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Hydrothermal deconstruction of single-use personal protective equipment during the COVID-19 pandemic

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ABSTRACT

To minimise the transmission of the SARS-CoV-2 virus, there has been a substantial increase in the production and usage of synthetic personal protective equipment (PPE) globally. Consequently, single-use PPE have been widely adopted without appropriate regulations for their disposal, leading to extensive environmental contamination worldwide. This study investigates the non-catalytic hydrothermal deconstruction of different PPE items, including isolation gowns, gloves, goggles, face shields, surgical masks, and filtering-facepiece respirators. The selected PPE items were subjected to hydrothermal deconstruction for 90 min in the presence of 30-bar initial oxygen pressure, at temperatures ranging between 250 °C and 350 °C. The solid content in form of total suspended solids (TSS) was reduced up to 97.6%. The total chemical oxygen demand (tCOD) and soluble chemical oxygen demand (sCOD) decreased with increasing deconstruction temperature, and at 350 °C the lowest tCOD and sCOD content of 546.6 mg/L and 470 mg/L, respectively, was achieved. Short-chained volatile fatty acids were produced after 90 min of deconstruction, predominantly acetic acid at concentrations up to 8974 mg/L. Ammonia nitrogen content (NH₃–N) of up to 542.6 mg/L was also detected. Carbon dioxide (CO₂) and unreacted oxygen (O₂) were the main gaseous by-products at up to 15.6% (w/w) and 88.7% (w/w), respectively. The findings suggest that non-catalytic hydrothermal deconstruction is a viable option to process and manage PPE waste.

1. Introduction

Personal protective equipment (PPE) such as isolation gowns, gloves, goggles, face shields, surgical masks, and filtering-facepiece respirators (FFRs) are essential items that protect individuals against the risk of contaminants and pathogen exposure. Conventionally, PPE is commonly used in hospitals to safeguard patients and staff from exposure to pathogens (Singh et al., 2020). However, with the advent of the global COVID-19 pandemic caused by the SARS-CoV-2 virus, single-use PPE has been routinely used to prevent further transmission in healthcare and other frontline roles to reduce virus transmission. This has resulted in an inadequate supply and a steady build-up of potentially contaminated PPE potentially contaminated PPE in municipal waste streams (Ogunseitan, 2020). With a steep increase in PPE demand, the market volume has markedly increased, with a projected global value of USD 81,790 billion by 2026. As a result, contaminated PPE of different types continues to accumulate in municipal solid waste streams (Theexpresswise, 2021).

The exponential increase in PPE waste and the potential mix up of COVID-19 contaminated PPE before disinfection with other solid household wastes creates a major problem (Wang et al., 2021b), resulting in potential cross-contamination and further spreading of the virus. Moreover, PPE wastes have been found in the environment (Kumar et al., 2021). With no standardised disposal regulations and widespread use of PPE, this waste stream has attracted global attention, resulting in a new challenge to different waste management and processing bodies.

Almost every PPE item is comprised mainly of plastics, such as polyethylene (PE), polypropylene (PP) and other polymers and rubbers, including polyurethane (PUR), polystyrene (PS), polycarbonate (PC),...
polyethylene terephthalate (PET), polyisoprene (IR), nitrile butadiene rubber (NBR), spandex and latex (cis-1,4-polyisoprene) (Table 1).

Most of these plastics are engineered using non-renewable fossil fuels, with versatile and robust physicochemical properties, making them resistant to chemical, photolytic, and biological decay (Chamas et al., 2020). Additionally, polyolefins like PE and PP that are predominantly used to produce PPE are highly durable polymers with no functional groups vulnerable to chemical, photolytic, or biological degradation. They also have high molecular weight and a hydrophobic nature, leading to an extended lifespan even after being discarded and processed by waste management organisations (Harshvardhan and Jha, 2013; Pathak, 2017).

Furthermore, different additives such as stabilisers and antioxidants (e.g., phthalates, bisphenol A (BPA), and polybrominated diphenyl ethers (PBDE)) have been often linked to endocrine-disruption in various organisms, and are introduced into the PPE polymers to enhance the properties of these items, further slowing down their environmental decay (Barnes et al., 2009; Galloway et al., 2011; Geyer et al., 2017; Habert et al., 2009; Hoppe and Carey, 2007; Maffini et al., 2006).

