylation, radical reactions play a critical role in PET-derived intermediate conversion within supercritical water. The autoionization of water at supercritical conditions generates reactive hydroxyl and hydrogen radicals, which initiate chain scission, hydrogen abstraction, and β-scission reactions. These processes facilitate

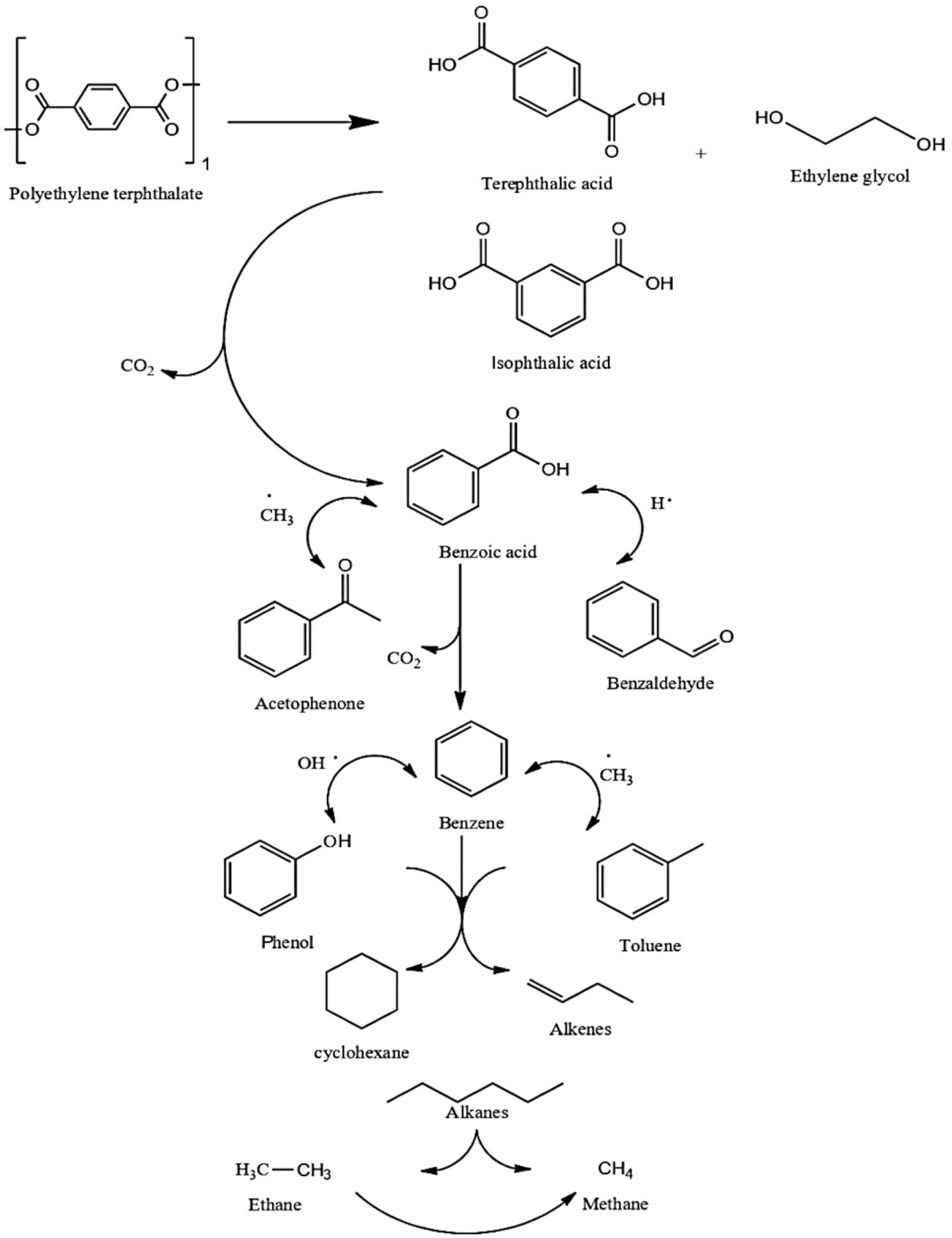

Fig. 6. Schematic representation of the reaction pathway of PET decomposition- Modified from (Čolnik et al., [21]; Sepini et al., [16]).

the breakdown of benzene and other aromatic intermediates, supporting the gradual increase in gaseous products, including methane, at prolonged residence times and elevated temperatures [23,27]. The conversion of PET-derived benzene to methane proceeds via phenyl radical formation, subsequent ring opening, and fragmentation, with radical propagation and termination reactions driving the final conversion to small molecular gases [16,51].

The reaction conditions employed in this study, particularly at 460 °C for 120 to 210 min, favoured these secondary cracking and radical-driven decomposition pathways. This is consistent with the highest methane yields and CO_2 evolution recorded in PET-rich systems. Moreover, the preferential partitioning of terephthalic acid and benzoic acid into the aqueous phase, coupled with the reduced oil yield at higher PET content, underscores the shift of carbon flow from hydrocarbon oil formation toward oxygenated aromatic acids and gases.

