



Continuous wet air oxidation of aqueous phase from hydrothermal liquefaction of sewage sludge

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ABSTRACT

The conversion of organic waste into advanced fuels through hydrothermal liquefaction (HTL) is a promising route. However, for the commercialisation of HTL technology, treatment and valorisation of the generated aqueous by-product are required for its economic viability. This study investigates subcritical non-catalytic continuous wet air oxidation (WAO) for the treatment of the aqueous phase from hydrothermal liquefaction (HTL-AP) of sewage sludge. A custom-made tubular reactor was used at temperatures and residence times similar to the HTL process (300–350 °C; 6–50 min), with excess air equivalent to 1.5–2 times the oxygen demand. The WAO process removed up to 95.3 % of the chemical oxygen demand and 91.8 % of the total organic carbon, generating volatile fatty acids, mainly acetic acid, as intermediary compounds from the oxidation reactions, and CO₂ and H₂O from the pollutant's complete degradation. The process effectively eliminated almost all of the organonitrogen compounds, generating NH₄⁺, which reached values of up to 97 % of the total nitrogen. Comprehensive molecular characterization performed by FT–Orbitrap MS analysis revealed that the main basic organonitrogen compounds in HTL-AP are distributed in the O₁N₁, N₂, O₁N₂, N₁ classes. For neutral to acidic organonitrogen species, O₃N₁ is the most representative chemical class. The energy consumption for heating the WAO reactor was up to 40 % lower using HTL-AP compared to blanks experiments. Despite good process water clean-up, autothermal operation was not achieved, and improvements in the reactor design are suggested.

1. Introduction

Hydrothermal liquefaction (HTL) represents a thermochemical technology with the capacity to convert organic matter, including sewage sludge, into bio-crude. This bio-crude can then undergo further upgrading and refinement into advanced fuels and value-added chemicals. The HTL process uses high temperatures (300–350 °C) and pressures over the saturation pressure of water. During HTL, the organic matter is converted, generating four product fractions: bio-crude, aqueous phase, gas phase, and solids. Product yields largely depend on feedstock type and processing conditions with typical ranges of 25–40 wt% bio-crude, 30–50 wt% of aqueous, 5–30 wt% solids and 5–20 wt% gas. Bio-crude is the main product of HTL; however, due to the high water content used during the HTL process (typically 20 wt% dry matter – 80 wt% water), high volumes of aqueous phase are generated, and its treatment and valorisation can improve the technical

scalability and economic viability of the HTL process [28].

The composition of the hydrothermal liquefaction aqueous phase (HTL-AP) varies according to the processed feedstock and operational conditions [28]. In general, HTL-AP can contain high levels of organic pollutants and nitrogen, presenting high chemical oxygen demand values (COD) (10–90 g/L) [23]. Typical major components present in HTL-AP, irrespective the processed feedstock, include carboxylic acids (acetic acid, propionic acid, formic acid, etc.), alcohols, ketones, phenols, amines and other nitrogen containing components [10,24,26]. These characteristics are detrimental to the environment and proper treatment is required. Several technologies have been proposed for the valorisation of post-HTL process water. They include biological processes, such as anaerobic digestion for biogas production [2] and microalgae cultivation [16], and thermochemical processes such as hydrothermal gasification (HTG). The main problem of using HTL-AP in biological processes are the possible inhibitory and toxic effects due to

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recalcitrant compounds, such as phenolics, organonitrogen and organosulfur compounds, present in the HTL-AP, which limits the conversion of the organic compounds into desired products, requiring heavy dilution or pretreatment for its successful use [14,31]. HTG uses temperatures higher than 400 °C and catalysts to reform the organic compounds into hydrogen, methane, carbon monoxide, and carbon dioxide [27]. However, operational cost for HTG is high compared to other technologies due to the use of metal catalysts, which can suffer from poisoning due to the presence of sulfur in the HTL-AP. Another option that has recently been the subject of investigation for the treatment of HTL-AP is wet oxidation.

Wet Oxidation (WO) is an advanced oxidation technology, also classified as a hydrothermal technology carried out in oxidative atmospheres (air, oxygen, or hydrogen peroxide). WO is usually used for the treatment of high-concentration, toxic, hazardous, and refractory wastewaters [34], characteristics also found in HTL-AP. Subcritical WO usually takes place at temperatures between 120 and 370 °C and pressures higher than the vapour pressure of water [19]. In the presence of an oxidative atmosphere and heat, the organic pollutants are oxidised and degraded to volatile fatty acids (VFAs), non-aromatic alcohols, ketones, ammonia, CO₂ and H₂O [22]. WO has been used for the treatment of diverse types of wastewater, including effluents from the production of chemicals, pharmaceuticals, textiles, paper mills, olive processing, and even urban wastewater [13,33] and several commercial WO plants have already been established worldwide.

WO has recently been investigated for the treatment of HTL-AP, and three papers can be found in the literature. Tews et al. [25] investigated the use of catalytic wet oxidation to treat thermochemical aqueous effluent, which includes HTL-AP from poplar, using char catalysts in microreactors. They successfully removed 76 % of the COD of the HTL-AP, with a residence time of 10 min at 90 °C, using hydrogen peroxide as the oxidant [25]. Thomsen et al. [26] investigated the use of non-catalytic WO for the treatment of the aqueous phase from HTL of sewage sludge in batch reactors, achieving more than 97 % COD removal at 350 °C with a residence time of 180 min [26]. Kilgore et al. [10] investigated catalytic WO of HTL-AP from wet wastes at relatively low temperatures (175–225 °C) in batch and continuous trickle bed reactors and achieved COD reductions of up to 50 % and increased levels of acetic acid post treatment. WO₃, ZrO₂, CeZr as well as the HTL solid residue were identified as potentially suitable catalysts for catalytic WO [10]. The significant content of transition metals in HTL solids was suggested to promote the formation of free radicals that are more reactive under oxidation. Even though the utilization of HTL solids as catalysts for WO was found to have only a weak catalytic effect, it can have a combined effect of reducing the organic content of both the aqueous and the solid phases, in case that solids need to be disposed (e.g. in landfill, land application, etc.) [10].

Wet oxidation can be performed using different types of reactors. The reactor design takes into consideration the type of wastewater and the operational conditions required for its treatment. Other factors, such as the degree of reactant mixing, reactant contact, the hydrodynamic regime, the use of catalysts, and heat recovery, are also taken into consideration [11]. Several types of WO reactors have been proposed and commercially used. The most used reactor is the Zimpro process, developed by F.J. Zimmermann in the 1930 s [35]. The Zimpro process comprises a co-current bubble column that might contain an internal baffling to improve mixing conditions [7]. Some examples of WO reactors design include the "Wetox" reactor, developed by Fassel and Bridges [6], the Kenox wet oxidation process developed by Kenox Corporation of Canada [6], and the Oxyjet reactor system, which was developed by researchers at the Universidad Politecnica de Catalunya, Spain and the Universite de Sherbrooke, Canada [8].

The use of WO for treating HTL-AP presents possibilities for integrating hydrothermal liquefaction and WO reactors. Unlike in other proposed HTL-AP valorisation processes, such as AD and HTG where value added products are produced (biogas and syngas, respectively),

the main advantage of employing WO for HTL-AP valorisation lies in the utilization of the excess heat generated during the oxidation of the organics. Additional benefits may arise from the extraction of acetic acid and ammonia from post-WO-AP, which have been shown to be present in increase concentrations [26]. The HTL process requires an external heat supply for its operation, and this heat could be generated from the treatment of HTL-AP using WO, which produces excess heat from the exothermic reactions. Continuous HTL reactors are mainly built using tubular design as described by Anastasakis et al. [1]. To facilitate the thermal integration of HTL and WO, WO should be operated using tubular reactors to allow heat exchange and employing temperatures similar to those required in the HTL process.

