



Full length article

Hydrothermal liquefaction of post-consumer mixed textile waste for recovery of bio-oil and terephthalic acid

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ARTICLE INFO

Keywords:

Hydrothermal liquefaction
Textile
Terephthalic acid
Bio-oil
Cotton
Polyester

ABSTRACT

Fast fashion trends lead to significant quantities of textiles produced and discarded, its waste is incinerated or landfilled due to a lack of recycling technologies for mixed textiles. Recycling of mixed textiles by hydrothermal liquefaction (HTL) is a novel approach to produce bio-oil and monomers, as no prior sorting or color removal is required. Herein, post-consumer polyester (polyethylene terephthalate (PET)) and cotton garments were subjected to HTL to produce bio-oil and terephthalic acid (TPA). The effects of blending ratio of PET and cotton, temperature and alkali catalyst on the product distributions are investigated. A maximum bio-oil yield of 26% was attained at 325 °C for a 95% Cotton/ 5% PET mix under alkali conditions. TPA yields ranged from 48 to 91%, where 50/50% PET/cotton resulted in a higher TPA yield than 95/5% PET/cotton textile wastes. The results obtained contribute to the development of sustainable recycling processes of mixed textiles.

1. Introduction

The fashion industry has devastating impacts on the environment, being the second most wasteful and polluting industry after the oil industry (Dhir, 2021). The manufacturing procedure of fibers is associated with a large consumption of petrochemical and natural resources, comprising cumbersome processes, such as spinning, bleaching, dyeing, etc., that generate a vast amount of pollutants and hazardous chemicals (Provin et al., 2021). The situation is worsened by current ‘cheap and fast fashion’ trends that greatly increase quantities of textiles and reduce the life span of garments. In Europe consumers reportedly discard about 11 kg of textiles per person annually (Saskia Manshoven et al., 2019) and only 1% of textile waste, mainly white colored, is recycled into new fibers (Mu and Yang, 2022), the rest is incinerated or landfilled (~87%).

Polyester, the common term for polyethylene terephthalate (PET) fibers, and cotton are the most widely used man-made and natural fibers, with production volumes of 55 and 26 million tons, respectively (Mäkelä et al., 2020). The production of polyester is a carbon-intensive process, consuming in excess of 70 million barrels of crude oil per year (Saskia Manshoven et al., 2019). PET is commercially synthesized from ethylene glycol (EG) and terephthalic acid (TPA). EG can be produced from renewable resources on a large scale via catalytic transformations, while TPA is synthesized from *p*-xylene which is predominately obtained

from the catalytic reforming of crude oil resources (Volanti et al., 2019).

Several physical and chemical recycling methods are available for valorization of PET wastes. Among them, chemical recycling via acid and base hydrolysis, methanolysis, glycolysis, etc., are the most suitable approaches according to the principles of ‘sustainable development’, as they lead to the formation of the original monomer (Achilias and Karayannidis, 2004) that can be used for the synthesis of new PET. However, only color-free PET bottles can be recycled at larger scale (Mu and Yang, 2022), while recycling technologies for PET fibers have not yet been developed due to the presence of dyes (Fei et al., 2020). In addition, chemical recycling methods require pure streams, whereas post-consumer textiles are a blend of synthetic and natural fibers. Therefore, the development of new recycling strategies for blended textile wastes is of great interest to minimize waste generation and recover monomers and other chemicals.

Hydrothermal liquefaction, a thermochemical depolymerization process commonly used for liquid fuel production from synthetic and biopolymers, could be used as an alternative approach to treat textile waste in order to produce bio-oil, a precursor for biofuels or chemicals, and value-added monomeric products. Mixed textile wastes can be treated by HTL without any prior sorting, separation and removal steps from dyes, pigments, coatings, etc. and this a key advantage compared to other chemical recycling methods.

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Received 3 May 2022; Received in revised form 25 May 2022; Accepted 27 June 2022

Available online 8 July 2022

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It has been previously reported that PET bottles can be depolymerized quantitatively into their monomers, TPA and EG in sub- and supercritical water (Čolnik et al., 2021; Goto et al., 2006; Seshasayee and Savage, 2020; Souza dos Passos et al., 2020). It has also been shown that co-liquefaction of synthetic polymers with lignocellulosic biomass or biomolecules can lower the decomposition temperature of polymers and act synergistically on the bio-oil production (Hongthong et al., 2020; Seshasayee and Savage, 2021). Owing to its high content of cellulose, the cotton part in the mixed textile can be converted simultaneously into the bio-oil during HTL (do Couto Fraga et al., 2021; Fang et al., 2004; Yin and Tan, 2012) and affect positively on the depolymerization of PET. It has recently been reported that about 26% of bio-oil can be produced under hydrothermal conditions at 320 °C from cotton textile waste (Zhao et al., 2022). To the best of our knowledge, no previous studies have been conducted on HTL of post-consumer mixed textile wastes containing PET and cotton.

Motivated by sustainability of the textile industry and the gap in the literature, we investigate the possibility to valorize post-consumer mixed textiles by HTL to produce bio-oil and TPA at temperatures of 300, 325 and 350 °C, as the higher bio-oil yields were obtained from biomass in the range of these temperatures (Seshasayee and Savage, 2021)

Liquefaction experiments were performed under neutral and alkali

$$HHV (MJ / kg) = 0.3491 C + 1.1783 H + 0.1005 S - 0.1034 O - 0.0151 N - 0.0211 A \quad (3)$$

conditions, as alkali catalyst have previously been reported to lead to higher quality bio-oil from cellulose (Pedersen and Rosendahl, 2015) and facilitate the cleavage of ester bonds during conventional hydrolysis of PET materials (Dutt and Soni, 2013). We also examine the composition of bio-oil, aqueous and solid fractions in order to elucidate the degradation pathway of mixed textile waste under HTL conditions and estimate the purity and recovery yield of TPA. The results obtained from the present study provide valuable insights for the sustainable design, production and recycling of post-consumer textile waste.

2. Experimental part

2.1. Materials

Post-consumer textile waste with three compositions (100% PET, 100% cotton, 51% PET/ 49% cotton) were supplied by Elis Danmark A/S. After manual removal of metallic zippers, buttons etc. the garments were shredded into small pieces and blended to obtain 95% PET/ 5% cotton, 50% PET/ 50% cotton, 5% PET/ 95% cotton mixed textiles.

Dichloromethane (DCM) (VWR, ≥98%), potassium hydroxide (KOH) (Sigma Aldrich, ≥98%) were used as received.