Recent studies by others (De-la-Torre and Aragaw, 2021; Wang et al., 2020) have confirmed different plastic forms in waterbodies globally. Recent COVID-19 studies by others (Ma et al., 2020; Peng et al., 2020). However, using medical waste incinerators leads to large carbon footprints (1074 kg CO2e/t) in the environment (Rizan et al., 2021). Also, the incineration of medical waste generates toxic emissions, including particulate matter and persistent organic pollutants (POPs) such as polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), hexachlorobenzene (HxCBz), polychlorinated biphenyls (PCBs), pentachlorobenzene (PeCBz), polycyclic aromatic hydrocarbons (PAHs), nitrous oxides (NOx), hazardous heavy metals and furans that resist photolytic, chemical, and biological decomposition (Hii et al., 2014; Kanan and Samara, 2018; Lee et al., 2004; Purnomo et al., 2021; Singh and Prakash, 2007).

These toxic gases have resulted in restrictions on medical-waste incinerators in different countries globally. New Zealand has prohibited medical-waste incinerators under the Resource Management Act 1991 (MEP, 2007). Additionally, under the Philippine Clean Air Act 1999, the Philippines has imposed a nationwide ban on the incineration of hazardous wastes (Lunag and Elauria, 2021).

Disinfection of used PPE via autoclaving followed by landfill disposal is a more sustainable treatment option. However, one of the major disadvantages of this technique is that it only sterilises but does not change the physical appearance and the chemical composition of the waste, making the waste look untreated (Lee et al., 2004). This often leads to double waste treatment, increasing disposal costs and undesired impacts on the environment. Furthermore, a lack of change in physical appearance might also lead to confusion between treated and untreated PPE, resulting in possible transmission of the virus. A lack of significant waste reduction after autoclaving is another drawback of this treatment technique (Windfeld and Brooks, 2015). Moreover, landfilling of plastic wastes, including PPE waste, results in the release of microplastics via landfill leachate (Alimi et al., 2018; Sundt et al., 2014), contributing to land and water contamination (Bergmann et al., 2015; Nizzetto et al., 2016). With the increase in scarcity of landfill disposal sites, growing environmental issues (Goh et al., 2000) and rise in waste volume, landfill disposal of municipal solid waste such as PPE waste is not a desirable option in many regions.

Hydrothermal deconstruction or wet oxidation of organic waste is a waste management technology that targets organic solid waste reduction in an environmentally friendly manner (Anthraper et al., 2018). Hydrothermal deconstruction focuses on the oxidation of organic waste material under high temperature (150–350 °C) and pressure (20–175 bar) reaction conditions (Aggrey et al., 2012; Anthraper et al., 2018; Javid et al., 2021a, 2021b, 2022; Mucha and Zarzycki, 2008), leading to the solubilisation and disintegration of waste. In contrast to other conventional waste treatment technologies, hydrothermal deconstruction not only is an environmentally benign option but also is easily scalable, time-efficient, cost-effective and does not generate toxic gaseous emissions such as nitrous oxides, persistent organic pollutants or dioxins, giving it a better technology readiness level (TRL) (Anthraper et al., 2018; Manir et al., 2018). Furthermore, hydrothermal deconstruction of PPE waste leads to the production of value-added by-products, such as volatile fatty acids, primarily acetic acid and ammonia–nitrogen, providing a potential resource recovery opportunity to revalorise the by-products produced for commercial and environmental benefits.

This study investigated the hydrothermal deconstruction of various single-use PPE during the COVID-19 pandemic and beyond, including isolation gowns, gloves, goggles, face shields, surgical masks, and filtering-facepiece respirators (FFRs). The effect of varying temperatures on the reduction of solid content and chemical oxygen demand of the selected PPE was examined. Additionally, the formation of valuable by-products such as volatile fatty acids, mainly acetic acid and

Table 1
Common polymeric materials and their monomers present in single-use PPE.