This study investigates the use of a tubular continuous wet air oxidation (WAO) reactor for the treatment of the aqueous phase from hydrothermal liquefaction of sewage sludge at conditions similar to HTL operating conditions to allow future integration of the two processes. This novel integration will allow a more efficient process in terms of managing heating and cooling duties as well as converting large amounts of COD to biogenic CO₂, thereby facilitating much easier process water handling. The aim of the study was to verify the effectiveness of such a WO process configuration in reducing the COD at temperatures and residence times comparable to the HTL process (300–350 °C, 6–50 min) and evaluating the energy release and requirements of the process. In addition, advanced analytical techniques such as FT-Orbitrap MS were employed to give an unprecedented insight into the molecular characteristics and transformations of HTL-AP during WO.

2. Experimental methods

2.1. Continuous wet air oxidation reactor

The continuous wet air oxidation (WAO) reactor was custom built with 11 Inconel 625 alloy tubes with 1.18 m length, 8 mm diameter with 1 mm wall thickness, and fittings composed 316 stainless steel, giving a total volume of approximately 400 mL. The reactor is divided into seven sections: Feed system, heat exchanger, air compression system, trim heater, main reactor, cooler, take-off system, and product collection, a visual representation of the reactor is provided in Fig. 1. The feed system uses a MT8 metering pump (Wanner Hydra-Cell, USA) at different flow rates to achieve the desired residence time. The heat exchanger comprises a double pipes counter-current heat exchanger (4 tubes). They are divided into two convolutions, where the tubes pass through a split aluminium block with two half circle grooves of 8 mm diameter. One side houses the feed pipe and the other the return flow of the main reactor section to heat the inflow.

After the heater exchange, compressed air is inserted into the reactor system, which uses an air-driven booster pump (model GBT7/30 USUN, China), and a needle valve to control the airflow. After air insertion to the system, the mixture of the aqueous phase and air passes through the trim heater composed of 2 tubes, where the feed is heated to reaction temperature. Afterwards, the feed passes through the main reactor section consisting of 4 tubes, where the feed is maintained at the reaction temperature. After the main reactor, the stream passes through the heat exchanger, where the temperature is reduced. Afterwards, it goes through the water cooler, where the temperature is further reduced before the take-off system which uses a back pressure regulator (H62 Equilibar, USA) to maintain the reactor pressure and, at the same time, release depressurised WAO products. The depressurised flow is directed to a collection tank, where the aqueous product is collected, and the gas fraction flows to a drum type wet gas flow meter.

The trim heater and the main reactor are heated using seven independently controlled heating tapes, 3×940 W heating tapes for the trim heater and 4×468 W for the main reactor. The power input to each heater is logged electronically and used to calculate the energy consumption for heating of the process. The temperature and pressure are measured in 13, and 6 points, respectively, as shown in Fig. 1.

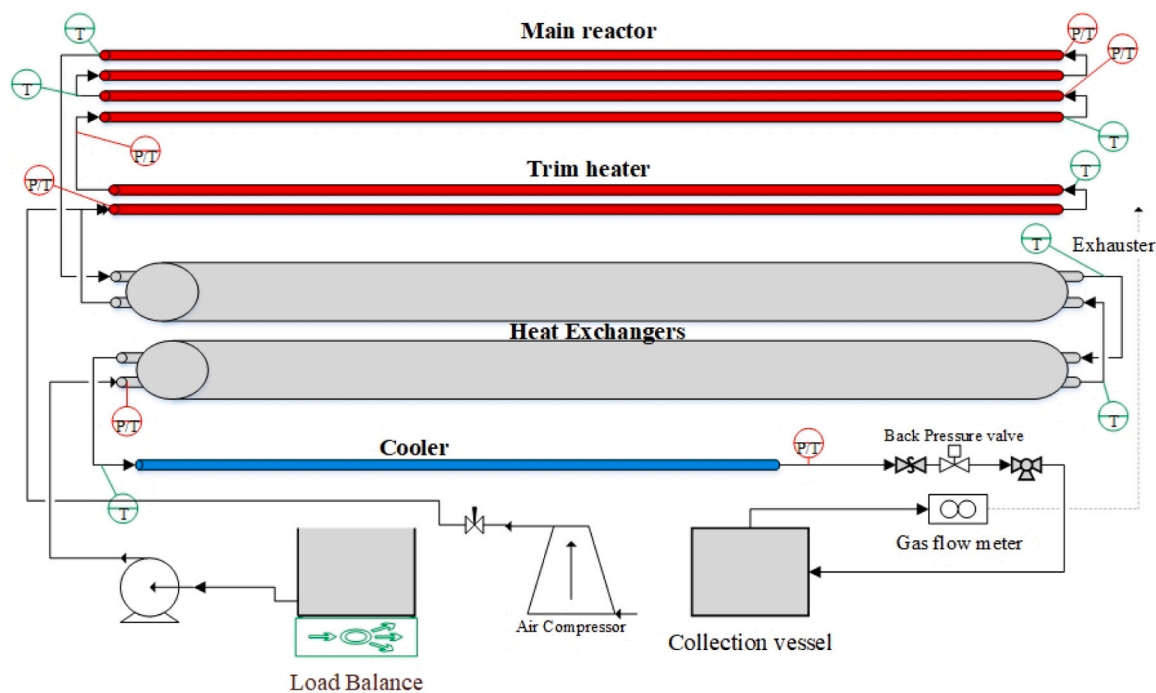


Fig. 1. Wet Air Oxidation reactor schematic.

2.2. WAO experiments

The WAO experiments were conducted at 300, 325, and 350 °C with different residence times and pressures higher than the equivalent water vapour pressure, as shown in Table 1.

The required airflow was calculated based on the COD of the HTL-AP, where excess O₂ between 1.5 and 2 times the COD requirement was provided, considering that the air is composed of 21 % O₂. Excess oxygen was supplied to ensure that the organics in HTL-AP can get completely oxidized and to drive the equilibrium towards the oxidation products. The residence time and reaction time were calculated based on the reactor's volume, flow rates, and the water density at the temperature gradient at each reactor section and pressure applied. The residence time is the total time of the HTL-AP in the reactor, from the pump until the collection vessel, and the reaction time is the time between the air injection until the cooler. Before the introduction of HTL-AP, the WAO continuous reactor is pre-heated to the desired temperature using water and air, with the regulated flows. After priming the reactor, a blank was performed for later comparison. When the reactor reached a steady state operation, 50 mL samples were collected at the beginning, middle and end of the experiment for further analysis to verify the reproducibility of the process by comparing it with the bulk collected product. Each experimental campaign collected around 4 L of aqueous product. After the experiments, the samples were stored at 2 °C, prior to analysis.

2.3. Analysis and calculation

The HTL-AP and post-WAO samples were analysed for chemical oxygen demand (COD), total organic carbon (TOC), total nitrogen (TN), and ammonium (NH₄⁺) using Merck Spectroquant cell tests (part numbers: COD-114541, TOC-114879, TN-114763 and NH₄⁺-114559).