Overall, the results of this work have shown the hydrothermal degradation of PET produces a significant amount of solid terephthalic acid and reduces the amount of oil produced, as reported by others [13,15]. We also report that the critical concentration of PET in mixed waste plastic should not exceed 30 wt%, since the terephthalic acid largely transfers from the aqueous phase to the solid phase. It is this formation of solid terephthalic acid precipitate into the liquid that can

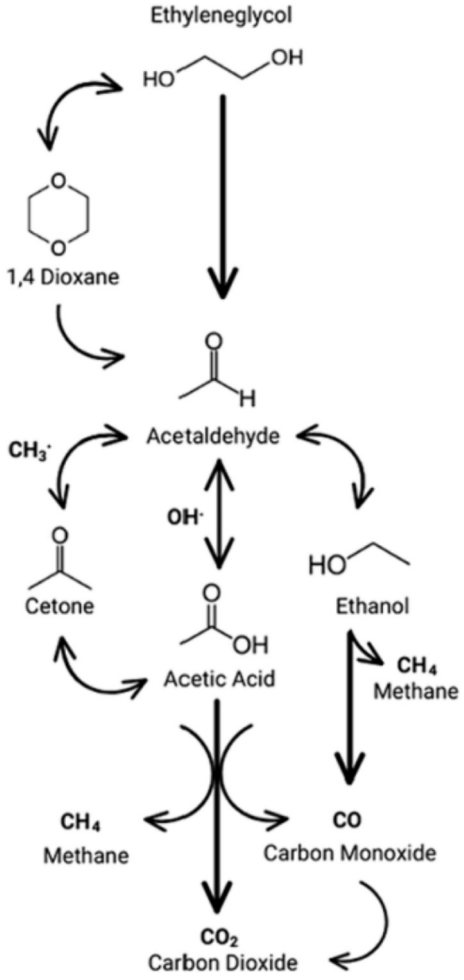

Fig. 6. (*continued*).

lead to fouling and blockage of process pipelines, valves and pumps that can disrupt the hydrothermal liquefaction process for the treatment of mixed plastic waste. However, managing PET decomposition directly within supercritical water liquefaction processes could enable integrated conversion without the need for pre-sorting or selective removal, provided the interactions between PET and polyolefin plastics are sufficiently understood and controlled, with the critical provision of not exceeding 30 wt% of PET in the mixed plastic waste. Further studies could also consider the application of co-solvents with the water or the use of catalysts to prevent terephthalic acid precipitation as solid into the liquid phase of the process. Another option would be the selective sorting of mixed waste plastic to remove the majority of PET. For example, Konarova et al., [15], proposed a pre-treatment route via alkaline depolymerization to recover terephthalic acid from PET prior to pyrolysis of the remaining polyolefins. Although effective, this approach increases process complexity and cost. Future work could consider the option of such pretreatment or sorting versus control of the feedstock and supercritical water process conditions via a techno-economic study.

4. Conclusions

The supercritical hydrothermal liquefaction of mixed plastic waste offers a viable thermochemical route for producing valuable liquid hydrocarbons from heterogeneous polymer streams. This study systematically evaluated the impact of PET content and process parameters on product phase distribution and composition. It was found that PET, due to its distinct hydrolytic decomposition behaviour, diverts carbon from the oil phase into solid and aqueous products, particularly terephthalic acid and related aromatic acids. Oil yields decreased substantially with increasing PET content, while gaseous product formation, especially carbon dioxide and methane were enhanced under higher severity conditions, owing to the intensified decarboxylation and radical-mediated degradation.

Gas and oil composition analyses confirmed that while polystyrene-rich blends favoured monoaromatic hydrocarbon formation, PET contributed additional aromatic content through decarboxylation of intermediate oxygenates. However, increasing PET content shifted a greater fraction of carbon into the aqueous phase as isophthalic and benzoic acids, which not only reduces oil yield but also poses challenges for downstream processing. At PET loadings above 30 wt%, the accumulation of terephthalic acid and related oxygenated aromatics can promote phase separation, resulting in increased equipment fouling, and substantially elevate the burden of aqueous-phase treatment. Therefore, to ensure efficient oil-phase recovery and maintain product quality, PET content in feedstocks should be limited to 30 wt% or less. Furthermore, the selective recovery of terephthalic acid from the solid and aqueous phases offers potential pathways for integrating hydrothermal processing into circular economy models.

CRediT authorship contribution statement

Maria Mathew: Methodology, Investigation, Writing – original draft. **Chloe Quarton:** Investigation. **Mohamad A. Nahil:** Methodology, Investigation. **Paul T. Williams:** Supervision, Funding acquisition, Conceptualization, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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