| Type of plastics/rubbers | Formula(s) | Physiochemical properties | Reference |
|-------------------------|------------|---------------------------|-----------|
| **PE**                  | (C2H4)n   | Melting point: 120–147 °C | (Chambers, 2011) |
|                         |           | Monomer: Ethylene (H2C – CH2) |           |
| **PP**                  | (C2H4)n   | Melting point: 170 °C | (Ozawa et al., 2019) |
|                         |           | Monomer: Propylene (CH2 – CH2CH) | (Maddavi et al., 2014) |
| **PUR**                 | C3H4N2O   | Melting point: N/A | (Ulrich, 1996) |
|                         |           | Monomer: Different polyol and diisocyanates |           |
|                         |           | Melting point: 215–230 °C | (Meiabadi et al., 2020) |
|                         |           | Monomer: Bisphenol A (BPA) (C12H10O2) | (Pianiec, 2017) |
| **PET**                 | (C10H12O4)n | Melting point: 260 °C | (De A. Freire et al., 1999) |
|                         |           | Monomer: Terephthalic acid (C9H6O4), Ethylene glycol (C2H4O2) |           |
| **IR**                  | C6H8      | Melting point: 54.5 °C | (Kent and Swinney, 1966) |
|                         |           | Monomer: Isoprene (2-methyl-1,3-butadiene) (CH2 – CH=CH2) |           |
| **NBR**                 | (C12H16)  | Melting point: > 108 °C | (Jose and Kasturbha, 2021) |
|                         |            | Monomers: Butadiene (CH2 – CH2) and acrylonitrile (CH2=CHCN) |           |
| **Spandex**             | –         | Melting point: ~ 250 °C | (Manie and Anbumanis, 2014) |
|                         |           | Monomer: ≥ 85% PUR | (Speight, 2019) |
|                         |           | Melting point: 30 °C | (Kirk and Ohmer, 1997) |
| **Latex**               | –         | Monomer: cis-1,4-polyisoprene (CH2 – C(CH2)CH – CH2) | (Mourad et al., 2012) |
ammonia–nitrogen, was also investigated. Moreover, gas analyses were performed to gain more insights into the composition of off-gases vented out after the PPE deconstruction process. Since there were no prior studies on the effect of hydrothermal deconstruction of PPE waste, the results from this study could assist develop a potential environmentally benign PPE waste treatment option.

2. Materials and methods

2.1. Materials

Personal protective equipment including isolation gowns, nitrile and latex gloves, goggles, face shields, surgical masks and FFRs were provided by Ministry of Health, New Zealand for hydrothermal construction experiments. The product and model details for all PPE items are presented in the supplementary material. Chromatographic grade acetic acid (C₂H₄O₂), propionic acid (C₃H₆O₂), butyric acid (C₄H₈O₂), and valeric acid (C₅H₁₀O₂) were acquired from Sigma-Aldrich (Auckland, New Zealand) for GC-FID analysis. Certified calibration standard gas mixtures of oxygen (O₂), carbon dioxide (CO₂), carbon monoxide (CO), nitrogen (N₂) and compressed oxygen gas (O₂) were purchased from the BOC Limited (Auckland, New Zealand) for GC gas analysis and reactor pressurisation. Test kits for chemical oxygen demand, total nitrogen and ammonia–nitrogen analyses were obtained from Hach Pacific (Auckland, New Zealand).

2.2. Hydrothermal deconstruction

Hydrothermal deconstruction of different PPE items was carried out in a 1.0 L high-pressure, high-temperature batch reactor (Amar Equipments Pvt. Ltd., Mumbai, India), which includes an integrated proportional-integral-derivative (PID) controller that enables accurate temperature control. For each reaction, the PPE items were first shredded to particle sizes of 0.1–0.5 cm followed by the loading up of the reactor vessel with different PPE items such as isolation gowns, nitrile and latex gloves, goggles, face shields, surgical masks and two categories of FFRs, with an initial concentration of 2.5 w/v% in distilled water (100 mL). The hydrothermal reactions were executed at temperatures ranging between 250 and 350 °C with 30 bar (gauge pressure) initial oxygen gas for 90 min with a stirring speed of 500 rpm. High stirring speed and excess oxygen gas were chosen to reduce the mass transfer limitations within the reaction system and improve the reaction kinetics. Gas sampling was performed to quantify the off-gas composition after cooling down of the reactor vessel. Liquid samples were taken at the end of the reaction and cool down period. The reactor set-up is shown in Fig. 1.

2.3. Analyses

2.3.1. Solid reduction

Solid reduction (%) in the form of total suspended solids (TSS) was measured based on the EPA Standard Method 2540D. Using a vacuum filter assembly, each hydrothermally treated sample (20 mL) was homogenously mixed and filtered through a dried 47 mm glass fibre filter paper (Microscience, Auckland, New Zealand). The filter papers were pre-rinsed with distilled water, dried at 105 °C overnight and weighed prior to filtration. After sample filtration they were again dried at 105 °C overnight, and the total increment in weight of the filter paper was used to calculate the corresponding TSS of the reaction mixture.
2.3.2. Chemical oxygen demand (COD)

Total chemical oxygen demand (tCOD) and soluble chemical oxygen demand (sCOD) were evaluated using the reactor digestion method via the high range (20–1500 mg/L) COD test kit (Hach Pacific, New Zealand). The tCOD assesses the overall organic content including particulates, and the sCOD quantifies the soluble organic content present within a reaction mixture. Hydrothermally treated samples were filtered using nylon syringe filters (0.2 μm pore diameter). The samples were digested in a DRB200 digital reactor (Hach Pacific, Auckland, New Zealand), with the resultant absorbance assessed via a DR3900 spectrophotometer (Hach Pacific, Auckland, New Zealand). Distilled water acted as a blank substrate for the analysis.