The COD and TOC removal were calculated using the following:

$$COD_{removal}(\%) = (COD_{initial} - COD_{end}) / COD_{initial} * 100 \quad (1)$$

$$TOC_{removal}(\%) = (TOC_{initial} - TOC_{end}) / TOC_{initial} * 100 \quad (2)$$

The energy released (ER) by the exothermic reactions during WAO was calculated based on the COD removal in each experiment. A general heat value for the oxidation reaction of 435 kJ per mole of O₂ reacted was assumed based on the investigation performed by [5].

$$ER = COD_{removed}(mol) * 435 \left(\frac{kJ}{mol} O_2 \right) \quad (3)$$

The volatile fatty acids (VFAs) concentrations were analysed with a GC-FID (System 7890 A, Agilent Technologies, USA) with an HP-INNOWAX column (30 m, 0.25 μm, 0.25 mm, Agilent Technologies, USA), with helium as carrier gas. To determine volatile and semi-volatile compounds in the samples both before and after wet air oxidation, gas chromatography-mass spectrometry (GC-MS) was utilised. The aqueous samples were derivatised using methyl chloroformate (MFC) as part of

Table 1

Wet air oxidation operational conditions at low (LF), medium (MF) and high flows (HF).

Temperature (°C)	Code	Residence time (min)	Reaction time (min)	Pressure (bar)	Flow rate (g min ⁻¹)	Airflow (NL min ⁻¹)
300	300-HF	10.1	5.3	180	47.0	12.1
	300-MF	16.5	8.8	180	28.9	8.2
	300-LF	46.5	24.3	170	10.2	3.0
325	325-HF	6.5	3.4	180	71.6	16.9
	325-MF	27.5	14.2	170	16.4	5.1
	325-LF	44.4	22.9	170	10.5	3.2
350	350-HF	6.9	3.7	190	64.2	16.1
	350-MF1	17.5	8.6	190	25.4	7.8
	350-MF2	27.1	13.4	190	17.0	5.2
	350-LF	49.5	24.8	190	8.9	3.1

the procedure. This method was described by [12].

Comprehensive chemical speciation analysis was conducted using the Orbitrap Exactive Plus instrument (Thermo-Fisher Scientific), coupled with a HESI-II probe. SHTL-AP and WAO samples were prepared at a concentration of 300 $\mu\text{g mL}^{-1}$ in methanol and were directly infused into the ionization source at a flow rate of 30 $\mu\text{L min}^{-1}$. Mass spectra were acquired at a mass resolution of 140,000 FWHM (full width at half maximum) at m/z 200. In the negative ion mode, operational parameters were set as follows: sheath gas flow at 10 arbitrary units (AU), ion source temperature at 100 °C, capillary temperature at 300 °C, and spray voltage at -3.8 kV. For the positive ion mode, conditions included sheath gas flow at 10 AU, auxiliary gas flow, and sweep gas flow at 2 and 1 AU, respectively. The ion source temperature was maintained at 120 °C, capillary temperature at 320 °C, and spray voltage at $+3.8$ kV. The scanning range for both ionization modes spanned 100–1000 Da. In each mode, the final mass spectrum of each sample was derived after subtracting the mass spectrum of the blank. Data processing was executed using Xcalibur 3.0.63 software (Thermo-Fisher Scientific, Inc.). To ensure precise assignment of molecular formulas, composition constraints were adjusted to facilitate the assignment of isotopic formulas containing ^{12}C , ^1H , ^{16}O , ^{14}N , and ^{23}Na , with a tolerance error ≤ 3 ppm. Criteria for assigning molecular formulas in the negative mode were established as follows: $^{12}\text{C}_{4-50}$, $^1\text{H}_{4-100}$, $^{14}\text{N}_{0-3}$, $^{16}\text{O}_{0-15}$; double bond equivalent (DBE) 0–35; and charge -1 . Conversely, in positive ion mode, the criteria encompassed $^{12}\text{C}_{4-50}$, $^1\text{H}_{4-100}$, $^{14}\text{N}_{0-3}$, $^{16}\text{O}_{0-15}$, and $^{23}\text{Na}_{0-1}$; DBE 0–35; and charge $+1$. Post-assigned elemental compositions, the data underwent transfer to Microsoft Excel for consistency analysis of molecular assignments, employing criteria outlined in [20]. Class histograms and contour plots were subsequently generated, with consideration given only to ions with relative intensities ≥ 0.01 .

3. Results and discussion

3.1. HTL aqueous phase origin and characteristics

The HTL-AP used in the WAO experiments was produced using the AU pilot-scale continuous HTL reactor. The HTL reactor is described by [1]. The HTL-AP was produced using the same sludge proportions as produced at the WWTP of Fredericia Spildevand og Energi A/S (Denmark) of 29 % primary sludge, 71 % secondary sludge, based on dry weight. The mixed sludge had a dry matter content of 12 % and was processed at 325 °C at a flow rate of about 50 L h^{-1} . The HTL-PW was separated from the biocrude by gravity and stored at ambient conditions until further use. For this specific HTL run the yields of bio-crude, gas, solids and AP were not quantified. The same sludge was however processed at the same conditions in batch reactors [21] and yielded 33 % bio-crude, 24 % solids residue, 34 % AP and 9 % gas; it is therefore expected that the continuous run would have resulted in a similar mass balance. The HTL aqueous phase characteristics are shown in Table 2. The HTL-AP contains a high concentration of COD, TOC, and TN. The carbon in VFAs corresponds to 16.3 % of the TOC, and the nitrogen in NH_4^+ and NO_3^- correspond to 37 % and 0.7 % of the TN respectively. The pH was slightly basic (7.6) due to the concentrations of NH_4^+ and VFAs. Regarding energy content, the HTL-AP can release 584.5 kJ L^{-1} , considering total COD removal.

3.2. WAO effectiveness

The effectiveness of the WAO process is assessed by its capacity to reduce COD and TOC concentrations. Fig. 2 shows the COD removed, the theoretical energy released, and the TOC removed in the WAO process at different temperatures and residence times. The highest COD and TOC removal were achieved at 350 °C with a residence time of 49.5 min, 95.3 and 91.8 %, respectively, as expected since higher temperatures and RT increase the degradation of organic compounds into

Table 2

Characteristics of the HTL-AP.

	mg L^{-1}	HTL-AP	$\pm$
COD		43000	800
TOC		12480	120
TN		4600	100
NH_4^+		2190	90
NO_3^-		146.5	4.8
pH		7.6	0.1
Acetic Acid		2654	140.1
Propanoic Acid		828.4	0.2
Isobutyric Acid		92.9	0.1
Butyric Acid		426.7	1.8
Isovaleric Acid		183.8	2.4
Valeric Acid		169.5	2.2
Isohexanoic Acid		70.4	8.3
Hexanoic Acid		29.4	1.5
Heptanoic Acid		15.2	2.9
Energy content	(kJ L^{-1})	584.53	10.9

CO_2 and lower molecular weight organic compounds.

The experiments at 325 and 350 °C showed similar results at the low residence time of 7 min, with a COD removal of around 40 % and TOC removal of approximately 35 %. At 300 °C, the removal was slightly lower if interpolating the result of 300 °C linearly, at 10 min its removals were 39.5 % COD and 30.6 % TOC. The higher removal rates at short residence times show that a high fraction of the organic compounds is easily degraded at the operational conditions investigated. At longer RT, the experiments at 300 and 325 °C presented similar COD and TOC removals, around 74 and 61 %, respectively. However, the degradation rate at 325 °C was higher in the first 30 min compared to the experiment at 300 °C. The difference between the COD and TOC removals, where the TOC values are lower than the COD, is due to the oxidation of organic compounds, which generated organic by-products that contain more C-O bonds, which reduces the COD values.