2.2. HTL experiments

HTL experiments were conducted in a 20 ml custom-built batch reactor with Swagelok fittings at temperatures of 300, 325 and 350 °C for 20 min. All experiments have been performed in duplicate. The procedure was described elsewhere (Matayeva et al., 2022). In a typical experiment, 1.0 g of blended feedstock and 8.0 g of water or alkaline solution (12.5 g/L KOH) were mixed and loaded into the reactor. The reactors were placed in a preheated fluidized sand bath for 20 min where heating occurred with the heating rate of 82 °C/min. After the reaction time, the reactors were quenched in water and weighed. After the gas was vented at room temperature, the reactors were re-weighed to determine the mass of gas formed. The reaction solution was transferred into a 15 mL polypropylene centrifuge tube, which was subjected to

centrifugation for 5 min at 5000 rpm to separate the aqueous and bio-oil/solid fractions. The aqueous phase was stored at 5 °C until further analysis. The precipitated solids and the reactor's contents were washed with DCM to recover the bio-oil. After separation by vacuum filtration, the solids were dried at 105 °C overnight, while DCM was evaporated under nitrogen. The solid residues and bio-oil were weighed and stored at room temperature until further analysis. The yields of bio-oil, gas, solid fractions were calculated according to Eq. (1), while the yield of aqueous phase was determined by difference (2).

$$Yield_{fraction} = \frac{mass_{fraction}}{mass_{feedstock}} \cdot 100\% \quad (1)$$

$$Yield_{aqueous} = 100 - Y_{bio-oil} - Y_{solids} - Y_{gas} \quad (2)$$

2.3. Characterization of HTL products

Ash content of feedstocks was determined by heating the samples at 550 °C in a muffle furnace (Nabertherm B180) for 3 h.

The elemental composition of feedstocks, solid residues and bio-oil products was determined by a Elementar vario MACRO cube analyzer (Langensfeld, Germany). The higher heating values (HHV) of the samples were calculated by the formula proposed by Channiwalwa S.A. and Parikh P.P. (Channiwalwa and Parikh, 2002) (Eq.3).

Carbon Recovery (CR) and Energy recover (ER) were calculated according to the following formulas (4) and (5), respectively:

$$CR (\%) = \frac{C_{bio-oil} \times Yield_{bio-oil}}{C_{feedstock}} \times 100\% \quad (4)$$

$$ER (\%) = \frac{HHV_{bio-oil} \times Yield_{bio-oil}}{HHV_{feedstock}} \times 100\% \quad (5)$$

Cellulose content in the cotton was determined according to the NREL LAP 002 method (Sluiter, 2008) Thermogravimetric analysis (TGA) coupled with DSC was employed to determine the purity of TPA in the solid residues using a Mettler Toledo TGA-3+. The samples were heated from 30 °C to 400 °C at 10 °C/min in a N₂ atmosphere. Sublimation phenomena were assessed in terms of their onset and peak temperatures. The TPA standard (98%,Sigma-Aldrich) was run in triplicate and the average heat enthalpy ΔH TPA standard (634.67 ± 4.3 J/g) was used to determine the mass of TPA in the HTL solid fractions (6) taking into account the mass of solids:

$$m_{TPA \text{ exp.}} = m_{HTL \text{ solid}} \times \frac{\Delta H_{HTL \text{ solid}}}{\Delta H_{standard}} \quad (6)$$

The TPA yield was calculated by Eq. (7) and (8) where 0.86 is the TPA mole fraction in PET:

$$m_{TPA \text{ theoretical}} = m_{PET} \times 0.86 \quad (7)$$

$$Yield_{TPA} (\%) = \frac{m_{TPA \text{ exp.}}}{m_{TPA \text{ theoretical}}} \times 100\% \quad (8)$$

FTIR analysis was performed using a Bruker Alpha FTIR Platinum diamond ATR. The spectra were recorded from 4000 to 400 cm⁻¹ with 20 scans. The resolution was 2 cm⁻¹, and the interval scanning was 0.5 cm⁻¹. Total organic carbon (TOC) analysis was performed using a scalar FORMACS^{HT-I} TOC/TN analyzer.

Gas chromatography-mass spectrometry (GC-MS) was employed for

the identification of the main components of the bio-oil and aqueous fractions. For the analysis of the aqueous phase, the samples were derivatized with methyl chloroformate. The derivatization procedure was described elsewhere (Biller et al., 2016). For the analysis of bio-oil samples, about 20 µg/L of 4-bromotoluene as an internal standard was added to the oil samples in DCM with the concentration 10 mg/mL.

The bio-oil and aqueous fractions were analyzed using an Agilent 7890 gas chromatograph coupled to a MS Agilent 5977A. GC-MS data analysis was performed using Agilent Masshunter Quantitative analysis software and only components with relative area higher than 5% and Match factor higher than 70 were considered.

3. Results and discussion

3.1. Product yields from HTL of mixed textiles

Product yields from the HTL of mixed textile waste with three different compositions according to the HTL temperature are depicted in Fig.1. Generally, a higher content of cotton in the mixed waste resulted in a higher bio-oil yield. The bio-oil yields from the 95% Cotton/5% PET blending ratio were in the range of 7–14% at neutral conditions. With temperature, the gas and oil yields increased gradually, while the solid yield decreased accordingly.

In previous studies (de Caprariis et al., 2021; do Couto Fraga et al., 2021; Feng et al., 2019; Yin and Tan, 2012) higher bio-oil yields between 14 and 28% were obtained from cellulose at 300 °C depending on the residence time, while further increase in temperature lowered the bio-oil yield (Feng et al., 2019; Yin and Tan, 2012).

In the present study, the post-consumer cotton fiber was found to contain only 60 wt.% cellulose that consists of unmodified glucose monomers. The low yield of glucose monomers after the acid hydrolysis of post-consumer garments can be explained by long-term wearing and laundering processes that can affect the degradation of cellulose and reduce its polymerization degree (Haslinger et al., 2019). For instance, after 50 cycles of industrial laundering man-made cellulosic textiles were shown to have a 20% lower degree of polymerization (Wedin et al., 2019), while a significantly higher reduction of intrinsic viscosity and molecular weight by 80–90% was found for natural cotton (Palme et al.,

2014). In general, laundering causes a reduction of molecular mass of cotton garments, while the crystallinity of cellulose does not change significantly (Palme et al., 2014), which is consistent with the results of the present study. FTIR spectra of post-consumer cotton-rich and poly-cotton samples (Fig.S1) showed only one characteristic peak for cellulose I_β (~3270 cm⁻¹) and no other peaks related to cellulose II and III were identified (Kafle et al., 2014), thus implying that cellulose in the cotton garments is still in the crystalline form.