2.3.3. Volatile fatty acids

Volatile fatty acids (VFAs) concentrations were quantified using a Shimadzu GC 2010 gas (Kyoto, Japan) chromatograph equipped with flame ionisation detection. A nitriloterephthalic-acid-modified polyethylene glycol (PEG) column (DB-FFAP, 30.0 m × 0.53 mm × 0.5 μm, Agilent Technologies, Santa Clara, California, US) was used. Helium gas was utilised as the carrier gas. The column was first heated to 40 °C, and the temperature was held for 2 min after sample injection followed by a temperature ramp-up to 180 °C at a rate of 10 °C/min, and the temperature was maintained for 26 min. Peak identification was achieved by calibrating reference standard solutions to sample peak retention times.

2.3.4. Nitrogenous by-products

The total nitrogen content (TNT) was measured using the high range (0–150 mg/L) TNT test kit (Hach Pacific, Auckland, New Zealand) based on the persulfate digestion method, following the kit instructions. The TNT was assessed using a DR3900 spectrophotometer. Deionised water acted as a blank substrate for the analysis.

Nitrogen in the form of ammonia (NH$_3$-N) was measured using the high range (0-50 mg/L) NH$_3$-N test kit (Hach Pacific, Auckland, New Zealand) in accordance with the AmVer (Salicylate) method. The NH$_3$-N content was evaluated using a DR3900 spectrophotometer. Ammonia-free water acted as a blank substrate for the analysis.

2.3.5. Off-gas composition

The off-gas composition released during the venting of pressure vessel at the end of the hydrothermal deconstruction process was measured using an SRI GC (8610c) 2010 gas chromatograph (California, USA) equipped with both thermal conductivity (for H$_2$ and O$_2$) and flame ionisation (CO and CO$_2$) detection. The gas was injected via a Hayesep D Pre-column (length 0.5 m) and subsequently the Hayesep D Column (length 2 m). Helium gas was used as the carrier gas. The column was first heated to 50 °C, and the temperature was held for 1 min followed by a temperature ramp-up to 90 °C at a rate of 10 °C/min, and the temperature was held for 3 min. Subsequently, the temperature was elevated to 270 °C at a rate of 30 °C/min. Peak identification was attained via calibration of reference standard gases to sample peak retention times.

3. Results and discussion

3.1. Reduction of PPE to residual solids

Total suspended solids are residual solids of organic and inorganic wastes present within a reaction mixture responsible for degradation of overall water quality, aquatic resources and increased water treatment costs (Bilotta and Brazier, 2008). A high TSS value contributes to increased accessibility to oxidisable organics, which lower the dissolved oxygen (DO) levels present in the water, leading to negative impacts on marine life (Verma et al., 2013). Therefore, evaluation of TSS is essential before discharging waste into water. During the hydrothermally deconstruction of PPE, a significant solid reduction (%) in the form of TSS reduction was achieved after the end of the deconstruction reaction (after 90 min) (Fig. 2). For isolation gowns, at 250 °C, 78.1% solid reduction was achieved. Similar reductions were evident at 300 °C (94.6%) and 350 °C (94.4%).

For the hydrothermal deconstruction of gloves, face shields and surgical masks, at 250 °C, a solid reduction of 73.4%, 77.5% and 89.1%, similar to isolation gowns, was observed. At a higher temperature of 300 °C, as expected, there was an increase in the solid reduction of 87.8% and 84.4% for gloves and face shields, respectively. However, at 300 °C, the solid reduction for the surgical masks showed negligible change (87.9%). A further increase in deconstruction temperature to 350 °C for gloves, face shields and surgical masks, resulted in an increased solid reduction of 92.2%, 94.2% and 91.9%, respectively. These results align with recent results on hydrothermal deconstruction by Anthraper et al. (2018); Javid et al. (2021a); Urrea et al. (2014); Yousefifar et al. (2017) who reported a solid reduction (%) of up to 99.3% for municipal solid waste, 93% for pharmaceutical waste and activated sludge and 100% for cellulose, respectively at deconstruction temperatures varying between 160 °C and 350 °C. This increase in solid reduction with elevation in reaction temperature is due to the improved solubility, reaction kinetics and rate of gas–liquid mass transfer at severe reaction conditions (Anthraper et al., 2018; Javid et al., 2021a).