3.3. Energy release

The theoretical energy released was calculated based on the COD removal, as shown in Eq. 3. Following the trend of COD removal in Fig. 1, the energy released in the first 7 min of RT at 325 and 350 °C, and after 10 min at 300 °C, was around 230 kJ L^{-1} . The highest energy released was 557 kJ L^{-1} at 350 °C after 49.5 min of RT, and at 300 and 325 °C, the energy released was approximately 435 kJ L^{-1} after 46.5 and 44.4 min, respectively.

The energy consumption reduction was calculated based on the collected data from each experiment and their corresponding blank, comparing the temperature profiles in the heat exchanger (HE) and the energy consumption of the trim heater and main reactor sections, as shown in Table 3. The reduction in energy consumption was between 18 % and 40 % at 300 °C, 13 and 37 % at 325 °C, and 14 and 21 % at 350 °C. The highest reduction at 300 and 350 °C was achieved in the experiments with high flow (HF), while at 325 °C, the highest reduction was at the lowest flow (LF). The energy consumption was reduced between 0.19 and 0.36 kWh L^{-1} at 300 °C, 0.08 and 1.17 kWh L^{-1} at 325 °C, and 0.13 and 0.43 kWh L^{-1} at 350 °C. These results show that heat was released by the WAO process, reducing the energy requirement compared to the blanks. The total WO energy requirement using the reactor including all heat losses ranged from 0.34 to 2.98 kWh L^{-1} . Taking into consideration the amount of COD converted in this window the energy requirement can be recalculated as $\text{kWh kg}^{-1} \text{COD}_{\text{removed}}$ for comparison. The current work results in values from 21 to 76 $\text{kWh kg}^{-1} \text{COD}_{\text{removed}}$. Although conventional WWTP would struggle with such high COD loads as found in HTL-AP they are estimated to only require between 0.03 and 7.1 $\text{kWh kg}^{-1} \text{COD}_{\text{removed}}$ [3], electrochemical oxidation, required 9–39 $\text{kWh/kg COD}_{\text{removed}}$ for HTL-AP [15]. It should be noted that the theoretical energy requirement to heat water from 25 to 350 °C

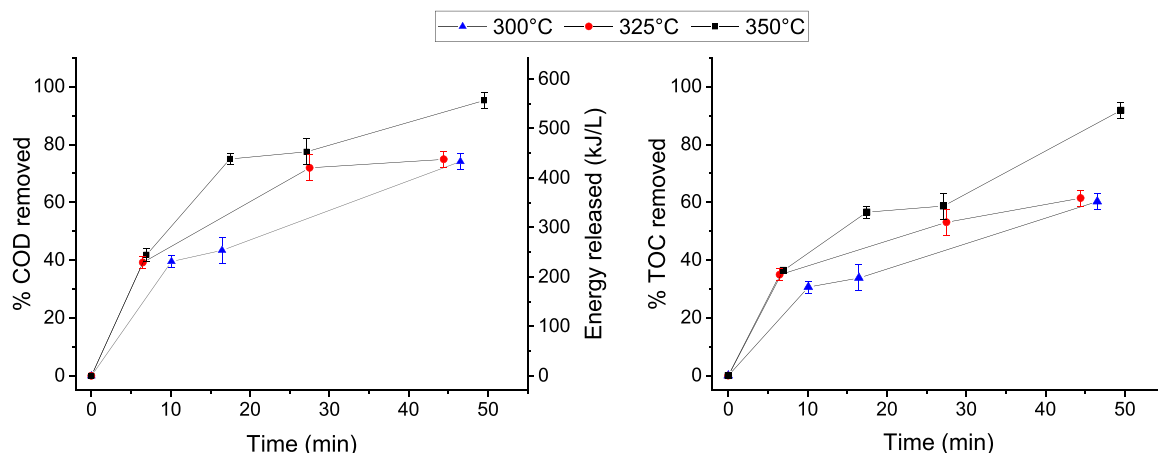


Fig. 2. COD removal and energy released (left) and TOC removal (left) at different temperatures and residence times.

Table 3

Heat recovery and Energy consumption of the WAO process.

T (°C)	Sample	Heat recovery – Heat exchanger (%)	Trim heater energy consumption (kWh L ⁻¹)	Main reactor energy consumption (kWh L ⁻¹)	Total energy consumption (kWh L ⁻¹)	Energy consumption reduction (kWh L ⁻¹)	Energy consumption reduction (%)
300	300-HF	76	0.16	0.19	0.34	0.23	40
	300-HF-blank	72	0.31	0.26	0.57		
	300-MF	69	0.22	0.36	0.58	0.19	24
	300-MF-blank	68	0.35	0.43	0.77		
	300-LF	61	0.98	0.72	1.70	0.36	18
	300-LF-blank	59	1.05	1.01	2.06		
325	325-HF	70	0.23	0.28	0.51	0.08	13
	325-HF-blank	65	0.24	0.35	0.58		
	325-MF	73	0.73	0.78	1.51	0.77	34
	325-MF-blank	72	1.00	1.29	2.29		
	325-LF	63	1.03	0.95	1.98	1.17	37
	325LF-blank	62	1.60	1.56	3.16		
350	350-HF	67	0.26	0.26	0.52	0.13	21
	350-HF-blank	62	0.26	0.39	0.65		
	350-MF1	67	0.61	0.55	1.16	0.19	14
	350-MF1-blank	63	0.66	0.69	1.35		
	350-MF2	58	0.60	0.60	1.20	0.24	16
	350-MF2-blank	50	0.72	0.72	1.43		
	350-LF	55	0.94	1.61	2.55	0.43	15
	350-LF-blank	50	1.09	1.89	2.98		

is only 0.384 kWh L⁻¹ without taking any heat exchangers into account vs the measured 0.52–2.98 kWh L⁻¹. Therefore, the current numbers should not be seen as actual energy requirements and accurate comparisons to other technologies, rather the aim is to highlight the heat release and differences of employing WAO or not.

The heat recovery in the heat exchanger only achieved efficiencies between 55 % and 76 % for the experiments using the HTL-AP and between 50 % and 72 % for the blanks. The heat exchanger results of the experiments using HTL-AP were consistently higher than the respective blank. This can be due to ongoing exothermic reactions at the heat exchanger, providing heat compared to the blank using water. The high energy consumption and low heat exchanger effectiveness highlight the importance of good reactor design and heat management.

Fig. 3a, 3b, and 3c show the WAO temperature profiles of the experiments with the HTL-AP and respective blanks at 300, 325, and 350 °C at the lowest flow rates. The temperature profiles for the remaining flow rates are included in the [supplementary information, Figures S1–S7](#). Auto-thermal operation was not achieved during the experiments. At the exit of the inflow heat exchanger the temperature dropped, e.g., at 350 °C the temperature dropped from 275 to 210 °C. This can be due to air insertion into the reactor at temperatures below the temperature of the aqueous flow. The air was inserted before the trim heater section, and the thermocouple was positioned at this point. The drop in temperature

after the heat exchanger was not observed when running with high flow, as observed in [Figure S1 and S3](#). This can be due to different HTL-AP to air ratio, where the high flows presented slightly higher ratio compared to the low flows.