Under subcritical conditions the crystallinity of cellulose plays a significant role, as more crystalline cellulose is less susceptible to attacks of water molecules and as a result, leads to lower liquefaction rates (Möller et al., 2013). Hence, the lower bio-oil yields obtained at 300 °C can be attributed to the lower cellulose content and its higher crystallinity. Therefore, for the enhanced hydrolysis of cotton fabrics higher temperature is required at neutral conditions.

For the 95% Cotton/ 5% PET and 50% Cotton/ 50% PET mixtures, the alkali environment greatly improved the bio-oil yields and reduced the amount of solids, which is in agreement with previous studies on the HTL of cellulose (Déniel et al., 2017; Fang et al., 2004). The maximum bio-oil yield of 26% was attained for the 95% Cotton/ 5% PET at 325 °C under alkaline conditions.

For all blending ratios, the solid yields correlated strongly with the PET content in the mixed textile wastes. When 95% PET/ 5% cotton fabrics were subjected to HTL, the maximum solid yields (61–64 wt.%) were obtained and oil yields were found to be low (<3 wt.%), which can be explained by the immiscibility of TPA in water and in the solvent used for the oil extraction process. Similarly, Seshasayee and Savage (2020) (Seshasayee and Savage, 2020) reported that no oil was formed from the HTL of PET pellets at 350 °C. Even at supercritical conditions (>400 °C) PET generated mainly solids and a maximum bio-oil yield of 16% was attained at 450 °C (Seshasayee and Savage, 2020).

With the addition of alkali catalyst, the solid yield decreased by 10 wt.% compared to those from non-catalytic HTL and consequently, aqueous phase yield increased due to the formation of water soluble dipotassium terephthalate salts.

Based on the results it can be concluded that HTL of PET rich textiles is not suitable for the production of bio-oil under subcritical conditions; however, recovering TPA in the solid fraction makes the HTL process attractive for blended textile wastes, providing value-added product in addition to the bio-oil.

3.2. Carbon balance

A carbon balance has been performed in order to confirm the accuracy of the results obtained on the HTL product yields. Fig. S2 illustrates the carbon recovery (CR) in the HTL fractions obtained from the HTL of mixed textiles at the same operating conditions as above. The carbon recovery in the gas phase was calculated theoretically by assuming that the gas primarily consists of CO₂.

It is important to note that the total carbon recovery was in the range 72–95 wt.% depending on the blending ratio and reaction conditions. However, the changes of carbon recoveries in the gas, bio-oil and solid fractions with temperature were consistent with the distribution of the HTL product yields, while the CR in the aqueous phase varied widely. This implies that the mass and carbon yields of bio-oil, solid phases have been determined accurately, while the carbon recoveries in the aqueous phase were underestimated. In fact, the formation of newly precipitated solid particles were observed during the storage of the aqueous phase. It is known that the liquid phase from the thermochemical conversion of cellulosic materials is not stable and form post-reaction solids, especially under acidic conditions (Chuntanapum and Matsumura, 2009). Therefore, the carbon loss is believed to be due to the formation of these post-reaction solids and the nature of the solid fraction is further elaborated in the Section 3.4.2.

It is confirmed that for the HTL of 95% PET/ 5% cotton mixed textile waste, substantial amounts of carbon are found in the solid fraction

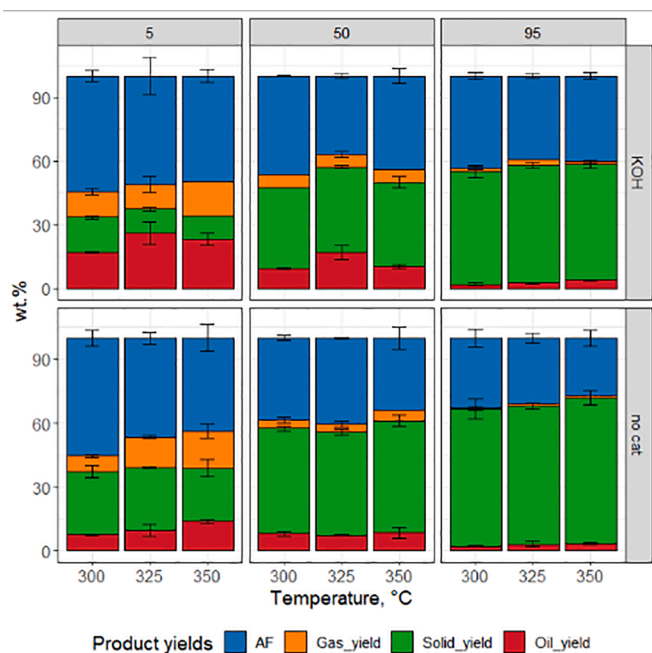


Fig 1. Product yields from HTL of mixed textile waste at 300, 325, 350 °C under neutral and alkali conditions (5 = 5% PET/ 95% cotton, 50 = 50% PET/ 50% cotton, 95 = 95% PET/ 5% cotton).