As for the deconstruction of goggles at 250 °C, the solid reduction was only 55.6%. This is primarily due to goggles being comprised of polycarbonate plastic, which undergoes a slow melting process because of two large methyl side groups and a rigid polymer chain (Table 1) (Hu and Lesser, 2004), resulting in higher solid content. However, at higher deconstruction temperatures of 300 °C and 350 °C, higher solid reductions of 95.3% and 97.6%, respectively, were achieved similar to the other PPE.

Based on their chemical compositions, different classes of FFRs were sub-classified into two different groups, namely FFR-I and FFR-II. In the case of FFR-I and FFR-II, at 250 °C, 54.8% and 35% solid reduction were observed. The solid reduction was lower compared to the other PPE items because of the presence of spandex with PP and PUR, which turns sticky at lower temperatures (175 °C) and only starts melting at 250 °C (Mani and Anbumani, 2014). At 300 °C, the solid reduction further increased to 67% and 81.6%, respectively. Additionally, at 350 °C, the solid reduction sharply increased to 88.9% and 87% for FFR-I and FFR-II, respectively. These results suggest that the hydrothermal deconstruction of selected PPE can effectively reduce the solids content up to 97.6% when present in a reaction mixture.
3.2. Effect of hydrothermal deconstruction on COD content

Chemical oxygen demand is a lumped parameter used to evaluate the mass of oxygen necessary to oxidise aqueous particulate matter, and it primarily denotes the oxidisable organics content available within the reaction mixture. Organic wastes like PPE waste are long-chained plastic, rubber molecules such as PE, PP, PUR, PS, PC, NBR, latex (cis-1,4-polyisoprene), spandex, natural fabrics like cotton, and hence, they are a significant potential source of COD. During the hydrothermal deconstruction experiments, excess oxygen gas was supplied to improve the reaction kinetics and ensure that the deconstruction of PPE waste occurred without mass transfer or stoichiometric limitations. In general, the final tCOD content for all the hydrothermally processed PPE decreased with an increase in reaction temperatures from 250 to 350 °C (Fig. 3).

For isolation gowns, at 200 °C, 9000 mg/L tCOD content was detected at the end of the hydrothermal deconstruction process after 90 min (Fig. 3a). A sharp decrease in the tCOD content was observed with the increase in reaction severity. After 90 min, at 300 °C and 350 °C, the tCOD content was 4493 mg/L and 1160 mg/L, respectively. These results are congruent with previous studies conducted by Javid et al. (2021a, 2021b, 2022), who confirmed a decrease in tCOD content with an elevation in deconstruction temperatures during the hydrothermal deconstruction of different pharmaceutical wastes including local anaesthetics, antibiotics and hormones. Additionally, the presence of VFAs, primarily acetic acid, at the end of the deconstruction process adds to the residual COD content detectable within the reaction mixture (Hii et al., 2014; Javid et al., 2021a, 2021b, 2022). The production of these VFAs could be deemed potential value-added by-products that might be utilised for commercial and environmental gains (Baroutian et al., 2016; Baroutian et al., 2015; Javid et al., 2021a, 2021b, 2022; Strong et al., 2011). Further degradation of these VFAs often results in the formation of water and CO₂ in the presence of sufficient heat energy and reaction time (Imteaz and Shanableh, 2004).

As for the other PPE, a similar drop in tCOD content was measured. In the case of goggles, by the end of the deconstruction reaction, at 250 °C, 300 °C and 350 °C, the tCOD content was 11333 mg/L, 4627 mg/L and 2030 mg/L, respectively (Fig. 3a). Compared to the isolation gowns, the tCOD content was slightly higher for gloves. This might have been due to the presence of extra double and triple bonds in the monomers of gloves which are fabricated from rubbers, NBR and latex (cis-1,4-polyisoprene), which require a higher bond dissociation energy as they have a higher melting point (Table 1) compared to the isolation gowns consisting of PP with only double bonds.

For surgical masks, the tCOD content detected at 250 °C, 300 °C and 350 °C was 12100 mg/L, 3900 mg/L and 1767 mg/L, respectively. At 250 °C, the tCOD content for FFR-I compared to FFR-II, which require a higher bond dissociation energy compared to other plastics (polystyrene) (Huang et al., 2020; Yeung et al., 2021), and therefore, increasing the tCOD content at harsh reaction conditions. An identical pattern was observed for sCOD, with the sCOD content also reducing with the elevation of deconstruction temperature (Fig. 3). After treatment at 250 °C, the sCOD content was detected up to 12927 mg/L (Fig. 3b) for the selected PPE, respectively. However, the sCOD declined sharply up to 3290 mg/L and 470 mg/L after deconstruction at 300 °C and 350 °C, respectively. Previous studies by Antraper et al., 2018; Javid et al., 2021a confirmed that the oxidation of municipal solid waste and pharmaceutical waste to CO₂ gas, resulting in a decrease in sCOD content.