When analysing the heat exchanger temperatures, it is possible to observe at the inflow heat exchanger that, if the increase in temperature followed the trend of the temperature in the middle of the heat exchanger higher temperatures after the heat exchanger could have been achieved, significantly reducing the energy consumption at the trim heater. Another point observed is the rapid temperature increase after the first part of the heat exchanger inflow of HTL-AP compared to the blank, e.g., at 350 °C, from 12 to 275 °C for HTL-AP and 21–210 °C for the blank. These significant differences can be due to exothermic reactions occurring in the inflow of the heat exchanger, which was not expected since the air was only inserted after the HE, the exothermic reactions can be due to oxygen mass transfer inside the reactor reaching the middle of the HE, or the presence of dissolved oxygen in the HTL-AP. If exothermic reactions were happening in this section, part of the possible heat recovery capacity could be lost. In addition, observing the temperature trend at the outflow of the heat exchanger, the temperature of HTL-AP was still high, e.g., at 325 °C the temperature was 196 °C before the cooler, and to fully recover the heat, a larger and more efficient heat exchanger would be required. To achieve auto-thermal

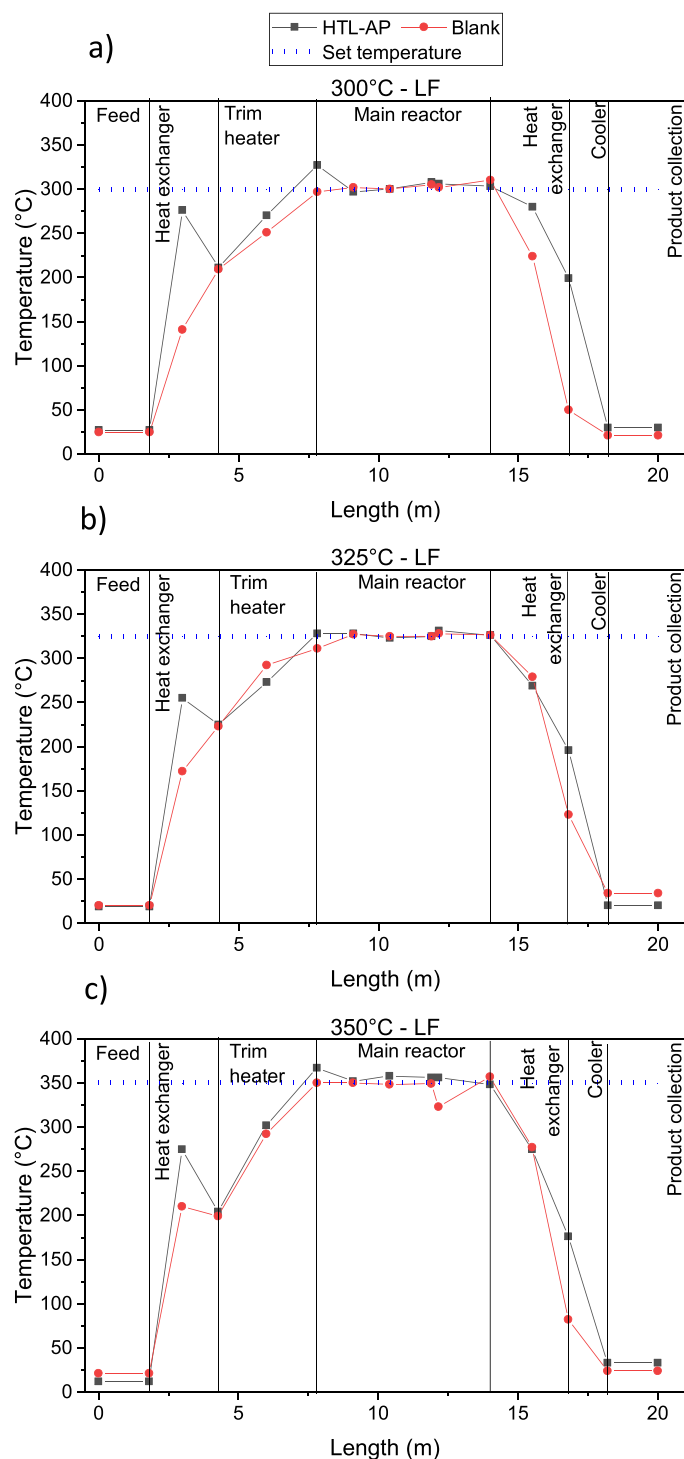


Fig. 3. Temperature profiles of the WAO reactor at different temperatures (a, b, c) and similar flow rates.

operations, the air should be at temperatures similar to the aqueous stream at the point of the air insertion, this can be done by inserting the air before the heat exchanger or by heating the air stream before injection. Improvements to the heat exchanger are also required, which needs to recover most of the heat of the outflow, this can be done by increasing its length or design. In addition, good isolation is required to reduce heat losses during WAO operation.

3.4. The fate of organic compounds

FT–Orbitrap MS spectra for HTL-AP encompassed 2254 and 2833 detected ions in the negative and positive modes, respectively, considering a signal-to-noise ratio higher than 3. The total number of peaks was significantly reduced after WAO treatment, primarily influenced by the residence time and process temperature. Acidic species ((–)-HESI) decreased by 42 %, 37 %, and 63 % at 300, 325, and 350 °C, respectively, while basic species ((+)-HESI) decreased by 59 %, 58 %, and 66 % for the same temperatures (Table S1). This corroborates the COD and TOC reductions discussed in Fig. 2 and is associated with the decrease in molecules from classes $NxOy$, Oy , and Nx (Figure S8). The basic compounds profile in HTL-AP exhibited the most intense region between 100 and 150 Da, with an average carbon number (CN) of 8 and a low presence of unsaturation (DBE= 3.7). Less intense ions extended up to 300 Da. Acidic compounds were found within the same mass range, with CN= 6 and DBE= 2.9. In general, the WAO process at 350 °C resulted in the aqueous phase containing fewer acidic oxygen-containing compounds (O/C = 0.45–0.12) and fewer acidic nitrogen-containing compounds (N/C = 0.10–0.02). Additionally, more basic oxygen-containing compounds (O/C = 0.10–0.21) were observed (Table S3).

The complex matrix of the HTL-AP compounds makes the estimation of reaction pathways difficult. However, the reaction pathways can be simplified by the decomposition of organic compounds into intermediaries, such as acetic acid, followed by their oxidation into CO_2 and H_2O . In this investigation, nine volatile fatty acids are quantified: acetic, propanoic, isobutyric, butyric, valeric, isohexanoic, hexanoic, and heptanoic acid. The complete list containing the VFAs concentrations in mg/L is provided in Table S3. In Fig. 4 is possible to observe the generation and decomposition of VFAs normalised to 100 % for the untreated HTL-AP.

Almost all experiments resulted in concentrations of acetic acid in the WAO products higher than the initial concentration in HTL-AP (2654 mg L^{-1}). At 300 °C after 16.5 min RT, the concentration of acetic acid was 1.8 times higher than the initial concentration, the highest achieved in this study (4789 mg L^{-1}). After 46.5 min RT, the concentration was 1.7 times higher, showing that the degradation of acetic acid can occur at 300 °C but at a low rate. The concentration of acetic acid at 325 °C peaked after 6.5 min (4038 mg L^{-1}), reaching 1.5 times more than the untreated sample. After that, the concentration decreases to 3508 mg L^{-1} after 27.5 min RT and increases to 3808 mg L^{-1} after 44.5 min RT. This shows that the generation and degradation of acetic acid occur simultaneously. At 350 °C, the concentration of acetic acid reaches approximately 4600 mg L^{-1} after around 7 min RT, equivalent to 1.7 times more than the HTL-AP. After 7 min, the concentration starts to decrease, reaching around 4170 mg L^{-1} after 17.5 and 27.1 min, and after 49.5 min, it reached 1198 mg L^{-1} , which is the lowest concentration found in this investigation, equivalent to approximately half of the initial concentration. This shows that, after around 27 min at 350 °C, the degradation of acetic acid occurs at a significantly higher rate than at the other temperatures investigated.