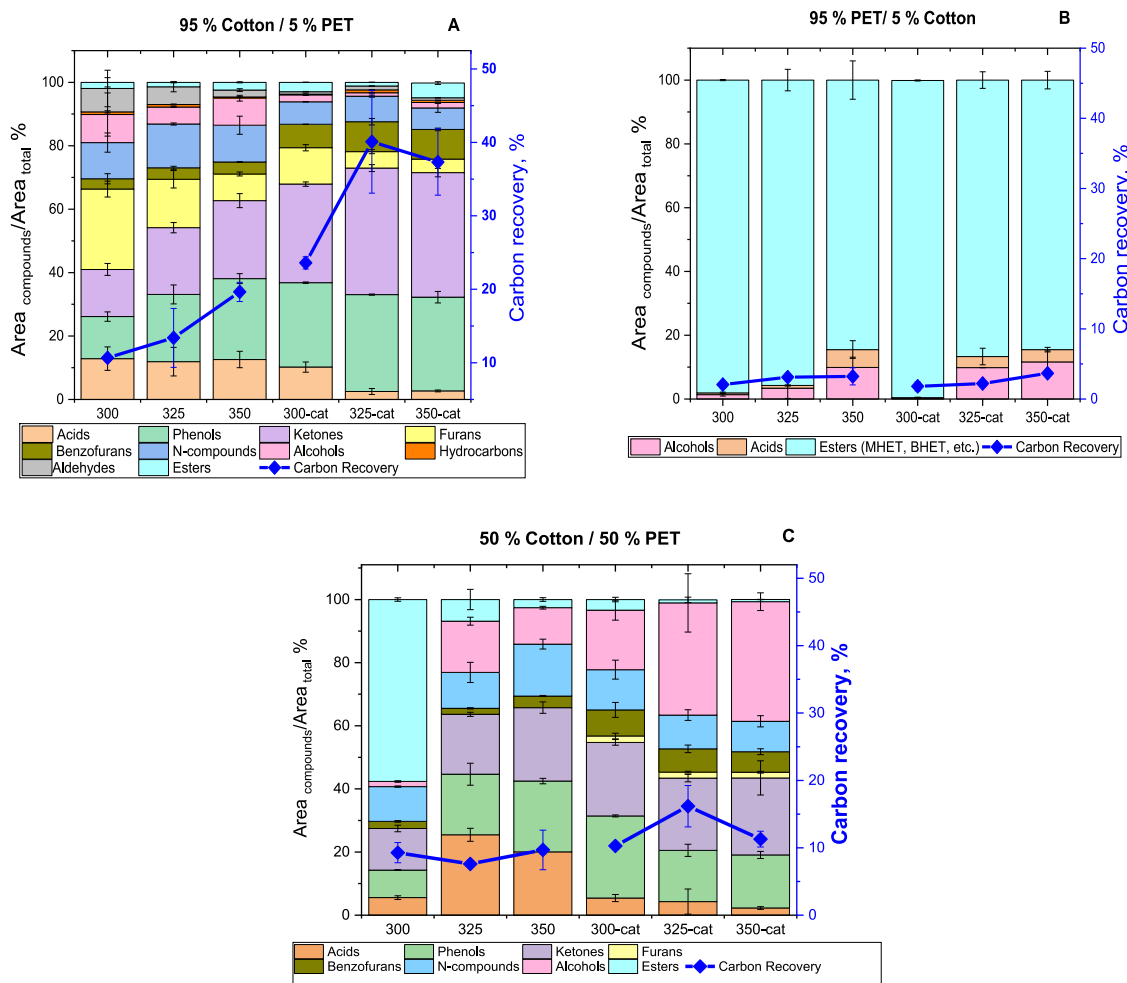


Fig 2. Composition of bio-oils produced from HTL of mixed textile waste at three temperatures (300, 325, 350 °C) under neutral and alkali conditions: A) 95% Cotton / 5% PET, B) 95% PET/ 5% Cotton, C) 50% Cotton/ 50% PET.

(61–64 wt.%) depending on the operating temperature. The bio-oil contained negligible carbon (<3.6 wt.%), while 13–14 wt.% was transferred into the aqueous phase. The addition of KOH catalyst resulted in the partitioning of around 10 wt.% of carbon from the solid fraction into the aqueous phase due to the formation of water-soluble dipotassium terephthalate salt.

For cotton-rich mixed textile HTL most carbon (36–42 wt.%) was also recovered in the solid fraction. The carbon recovery in the bio-oil phase increased from 10 wt.% to 19 wt.% with an increase in temperature from 300 to 350 °C. The organic carbon content of the aqueous phase was in the range of 14–16 wt.% and did not change significantly with temperature. Adding alkali catalyst significantly increased the carbon recovery in the bio-oil to 40 wt.% at 325 °C, while the CR in the solid fraction decreased almost three times. The positive effect of KOH on the CR to the bio-oil is associated with the stabilization of the bio-oil components and prevention of the formation of char-like materials.

In the case of 50% PET/ 50% cotton, most carbon (53–62 wt.%) was recovered in the solid fraction and bio-oil contained about 7.5–9 wt.% of the carbon. The addition of catalyst decreased the CR in the solid fraction to 40–42 wt.%, whereas more carbon was distributed into the bio-oil and aqueous fractions.

3.3. Elemental composition of bio-oil

Bio-oil cannot be used directly as transport fuels due to high contents of nitrogen and oxygen and therefore, has to be upgraded. The

information regarding the elemental and molecular composition of the HTL oils determines the harshness of the upgrading process required. In this context, Table 1 represents the element composition, HHV and ER values for bio-oil products obtained from the HTL of mixed textiles. Bio-oils from all mixed textiles were found to contain high oxygen contents and some levels of nitrogen that could be derived from different impurities such as dyes, acrylic or elastane fibers etc.

The higher amount of PET in the mixed textile resulted in higher oxygen contents and lower HHV values of bio-oil products. For 95% Cotton/ 5% PET and 50% Cotton/50% PET mixed wastes, elevating the temperature from 300 to 350 °C in alkali conditions resulted in an increase of the carbon content, while the oxygen content decreased, improving HHV values. A maximum ER of 42% was achieved for the 95% Cotton/ 5% PET blending ratio at 325 °C due to the highest bio-oil yield obtained.

The lower energy content of bio-oil products produced from the 50% Cotton/ 50% PET samples can be explained by the higher thermal stability of degradation products from the polyester part. Due to the lower bio-oil yields and HHV values, HTL of PET-rich textile waste led to the lowest ER in the bio-oil (<3%).

3.4. Characterization of HTL products

3.4.1. Molecular characterization of bio-oil products

The composition of bio-oil and aqueous phases was characterized by GC–MS analysis and identified compounds were sorted into several chemical families according to their functional groups. Fig.3 illustrates

Table 1
Element analysis, HHV and ER values of bio-oil products.

T, °C	Catalyst	C	N	H	S	O*	HHV,MJ/kg	ER,%
<i>95% Cotton/ 5% PET</i>								
300	KOH	61.1 ± 3	0.4 ± 0.1	7.8 ± 0.4	0.04 ± 0.1	30.6	27.4 ± 3.5	26.2 ± 0.9
325	KOH	68.4 ± 2.5	0.4 ± 0.0	7.8 ± 0.2	0.04 ± 0.0	23.4	28.7 ± 3.9	41.7 ± 8.2
350	KOH	72 ± 2.3	0.5 ± 0.1	7.2 ± 0.9	0.1 ± 0.0	20.5	31.4 ± 1.6	40.5 ± 4.9
300	No cat	62.3 ± 6.1	0.4 ± 0.1	6.2 ± 0.5	0.2 ± 0.0	31.0	25.9 ± 2.3	11.0 ± 0.5
325	No cat	65.7 ± 1.8	0.6 ± 0.4	6.9 ± 0.2	0.1 ± 0.0	26.8	28.2 ± 0.8	15.0 ± 4.5
350	No cat	63 ± 3.0	0.3 ± 0.1	7.6 ± 0.4	0.1 ± 0.0	29.1	27.9 ± 1.5	21.5 ± 1.4
<i>50%/50% polycotton</i>								
300	KOH	49.6 ± 2.3	0.9 ± 0.1	6.5 ± 0.9	0.1 ± 0.0	42.9	20.6 ± 3.7	9.1 ± 0.5
325	KOH	52 ± 6.6	1.2 ± 0.1	6.8 ± 0.5	0.5 ± 0.0	39.7	22.0 ± 4.1	17.7 ± 3.4
350	KOH	59.7 ± 1.8	1.6 ± 0.4	7.6 ± 0.2	0.1 ± 0.0	31.0	26.5 ± 0.4	12.9 ± 1.3
300	No cat	63.5 ± 0.5	1.1 ± 0.1	5.9 ± 0.3	0.2 ± 0.0	29.3	26.1 ± 0.1	9.85 ± 1.6
325	No cat	56.1 ± 1.6	1.5 ± 0.8	7.1 ± 0.3	0.2 ± 0.0	35.2	24.3 ± 1.3	8.49 ± 0.2
350	No cat	61.8 ± 0.6	1.4 ± 0.0	6.6 ± 0.2	0.2 ± 0.0	30.0	26.3 ± 0.4	10.6 ± 3.2
<i>95% PET/ 5% Cotton**</i>								
300	KOH	55.6	0.9	3.5	0.2	39.8	19.4	1.7
325	KOH	51.52	1.1	4.3	0.6	37.6	19.7	2.4
350	KOH	52.2	1.0	4.5	0.5	41.9	19.2	3.4
300	No cat	59.8	0.8	4.7	0.3	34.4	22.9	2.10
325	No cat	61.0	2.4	5.8	0.5	30.2	25.0	3.40
350	No cat	55.5	1.4	3.6	0.8	38.7	19.7	3.04