A general trend for the tCOD and sCOD content was observed during the hydrothermal deconstruction of all PPE items. The COD contents declined sharply with an increase in deconstruction temperature. The complex synthetic PPE items broke down into short-chained carboxylic acids, water and CO₂, resulting in a dramatic drop in tCOD and sCOD contents.

3.3. Volatile fatty acids formation

Hydrothermal deconstruction of organic wastes such as PPE results in the breakdown of complex long-chain compounds into short-chain volatile fatty acids, primarily acetic acid, as well as CO₂ and water. The gas chromatography results identified acetic acid (Fig. 4) as the main final product and a considerably lower concentration of propionic acid formation during the hydrothermal deconstruction of different PPE items. Previous studies on hydrothermal deconstruction of...
pharmaceutical waste, waste activated sludge and sewage sludge also verified the formation of VFAs, predominantly acetic acid, propionic acid and methanol (Baroutian et al., 2016; Baroutian et al., 2015; Javid et al., 2021a, 2021b, 2022; Strong et al., 2011). With the market volume of acetic acid being projected to spike up to 18.68 metric tonnes by 2026 (Statista, 2021), acetic acid produced during the hydrothermal deconstruction of PPE waste could be re-utilised for economic and environmental gains. Additionally, acetic acid can act as an effective disinfectant to destroy numerous microbes (Cortesia et al., 2014; Zinn and Bockmühl, 2020).

The hydrothermal deconstruction of isolation gowns at 250 °C produced 6965.4 mg/L after 90 min (Fig. 4). However, at higher deconstruction temperatures, 300 °C and 350 °C, the acetic acid concentration dropped to 4544 mg/L and 1776 mg/L, respectively. Presumably, at severe deconstruction conditions of 300 °C and 350 °C, after 90 min, sufficient energy was available to degrade the acetic acid molecules into water and CO₂ gas. Recent hydrothermal deconstruction studies by Baroutian et al. (2015); Javid et al. (2021a, 2021b, 2022) also proposed the degradation of the produced VFAs, primarily acetic acid. Another research on the hydrothermal deconstruction of cellulose by Yousefifar et al. (2017) suggested a decline in acetic acid concentration at temperatures greater than 260 °C due to the availability of sufficient energy to overcome the activation energy (167.7 kJ/mol) of acetic acid deconstruction. Furthermore, the decrease in VFAs concentration after a prolonged hydrothermal deconstruction could be attributed to a faster rate of VFAs degradation than that of formation, resulting in an overall concentration drop (Imteaz and Shanableh, 2004). No propionic acid was produced for the deconstruction of isolation gowns.

As for the deconstruction of other PPE items except for goggles, a linear decrease with an increase in deconstruction temperature in the concentration of acetic acid content similar to isolation gowns was noticeable by the end of the deconstruction process, for a fixed time period. At 250 °C, the acetic concentration ranged between 3417 mg/L to 8974 mg/L for gloves, face shields, surgical masks, FFR-I and FFR-II deconstruction. At higher deconstruction temperatures of 300 °C and 350 °C, the acetic concentration varied between 418.6 mg/L and 6017.9 mg/L for these PPE items. An identical decreasing trend for propionic acid formation was observed for the surgical masks, FFR-I and FFR-II, deconstruction process. At 250 °C, propionic acid concentrations of 262 ± 70.2 mg/L for surgical masks, 134 ± 7.6 mg/L for FFR-I and 701.5 ± 70.5 mg/L for FFR-II was generated after 90 min of deconstruction. At 300 °C, only FFR-II deconstruction with a concentration of 322.6 ± 86.5 mg/L resulted in propionic acid formation. As expected, no traces of propionic acid were found at the harshest reaction temperature of 350 °C.

In the case of goggles, contrarily to the hydrothermal deconstruction of other PPE items, a different pattern was observed. At 250 °C, only 587.1 mg/L acetic acid was generated, which is relatively low compared to other PPE items. This might be due to the robustness of the polycarbonate goggles and the methyl groups causing steric hindrance and restricting the cleavage of the complex polymer chain into simpler short-chain molecules, such as acetic acid. However, at 300 °C, after 90 min, the concentration roughly doubled up to 1181.9 mg/L. Moreover, at 350 °C, a steep decrease to 337 mg/L, similar to all the other chosen PPE items, was measured for the formation of acetic acid.