The other VFAs present significant lower concentrations than acetic acid. Isobutyric acid appears as a WAO intermediary compound at 300 °C reaching concentrations 1.4 times higher than HTL-AP, and at the low RT at 325 and 350 °C, it reached a 1.3 times increase. The concentration of propanoic and heptanoic acid increased after 46.5 min at 300 °C, reaching 1130 and 29.3 mg L^{-1} , respectively, which is 1.4 and 1.9 times higher than the initial concentration of the untreated sample.

The other VFAs, besides the previously mentioned, presented the same or lower concentrations after WAO. At 300 °C, the concentration of butyric, isovaleric, valeric, isohexanoic, and hexanoic acids was between 0.4 and 0.7 times lower than the initial concentration. At 325 °C, the concentration of heptanoic acid remains almost the same regardless of the RT. At 350 °C after the highest RT, practically complete degradation of all VFAs, besides acetic acid, was achieved.

The degradation and formation of VFAs are correlated to the

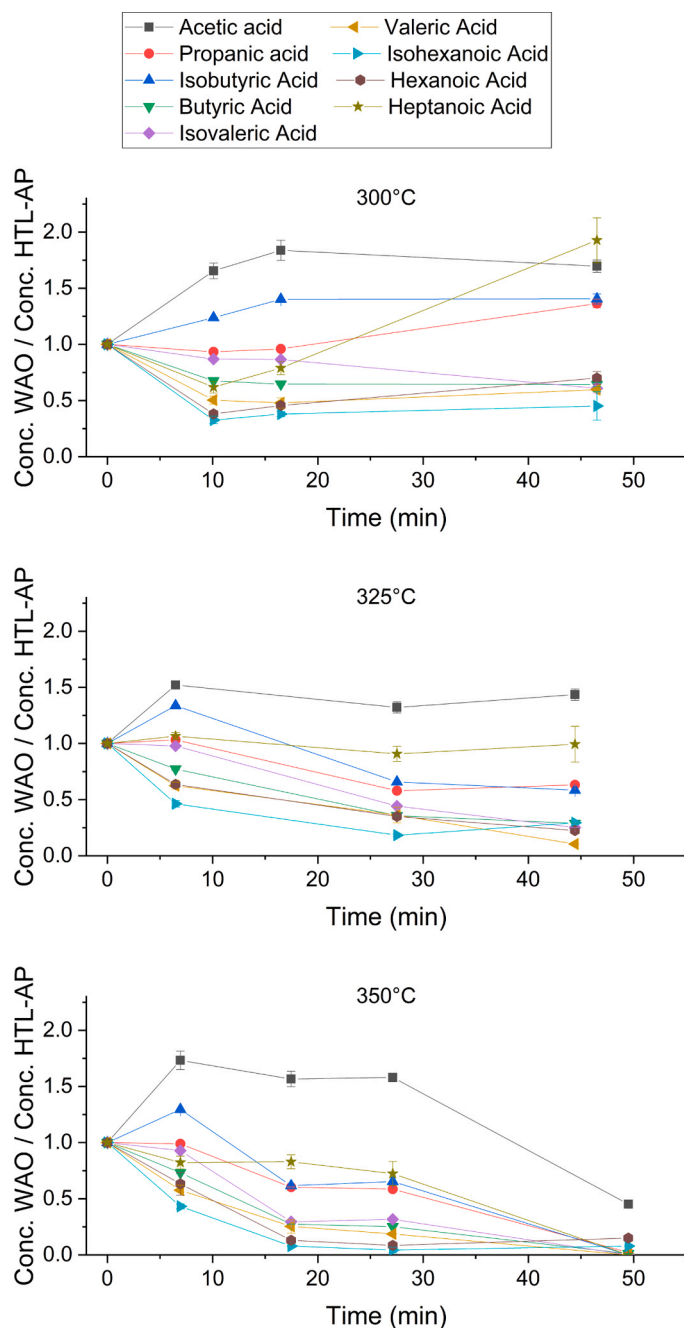


Fig. 4. VFAs generation and degradation during WAO at different temperatures and residence times.

reduction of the TOC during the WAO experiments. The degradation of the organic compounds and the formation/degradation of VFAs were evaluated, taking into consideration the carbon content of the VFAs, as shown in Fig. 5. The highest portion of VFAs-TOC was achieved at 300 °C, after 46.5 min, VFAs-C corresponded to 55.4 % of the TOC. At 325 °C the highest fraction of VFAs in TOC was 40.3 % after 44.5 min, and at 350 °C was 48.5 % after 49.5 min. Besides the experiment at 300 °C, it is possible to observe that the concentration of VFAs increases at short RT followed by a decrease, showing that their degradation at 325 and 350 °C is higher than their formation as WAO intermediaries. At 300 °C, the VFAs concentration only increases, presenting a higher formation than degradation rates. The reduction of TOC presents a higher rate than the reduction of VFAs, as observed in Fig. 4, the fraction of VFAs increases over time at all temperatures investigated. The proportions of VFAs-TOC

obtained in this study are similar in comparison to the investigation made by Thomsen et al. [26], where around 57 % reduction at 300 °C and 50 % at 350 °C of the TOC was achieved in the form of VFAs after 60 min of residence time [26]. This effect confirms that the oxidation of VFAs, mainly acetic acid, is harder, requiring higher RT or catalysts.

The high concentration of VFAs in the post-WAO process water brings attention to their possible valorisation. VFAs have diverse applications in different types of industries, such as chemical, tanning, food-beverage and pharmaceutical [18]. In addition, VFAs are essential as an energy and carbon source for various microorganisms used in the different biotechnological processes, e.g., anaerobic digestion for biogas production, microbial lipid accumulation, microbial electrolysis for hydrogen production, and polyhydroxyalkanoates (PHA) production.

GC-MS was used to identify 101 organic compounds, which were separated into two categories, organic compounds containing Nitrogen or Sulfur, which correspond to 62 compounds, and oxygenated organic compounds containing 39. In this section, the 39 oxygenated organic compounds were classified into six different groups, taking into consideration their structure and nature: Alcohols (2-Butanol), aromatic compounds (phenolic compounds), cyclic ketones (cyclopentanone, butyrolactone), esters/ethers (Methyl acetoxyacetate), ketones (3-Pentanone), and organic acids (Propanoic acid, Butanedioic acid). To better visualise the degradation of the compounds in the organic acids group, acetic acid was not included in the list due to its increase in concentration as previously observed. The complete list of compounds, including the area, the sum of the compounds' area of the different groups, the retention time, and the match factor, are included in Tables S4-S6.

Fig. 6 depicts the degradation patterns of the determined groups after WAO at 300, 325, and 350 °C based on the sum of the peak areas of the specific group before and after WAO. From the groups' list, cyclic ketones present the lowest degradation rate during WAO, where around 80 % can be found in the WAO product at 300 °C in all RT and at 325 °C in the first 27.5 min reducing to approximately 60 % after 44.5 min RT. At 350 °C, around 65 % of the cyclic ketones can be found, and after 49.5 min, they are completely degraded. Cyclic ketones can be intermediary compounds generated from the oxidation of aromatic compounds, as proposed by Joglekar et al. [9], which investigated the kinetics of WAO of phenols and substituted phenols [9].