*calculated by difference.

**analysis has been performed only once due to the low amount of bio-oil.

an overview of bio-oil components categorized in several chemical groups. The values of the carbon recovery (CR) in the bio-oil are also presented. The detailed list of identified individual compounds in the bio-oil and aqueous phases are given in electronic supplementary Tables S.1 and S.2, respectively.

As shown in Fig.3a, the bio-oil obtained from the HTL of cotton-rich mixed textile under neutral conditions contains furanic compounds (5-hydroxymethylfurfural, furfural, 2-acetyl-5-methylfuran, etc.), benzofurans (2-methylfurfurbenzofuran, 2-methyl-5-hydroxybenzofuran, etc.), phenols (phenol, cresol, catechol, hydroxyquinone, etc.), ketones (cyclopentenones, cyclopentanedione, ketone adducts, etc.) and organic acids (levulinic acid, etc.). By increasing the temperature from 300 to 350 °C, the amount of furanic compounds decreased, while the content of ketones and phenols increased.

Under subcritical conditions, glucose from the hydrolysis of cellulose, undergoes isomerization and dehydration reactions to form 5-hydroxymethylfurfural (5-HMF) (Taghavi et al., 2020). Different furan derivatives can be formed from 5-HMF through a series of reactions, such as decarbonylation, hydrogenation, isomerisation, etc. (de Caprariis et al., 2021). Benzofurans were previously reported to be generated through Diels-Alder self-condensation reactions of furan derivatives (Gilbert et al., 2014).

Due to the lower thermal stability of furan rings at higher temperature, the hydrolytic ring cleavage of furanic compounds takes place followed by several rearrangement and dehydration reactions generating more benzendiols and benzenetriols (Srokol et al., 2004). The formation of cyclic ketones and aromatics could also occur via aldol condensation and Michael reactions between aldehydes and ketones (Kröger et al., 2013).

Under alkaline environment, the bio-oil is composed of more alkylated phenolic compounds (methyl-, ethyl-, dimethylphenols) and cycloketones (methyl-, ethyl-, dimethylcyclopentanones, etc.) and dibenzofurans. Based on the results obtained, the alkali catalyst shifted reaction pathway towards the retro-aldol cleavage to form C2-C3 aldehydes, ketones, alcohols that can undergo acetylation reaction.

It is known that polymerization reactions are the dominant pathway for the transformation of furanic compounds into char in acidic conditions, while using an alkali catalyst results in a lower amount of char and slightly higher content of benzofurans, which can be explained by the higher stability of benzene rings in the benzofurans.

The bio-oil from the PET rich textile waste consists primarily of bis(2-

hydroxyethyl) terephthalate and monohydroxyethyl terephthalate (BHET and MHET, respectively), in addition to TPA, diols (diethylene glycol) (Fig.3b). With increased temperature and using KOH, the content of BHET and MHET decreased and the amount of organic acids (mainly TPA, benzoic acid) increased due to the enhanced hydrolysis. It has been previously reported that the depolymerization of PET occurs predominantly through chain-end scission mechanisms under alkali conditions, while random cleavage takes place under neutral conditions (Wan et al., 2001), forming more by-products, such as MHET and BHET.

The bio-oil produced from the 50% PET/ 50% cotton mixture showed a lower amount of furanic compounds, but more carboxylic acids, phenolics and cyclic ketones. Among the identified carboxylic acids, levulinic acid (LA) was the main compound with a relative peak area of 50%, which formed through decomposition of 5-HMF. The high selectivity for LA can be associated by the lower loading of cellulose or in situ catalytic activity of TPA released from the PET degradation. The addition of KOH decreased the content of organic acids and increased the amount of phenolic compounds, cyclic ketones and diols in the bio-oil.

According to the FTIR analysis (Fig.S3 b), the main stretching vibrations for -OH groups (3200–3600 cm⁻¹), for alkyls (2830–2920 cm⁻¹), C=O groups in carboxylic acids (1709 cm⁻¹), aromatic C=C (1570 cm⁻¹), and 750 cm⁻¹ (aromatic out of plane bending) were observed for the bio-oils from the 50% PET/ 50% cotton mixture. Using KOH catalyst resulted in the reduced intensity of the peak at 1709 cm⁻¹, while the peaks at 1604 cm⁻¹ (conjugated C=O), 1505 cm⁻¹ (furan ring) and 750 cm⁻¹ (aromatic out of plane bending) become more prominent, thereby confirming the increase in the phenol derivatives, cyclic ketones and furan derivatives.

It is worth mentioning that bio-oil from the 95 and 50% cotton containing textiles contained some heterocyclic nitrogen containing compounds, while in the case of PET rich textiles, the content of nitrogen compounds was negligible. Previously the high synergy for bio-oil production was attained for the co-liquefaction of polyurethane and Miscanthus due to the formation of nitrogen containing heterocyclic compounds through Maillard reactions (dos Passos et al., 2021). Likewise, in this study the nitrogen compounds could be originating from the combination reactions between cotton-derived intermediates and different additives, such as azo dyes, elastane etc. that contain azo, nitroso and nitro groups.