3.4. Formation of nitrogenous by-products

Plastic materials such as PPE items are made up of different elements, including carbon, hydrogen, oxygen, and nitrogen and hence, being a potential source of nitrogenous by-products primarily in the form of ammonia (NH₃-N), nitrate (NO₃-N) and nitrite (NO₂-N). In excess, these nitrogen forms contribute to land and water pollution, resulting in detrimental effects on numerous organisms (Luo and Jin, 2002). To measure the concentrations of different nitrogenous compounds, TNT and NH₃-N analyses were conducted. During the hydrothermal deconstruction of chosen PPE items, the TNT content comprising NH₃-N, NO₃-N and NO₂-N largely remained constant, with NH₃-N being the nitrogenous source which increased at higher deconstruction temperatures. After the deconstruction of isolation gowns, after 90 min, the TNT and NH₃-N content showed little change over the selected temperature range. At 250 °C, 300 °C and 350 °C, the concentrations were 8.2 mg/L, 10 mg/L, 6 mg/L for TNT content and 1.2 mg/L, 1.06 mg/L and 1.7 mg/L for NH₃-N.
N content (Fig. 5a and b).

As for the deconstruction of goggles, as expected, no nitrogenous compounds were detected after the deconstruction of goggles because they lack the nitrogen element in their materials of construction. Hence, they behaved as a “blank substrate” for the TNT NH$_3$-N analyses.

In the case of gloves, after 90 min, similar to gowns, no significant change in TNT content was observed, with 607.5 mg/L, 616.6 mg/L and 578.3 mg/L TNT concentration at 250 °C, 300 °C and 350 °C, respectively. However, an increase in NH$_3$-N content was noticed with an increase in deconstruction temperatures, at 250 °C, 300 °C and 350 °C, with values of 403 mg/L, 534.6 mg/L and 542.6 mg/L, respectively. These results are congruent with previous hydrothermal deconstruction studies by Javid et al. (2021a, 2021b, 2022), who confirmed increasing NH$_3$-N content during the hydrothermal deconstruction of various pharmaceutical wastes at deconstruction temperatures ranging between 200 and 350 °C. Furthermore, Ekpo et al. (2016) also reported a significant rise in NH$_3$-N with an increase in reaction temperature from 170 °C to 500 °C during the hydrothermal deconstruction of swine manure.

A pattern comparable to the deconstruction of gloves was visible for TNT and NH$_3$-N formation for all other selected PPE items. No dramatic change in TNT content was found with elevating deconstruction temperature at 250 °C, 300 °C and 350 °C with values of 272.5 mg/L, 234.2 mg/L and 242.1 mg/L for face shields, 131 mg/L, 116.7 mg/L and 182 mg/L for surgical masks, 22.6 mg/L, 18.8 mg/L, 29 mg/L for FFR-I and 130.6 mg/L, 115 mg/L, 130.2 mg/L for FFR-II, respectively. Understandably, an increase in NH$_3$-N concentration was detected at the more severe deconstruction temperatures with values of 145 mg/L, 163.5 mg/L and 209.5 mg/L for face shields, 65.6 mg/L, 76.2 mg/L and 147.9 mg/L for surgical masks, 4.2 mg/L, 7.4 mg/L, and 18.5 mg/L for FFR-I and 49.6 mg/L, 59.4 mg/L, 97 mg/L for FFR-II, respectively.

The concentrations of TNT and NH$_3$-N versus time for the deconstruction of all PPE items but goggles showed a similar trend. The TNT concentrations remained constant with an increment in NH$_3$-N concentrations with increasing reaction severity. The difference between TNT and NH$_3$-N concentrations can be attributed to the formation of other nitrogenous compounds, including NO$_x$ and NO$_2$. With the global demands for NH$_3$-N reaching an all-time high, the amounts of these nitrogenous compounds generated during the hydrothermal deconstruction of different PPE items can be extracted from the final reaction mixture and reutilised for commercial benefits. With the global demand for NH$_3$-N as a fertiliser expected to hit 190 million tonnes by the end of 2022 (FAO, 2019), the NH$_3$-N generated during the hydrothermal deconstruction of PPE waste can be recovered via numerous technologies such as absorption, air stripping, membrane distillation, reverse osmosis, ion exchange, hollow fiber membrane contactor and electrodialysis to fulfil the high production needs (Chen et al., 2021; Guida et al., 2022).

3.5. Effect of hydrothermal deconstruction on Off-gas composition

Personal protective equipment mainly comprises of long-chained carboxylic compounds such as PE, PP, PUR, PS, PC, NBR, spandex, latex and at times cotton. Hydrothermal deconstruction of such compounds results in the release of off-gas as well as other waste management techniques. With the increasing carbon footprint from different processes attracting global attention, it is essential to quantify the composition of gaseous products released in the environment after the deconstruction of PPE waste.