Aromatic compounds appear as the second most difficult to degrade; at 300 °C, the concentration remains almost stable, representing around 42 % of the initial concentration in the HTL-AP. At 325 °C, the concentration represents 58 % in the short RT, reducing to 13 % after 44.5 min. Their reduction at 350 °C is faster, containing around 20 % after 7 min, and almost complete degradation at the highest RT. Esters/Ethers presented an increase after 16.5 min at 300 °C, possibly due to their formation as intermediaries to the degradation of other organic compounds. The removal of the other groups presents a higher rate, increasing with higher temperatures, reaching almost complete degradation of all investigated compounds at 350 °C after 49.5 min RT.

3.5. The fate of organonitrogen and organosulfur compounds

The HTL-AP can present different compositions due to the composition of the feedstock and operational conditions. In the case of this study, the feedstock used was sewage sludge, which contains significant levels of proteins in its composition, which can generate soluble organonitrogen compounds in the HTL-AP; the same effect is proposed for organosulfur compounds present in sewage sludge that can end in the HTL-AP.

In this section, 60 organonitrogen compounds were detected by GC-MS; these compounds were then classified into two groups, N compounds (24 compounds, e.g. amines, amides, and carbamates) and N cyclic compounds (36 compounds, e.g. pyridine, pyrazine). Two organosulfur compounds were detected, Ethanone, 1-(2-thienyl)- and 3-Thiophenecarboxylic acid, and were classified as S compounds. As for the

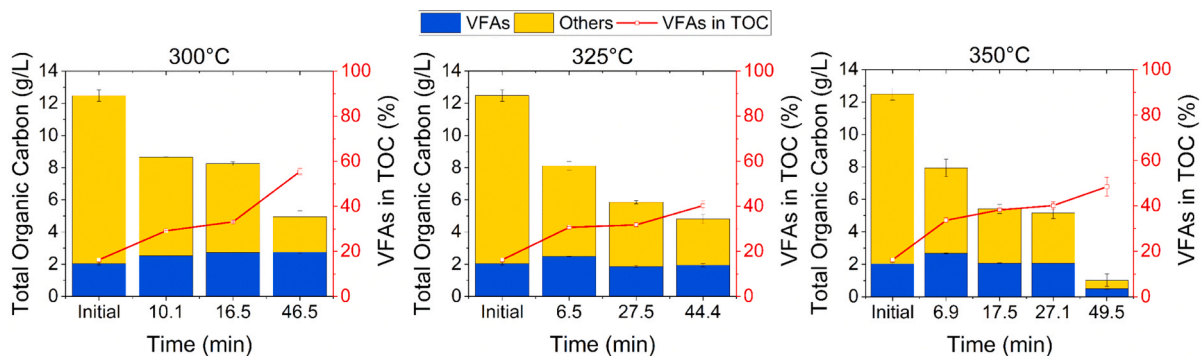


Fig. 5. TOC removal and VFAs proportion during the WAO process.

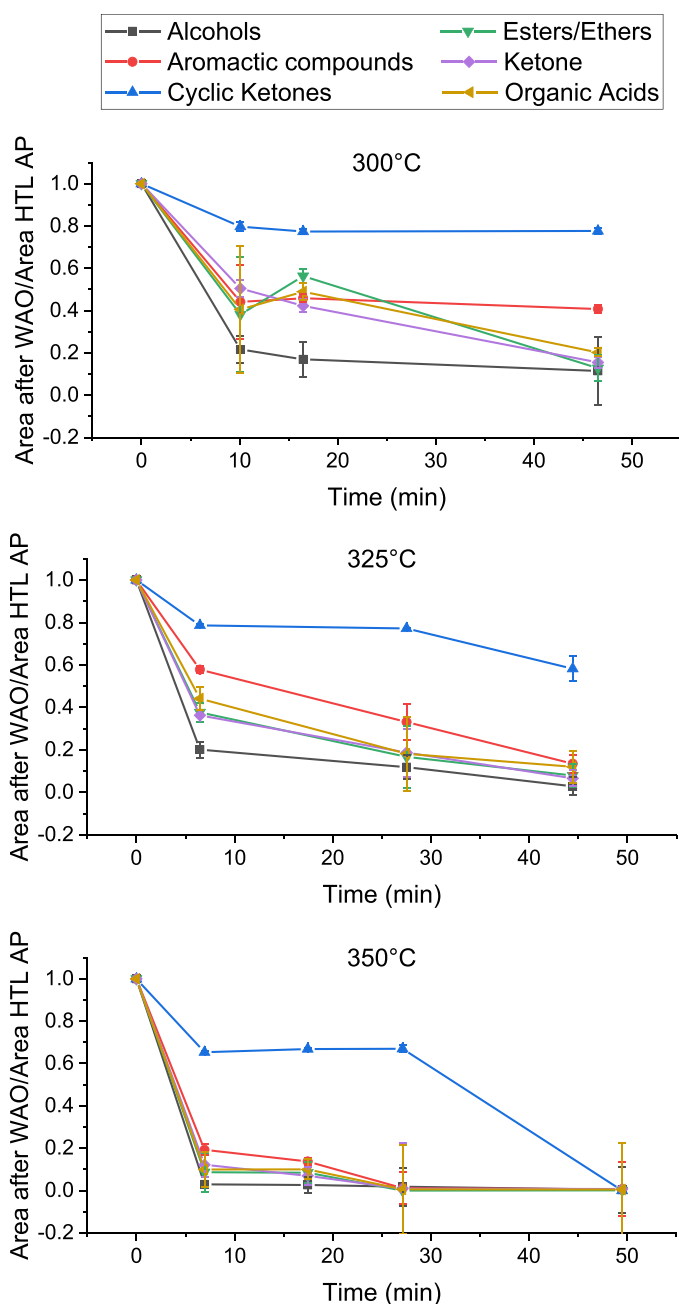


Fig. 6. Degradation of oxygenated organic compounds during WAO detected by GC-MS.

previous section, the sum of the peak areas of the groups was compared to the initial values in the HTL-AP, as shown in Fig. 7.

The organonitrogen and organosulfur compounds were degraded at a high rate at short RT, followed by a slow degradation. The N compounds presented the highest degradation in all temperatures, presenting around 20 % of the initial concentration in the HTL-AP in short RT at 300 and 325 °C. N cyclic compounds and S compounds had a lower rate of degradation compared to N compounds due to the structure of the compounds, which contains rings that are harder to oxidize. At 350 °C, all the compounds were almost completely degraded after 27.1 min. At the highest RT, 31 % of the N cyclic compounds remained in the WAO product at 300 °C; at 325 °C, it was 18 %.

The degradation of organonitrogen during WAO generates NH_4^+ and NH_3 since the oxidation of nitrogen is not expected in the reaction conditions used in this investigation. At lower WAO temperatures (<200 °C) organonitrogen compounds can initially form NO_3^- but as the severity increases these are consumed to produce additional NH_4^+ . At the lowest WAO severity NO_3^- concentrations reduced from initially 147–110 mg L^{-1} to finally 1.6 mg L^{-1} at 350-LF, in line with previous published literature on WAO of N containing wastes [30]. The total nitrogen and NH_4^+ of the samples before and after WAO were measured to better understand the degradation of organonitrogen during the process at different temperatures and RT, as shown in Fig. 8.