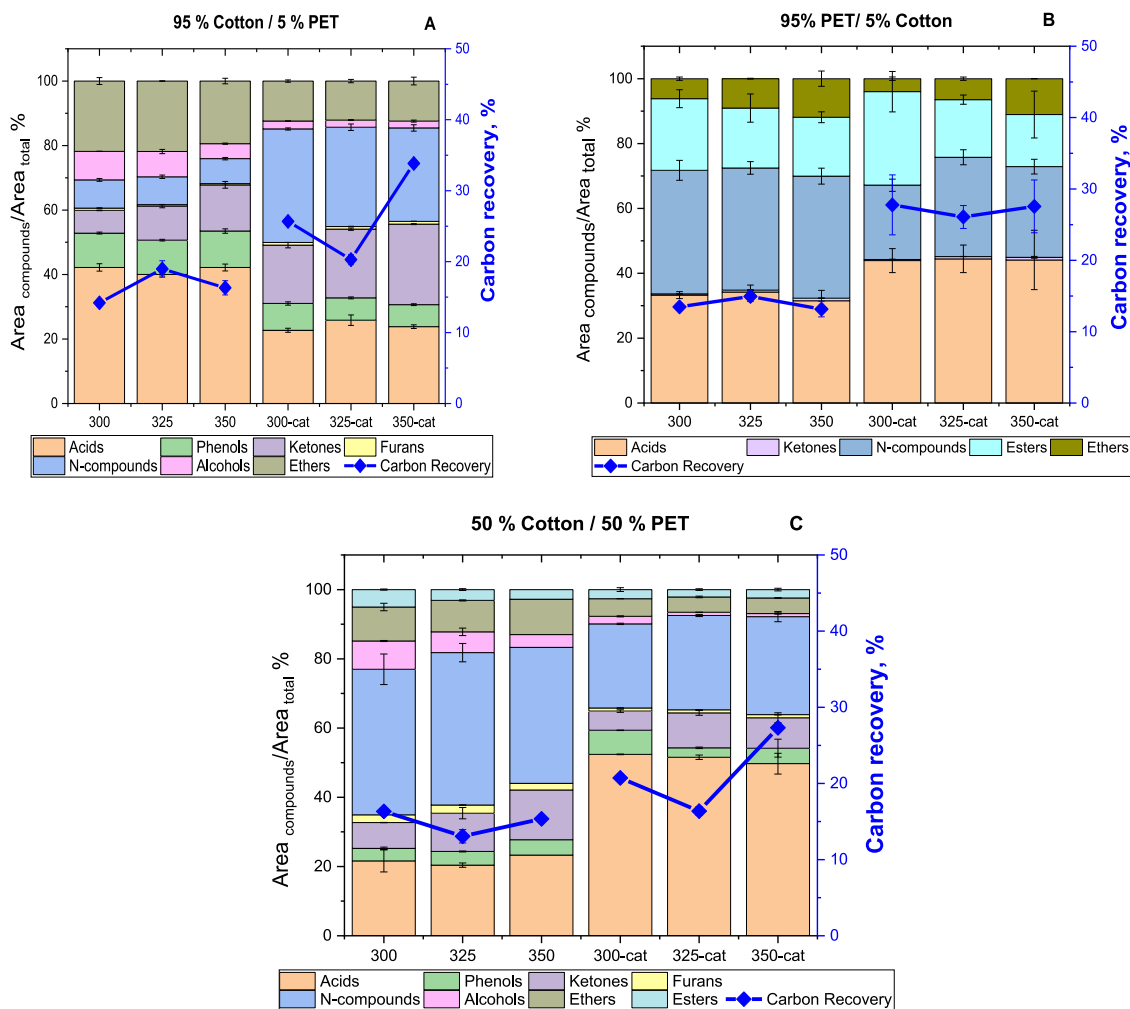


Fig 3. Composition of aqueous phase produced from HTL of mixed textile waste.

3.4.2. GC-MS of aqueous phase

The management of the HTL aqueous phase is a big challenge, as it considered as a waste stream that causes obstacles in the commercialization of the HTL process. Many attempts have been made to valorize the aqueous phase by different technologies, such as hydrothermal gasification, anaerobic digestion (Zheng et al., 2017), electrochemical oxidation (Matayeva and Biller, 2021), aqueous phase reforming (Pipitone et al., 2020) and wet oxidation (Silva Thomsen et al., 2022). The presence of a wide variety of organic species, dyes, pigments, etc. in the process water from the HTL of textile waste could result in an insufficient treatment efficiency by these technologies. Therefore, the information on its characteristics and chemical composition is important in order to select the most optimal method to treat the process water. The aqueous phase produced from the mixed textiles was acidic (pH 2.6–3.2), whereas with the addition of KOH, the pH of post-reaction solutions ranged from 4.8 to 5.4. TOC values of the aqueous phase ranged between 12,600 and 30,400 mg/L depending on the feedstock composition and reaction conditions. It has been previously reported that the TOC removal can be achieved up to 99% for effluents with the TOC of >30,000 mg/L by electro-oxidation (Matayeva and Biller, 2021) and wet oxidation (Silva Thomsen et al., 2022). Additionally, hydrogen and heat can be valorized, respectively, by applying these processes.

Based on the initial TOC values and complex chemical composition of the process water from the HTL of mixed textile, wet oxidation and electro-oxidation can be more efficient treatment processes in terms of TOC removal and hydrogen or heat recovery.

In general, the aqueous fractions were found to contain similar

chemical families, but with the different relative contents.

For the 95% cotton/ 5% PET mixed textiles, the aqueous phase was composed of short chain carboxylic acids, ethers (tetraglyme), cyclic ketones, nitrogen compounds and phenol derivatives. Nitrogen compounds are present in the form of hydrazines, hydrazides, heterocyclic compounds, amino acids, amides. Overall, the same classes of nitrogen compounds are present in the aqueous phase for all blended textiles, implying that these components originate from the same sources, such as azo dyes, and other additives used in textiles. For instance, hydrazine is used for mercerization of fabrics, rendering wrinkle proof, flame retardant properties (Eckart, 2001). It is also utilized for de-sizing polyurethane (Eckart, 2001) that can present as coatings in mixed textile.

With the addition of KOH catalyst, the carbon recovery in the aqueous phase from the 95% cotton/ 5% PET increased by 10–20% depending on the temperature. In this case, the nitrogen compounds were the dominant compounds and the relative sum of carboxylic acids decreased, as more nitrogen moieties, such as hydrazine, amine, etc. reacted with short chain carboxylic acids forming hydrazides. The increase in the relative content of nitrogen compounds under alkaline conditions can be explained by two reasons. Firstly, using KOH catalyst could weaken considerably the chemical bonds between fiber and contaminants containing nitrogen species (dyes, flame retardant additives, coatings, dyes, etc.). However, the content of nitrogen compounds did not increase for the 95% PET/ 5% Cotton and 50% PET/ 50% Cotton mixtures at alkali conditions. On the other hand, 95% Cotton containing textile produced the highest amount of char at neutral conditions, which could act as an adsorbent, removing these nitrogenated species from the

aqueous phase. In fact, the color of the aqueous phase obtained at neutral conditions was light brown, while it changed to dark blue under basic conditions. Several hydrochar properties, such as surface area, porosity, surface functional groups, etc. have been reported for the abatement of pollutants using hydrochar produced from lignocellulose (Leng et al., 2015). The liquefaction char has a lower surface area and is more microporous than pyrolysis char; however, it possesses more surface functional groups (Leng et al., 2015; Leng et al., 2015) that can selectively react with different contaminants.