During the hydrothermal deconstruction of organic wastes, the long-chained complex organic compounds were oxidised into simpler short-chain carboxylic acids (ROOH) via a free radical mechanism (Thompson et al., 2020) until the formation of formic or acetic acid. However, with only one active oxygen available, these carboxylic acids are unstable at high temperatures (Swern, 1981) and hence, further breakdown to produce CO$_2$ and water (in the case of complete oxidation) (Imteaz and Shanableh, 2004). Concurring results were found during the hydrothermal deconstruction of numerous PPE items, with O$_2$ and CO$_2$ being the predominant gases vented out with traces of CO and H$_2$ gases after the reactor was cooled down. Overall, the O$_2$ concentration (% w/w) remained essentially constant due to the large stoichiometric excess, and the CO$_2$ concentration (% w/w) was observed to increase in the off-gas as the deconstruction temperature increased. The unreacted excess oxygen gas can be collected in a gas tank and further be reused for further hydrothermal deconstructions, reducing the overall operational costs. For isolation gowns, at 250 °C, 350 °C and O$_2$ gas was detected in the off-gas at the end of the reaction (Table 2). At 300 °C and 350 °C, the CO$_2$ gas concentration rose to 13.1% and 13%, respectively, and O$_2$ gas concentration remained nearly constant with values of 75.1% and 74%, respectively.

As for the deconstruction of other PPE items, the concentrations of CO$_2$ and O$_2$ gases were analogous to those in the case of deconstruction of isolation gowns. During the deconstruction of goggles, the lack of CO$_2$ gas may be due to incomplete oxidation of the robust polycarbonate plastic, which requires more heat energy to dissociate into shorter-chained carboxylic acids such as acetic acid, and finally into CO$_2$ and water. A proportional increase in CO$_2$ concentration was evaluated at 300 °C and 350 °C with values of 12.1%, 11.8%, 7.7%, 9.7%, 10.3% and 13.6%, 13.3%, 11%, 15.6%, 11.4% and 11.6% for gloves, goggles, face shields, surgical masks, FFR-I, FFR-II deconstruction, respectively. There was no significant change in O$_2$ concentration in the off-gas, with values ranging between 74.2% and 79.7% at 300 °C and 350 °C. H$_2$ and CO were at a concentration of ≤1.5% in all samples analysed. The CO$_2$ gas vented out at the end of the hydrothermal deconstruction process can be absorbed using a wet scrubber. Moreover, the NH$_3$-N produced during the hydrothermal deconstruction of PPE waste can also be recovered and reutilised for capturing the CO$_2$ via wet scrubbing (Diao et al., 2004; Jiang et al., 2020).

4. Conclusions

Non-catalytic hydrothermal deconstruction can effectively destroy up to 97.6% of single-use PPE over 90 min at 350 °C. Under these conditions, the resulting aqueous waste had relatively low organics concentrations of 547 and 470 mg/L as measured by tCOD and sCOD, respectively. The PPE items tested were deconstructed into short-chained volatile fatty acids, including acetic acid and propionic acid, as well as NH$_3$-N, CO$_2$ (off-gas) and water. Among the volatile fatty acids, acetic acid was predominantly detected with a concentration of up to 8974 mg/L. The flue-gas primarily comprised CO$_2$ and O$_2$ gases with concentrations of up to 15.6% and 88.7% (w/w). The unreacted oxygen gas can be potentially retrieved in a gas tank and reused for future hydrothermal deconstruction experiments using a gas compressor, reducing the operational costs of the PPE deconstruction process. The NH$_3$-N generated during the hydrothermal deconstruction process can be recovered and reutilised for the wet scrubbing of CO$_2$ gas. The hydrothermal deconstruction technique reduces the waste volume requiring landfiling and leads to the production of value-added final products in the form of acetic acid and NH$_3$-N. Moreover, with a shortage of raw materials and an ever-increasing consumer, producing these value-added products during the hydrothermal deconstruction of PPE waste enhances the possibilities of resource recovery when scaled up to a large scale, making it a potentially commercially and environmentally beneficial waste management technique.

Future studies and examination into the hydrothermal deconstruction of a mixture of different categories of PPE waste using oxygen gas and air, process water reusability and techno-economic analysis would provide valuable insights to this technique’s industrial feasibility. Although hydrothermal deconstruction requires additional development in contrast to the traditional PPE waste management techniques, the results indicated that hydrothermal deconstruction shows excellent potential as an environmentally friendly manner of processing PPE.
waste with minimal land, air or water impacts.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.wasman.2022.09.006.

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