For PET rich mixed textile, about 13–14% of carbon remained in the aqueous phase as carboxylic acids (terephthalic acid, benzoic acid, hexedionic acid, etc.), nitrogen compounds (hydrazides), ethers (tetraglyme, 1,4-dioxane) and esters (MHET). Temperature did not affect the composition significantly, but the relative content of organic acids increased by 10% with the addition of basic catalyst that enhances the hydrolysis of PET into the TPA monomer. The increase in the carbon recovery of 10% in the aqueous phase was due to the relocation of TPA from the solid phase after the formation of water soluble dipotassium terephthalate. The presence of piperonylic acid, benzoic acid was also observed for the 95 and 50% PET- containing textiles with the addition of KOH catalyst.

The aqueous phase from the 50% PET/ 50% cotton contained degradation products from both cotton and PET. Under alkali conditions, the increase in the carbon recovery in the aqueous phase was due to generation of more carboxylic acids, mainly short chain acids, and the relocation of TPA from the solid phase.

As already stated in the Section 3.2, HTL of mixed textile wastes resulted in a carbon loss between 4 and 25 wt.% due to the formation of post-reaction solids in the aqueous phase. In the case of cotton rich textiles, the aqueous phase was shown to contain furanic compounds, aromatic and heterocyclic compounds that are not stable and undergo condensation reaction to form insoluble solids, referred to as humins, that can account for 10–50 wt.% carbon loss of the feedstock (Cheng et al., 2018).

In the case of the PET rich mixed textiles, MHET and BHET are known to have higher solubility in water at ambient temperature, but at lower temperature they undergo crystallization. In order to confirm this, the precipitated solids from the aqueous phase obtained from the 95% PET/ 5% cotton mixture were separated, dried and analyzed by TGA-DSC analysis. The DSC curve showed the intense peak at 173 °C that corresponds to BHET dimer (Imran et al., 2010) (Fig. S4).

3.5. Recovery of TPA in solid phase

For the production of renewable PET, its monomers have to be obtained from renewable resources. However, currently only EG is derived from bio-ethanol (the biomass derived carbon content >20%), while the remaining 80% (mainly TPA) is still synthesized from petroleum resources (Tachibana et al., 2015). Therefore, recycling PET fibers by HTL for producing commodity monomers is crucial for minimizing the generation of plastic waste and consumption of natural resources.

The HTL solids obtained from the 95% PET/ 5% Cotton and 50% PET/ 50% cotton mixtures were characterized by FTIR, element analysis and TGA-DSC. The HTL solid fractions were characterized as dark colored powders due to the presence of impurities, such as disperse dyes, pigments, etc. that are insoluble in water and stable at higher temperatures. Notwithstanding, the solids from both blended textiles exhibited the same characteristic bands as the commercial standard of TPA: 3065 cm^{-1} (C–H aromatic), 1676 cm^{-1} (C=O), 1280 cm^{-1} (C–O) (Fig.S5). Moreover, the element analysis of solids was consistent with the theoretical composition of TPA (C 57.84%, H 3.64%, O 38.62%) (Table S3).

The purity of recovered TPA was determined by DSC analysis and the yield of TPA was calculated taking into account the solid yield and its purity (Fig. 4). The carbon contribution of the char or by-products was also calculated as the difference of the carbon recovery in the solid fraction and the carbon recovery as TPA.

The yields of TPA were in the range of 48–91 wt.% depending on the blending ratio and reaction conditions. It should be pointed out that the conversion of PET under hydrothermal conditions was complete, as the melting peak related to the PET (~250 °C) was not detected for any solid samples. However, DSC curves revealed the presence of BHET dimer in the solids from the 95% PET/ 5% cotton mixture at ~173 °C under neutral conditions (Fig. S6), while under alkali conditions this peak disappeared due to the enhanced hydrolysis. The amount of residual carbon did not decrease greatly with the addition of KOH, thus implying that these carbons are very hydrothermally and chemically stable compounds that are most likely derived from disperse dyes. It is worth noting that the TPA was isolated straightforwardly from the residual char by-products and other impurities by acid-base extraction (Fig. S7).

HTL of the 50% PET/ 50% cotton mixture resulted in a higher TPA yield than that of 95% PET/ 5% Cotton blended mixture. The maximum TPA yield of 91 wt.% was obtained from the HTL of 50% PET/ 50% cotton mixture at 350 °C at neutral conditions. However, in this case residual carbon accounted for 29% in the solid fraction. In comparison,

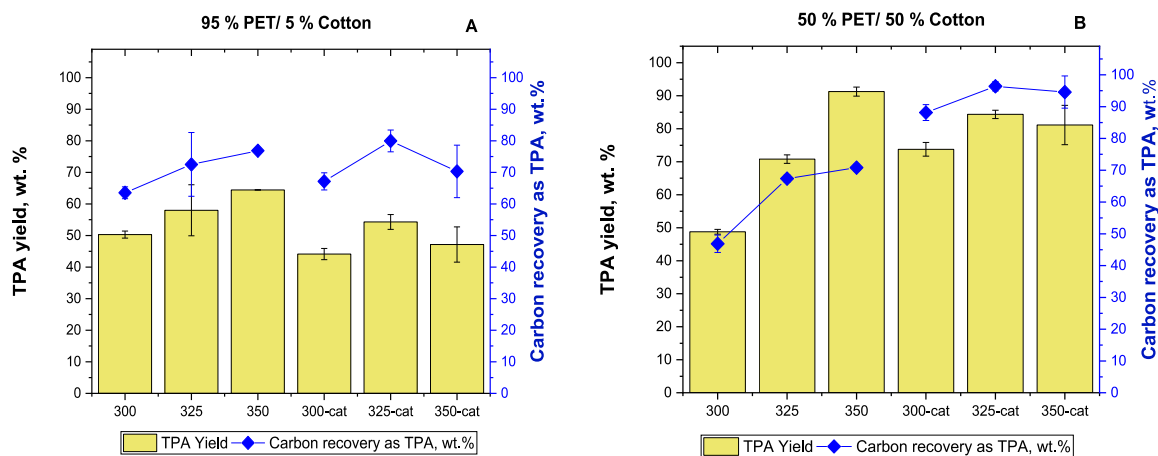


Fig. 4. Recovery rate of TPA in solid fractions produced from HTL of mixed textile waste at three temperatures in water and alkali conditions: A) 95% PET/ 5% Cotton, B) 50% PET/ 50% Cotton.

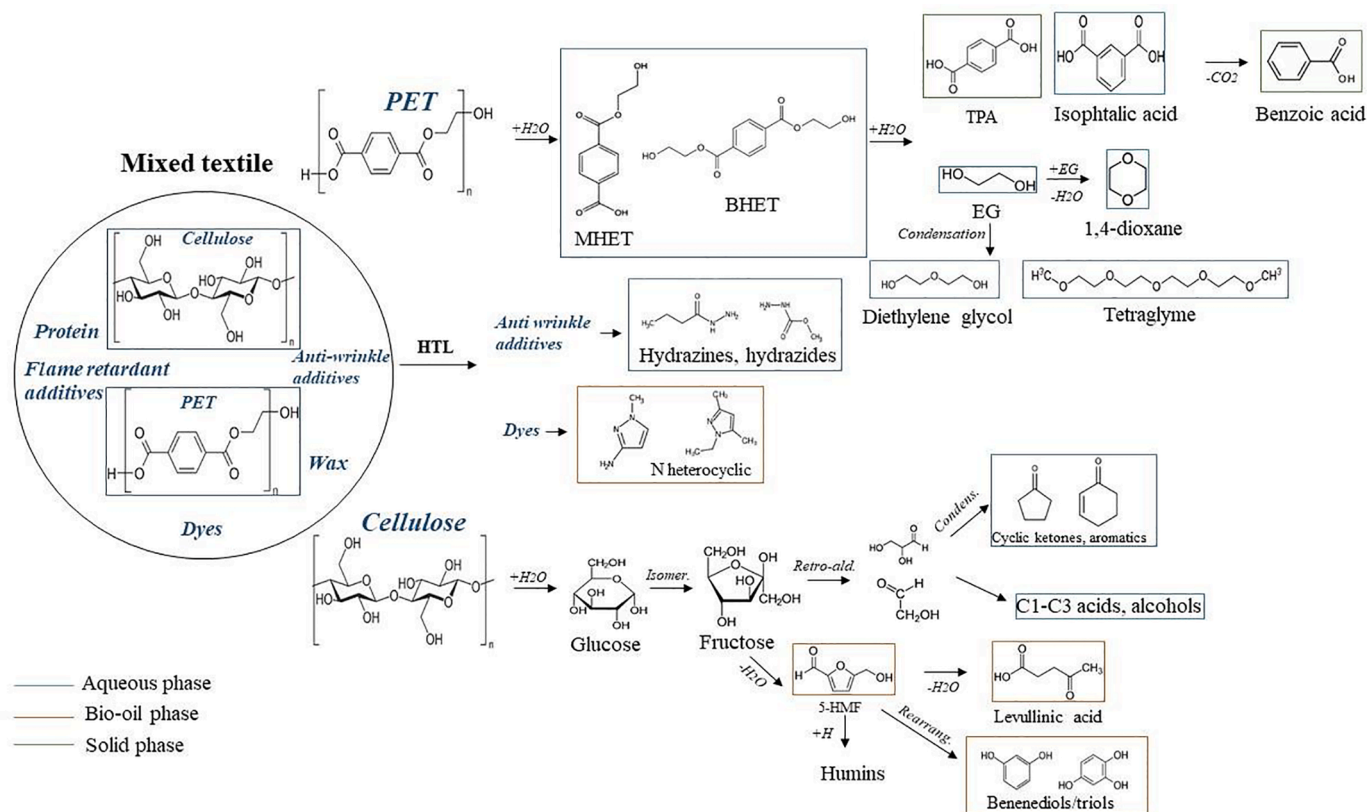


Fig 5. Simplified reaction pathway of the HTL of mixed textile wastes.

relatively lower TPA yield of 81 and 84% were attained at 350 and 325 °C using KOH catalyst due to the formation of dipotassium terephthalate; however, the residual carbon corresponded only 4 and 5%, respectively, due to the lower amount of char formed.

From literature, the hydrolysis of esters can proceed through several mechanisms: proton catalyzed, direct nucleophilic attack, direct hydroxide attack and radical mechanism. It is believed that direct hydroxide mechanism is the fastest and it is dominant initially until acids release, so hydrolysis reactions continue by acid catalyzed mechanism (Oka et al., 2002). On the other hand, adding cation-inclusion components, such as ethers or aprotic solvents, in alkali solutions was reported to facilitate the hydrolysis of PET by enhancing the percolation of hydroxide ions into the hydrophobic surface of PET (Hu et al., 1997; Sinha et al., 2010). Cotton can be considered as the material that comprises the attributes of ethers and alcohols that can enhance the action of alkali catalyst for the degradation of PET fractions. Therefore, the highest TPA yield was observed for the 50% PET / 50% cotton mixture using alkali catalyst.

Based on the observations from this study and literature results the reaction pathway of mixed textile containing cotton and PET under hydrothermal conditions is proposed and depicted in Fig. 4.

4. Conclusion

In the present study HTL experiments have been performed using post-consumer mixed textile waste in varying proportions of PET and cotton. It is shown that the HTL operating parameters employed in this study allowed the degradation of cotton and PET to produce bio-oil and TPA. For all blended mixtures, using alkali catalyst favored hydrolysis, increasing the selectivity towards the target products. HTL of cotton rich mixed textiles produced a bio-oil yield of 26% and a HHV of 28 MJ/kg,

while the oil production from PET rich textile was insignificant. On the other hand, a maximum 91% TPA was recovered in the solid fraction. HTL of 50% PET/ 50% cotton resulted in the highest TPA recovery due to the synergistic effect of cellulose and KOH catalyst on the hydrolysis of PET. It was shown that the TPA in the solid fraction can be simply isolated from by-products by acid-base extraction.

CRedit authorship contribution statement

Aisha Matayeva: Conceptualization, Methodology, Investigation, Writing – original draft, Visualization, Project administration. **Patrick Biller:** Conceptualization, Writing – review & editing, Resources, Supervision, Funding acquisition.

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.

Acknowledgement

This research was funded by the Innovation Fund Denmark Grand Solution project ReSuit: Recycling Technologies and Sustainable Textile Product Design, grant number 0224-00084B.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.resconrec.2022.106502](https://doi.org/10.1016/j.resconrec.2022.106502).

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