In Fig. 8, it is possible to observe the increase in the ammonium fraction of the TN over time (nitrate was insignificant). These results are in line with the degradation of the organonitrogen compounds observed in the GC-MS and FT-Orbitrap MS analysis. Before the treatment, the HTL-AP contained 4600 mg L^{-1} of TN, of which 37 % composed of ammonium. After WAO at the respective longest residence times, the ammonium fraction of the TN increased to 84 % at 300 °C, 76 % at 325 °C, and 97 % at 350 °C. The ammonium fraction of TN at 325 °C was lower than at 300 °C, but the ammonium concentration was similar, around 4000 mg L^{-1} . The difference is due to the reduction of the TN in the samples due to the release of NH_3 in the gas phase. Overall, the nitrogen balance shows that up to 22 % of nitrogen is removed at the most severe conditions where the ammonium is also at the highest levels, this reduction in TN is hence attributed to loss of NH_3 to the gas phase.

Degradation of organonitrogen compounds in the continuous process is similar to the batch reactor investigation performed previously, which achieved around 70 % of ammonium in the wet oxidation product after 60 min at 300 °C, and about 90 % at 350 °C [26]. The presence of organonitrogen compounds, especially N-containing heterocyclic compounds present in the HTL-AP from sewage sludge, is a challenge for biological processes [29], and the WAO process could almost completely degrade such compounds. However, a high concentration of ammonium can also inhibit some biological process, e.g. anaerobic digestion for biogas production [32].

The high concentration of ammonium in the WAO product, up to 4600 mg L^{-1} , brings the opportunity for its recovery. Ammonium can be recovered for the production of fertilisers, and several methods can be

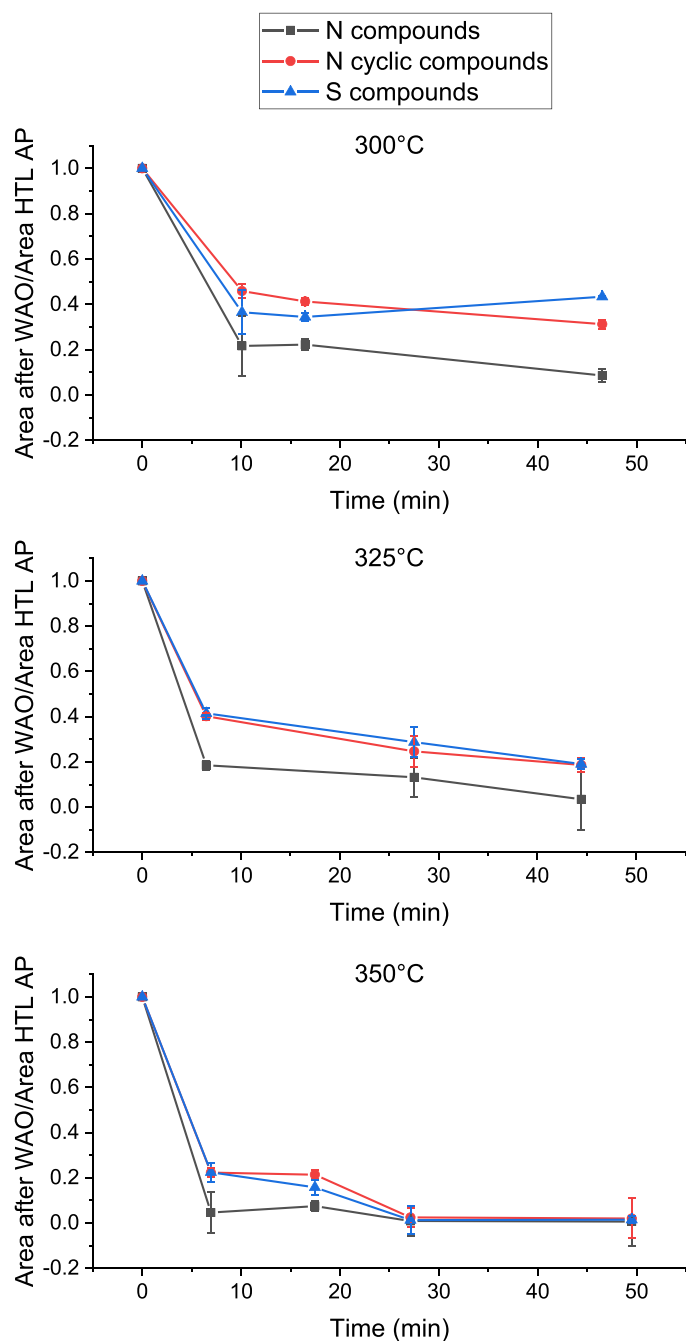


Fig. 7. Degradation of organonitrogen and organosulfur compounds during WAO detected by GC-MS.

used, Cruz et al. [4] listed the mainstream ammonium recovery technologies, which include air stripping, membrane technologies, electrochemical processes, bioelectrochemical systems, electrodialysis, struvite precipitation, ion exchange and adsorption, and biological assimilation [4]. In the context of integrating wastewater treatment plants, HTL and WAO, struvite precipitation appears as a good option for fertiliser production (as shown previously by e.g. Ovsyannikova et al., [17], where phosphorus present in the HTL solids can be extracted and then precipitated using the ammonium present in WAO products.

3.6. FT-Orbitrap MS analysis for assessment of changes on polar organic compounds of HTL-AP caused by WAO

HTL-AP presents an analytical challenge in understanding the impact of the treatment process on its chemical constituents. This challenge primarily arises due to the high polarity and solubility of the compounds and, secondarily, from the large quantity of representative compounds from various chemical classes, which together constitute a highly complex mixture. Directly infusing the sample into ($\pm$)HESI-FT-Orbitrap MS analysis without prior pre-treatment can help understand the molecular changes of organic compounds. The use of ultra-high resolution mass spectrometry analysis is not used for reactivity investigation but as a qualitative proposal to separate hundreds of compounds by their atom constituents.

Considering the WAO at 350 °C with 50 min of RT as the most representative for evaluating the chemical changes, the modifications are presented in Fig. 9 in the form of Kendrick and van Krevelen diagrams. Comparing the diagrams A (1–4) and B (1–4), which are associated with acidic species, it is evident that the WAO process increased oxygenated species of low molecular mass (100–150 Da). The B2 diagram demonstrated an increase in compounds with O/C ratios ranging from 0.2 to 0.8, primarily due to the compounds distributed in the O₂ and O₄ classes (Figure S9). In the B3 diagram, it is observed that while organonitrogen compounds remain unaffected, in the treated sample there is an increase in the H/C ratio, likely attributed to the defunctionalization of oxy-nitrogen groups, such as O₃N₁ (Figure S10). The B4 diagram confirms the oxygenation of compounds, particularly evident in compounds with N/C = 0, resulting in an increase in the O/C and H/C ratios among the remaining compounds.

For basic species, the diagrams showed more pronounced changes in the molecular composition of HTL-AP after the WAO process at 350 °C. The degradation of compounds is pronounced in D1, with compounds having a molecular mass higher than 200 Da being the most affected. The remaining few compounds are less oxygenated and nitrated, as evidenced by van Krevelen diagrams D2 and D3. Diagram D4 shows that classes Nx (O/C = 0) are most affected. Detailed analysis (Figure S11) shows that the classes N₁ and N₂ are predominantly influenced by the treatment, which aligns with previous results, including TN analysis. Decrease in the intensity of NxOy (N/C = 0.1–0.4; O/C = 0.1–0.4) classes in diagram D4 are related to the impact of WAO in the N₁O₁ class. The relative increase in the intensity of N₁O₂ and N₁O₃ can be caused by the

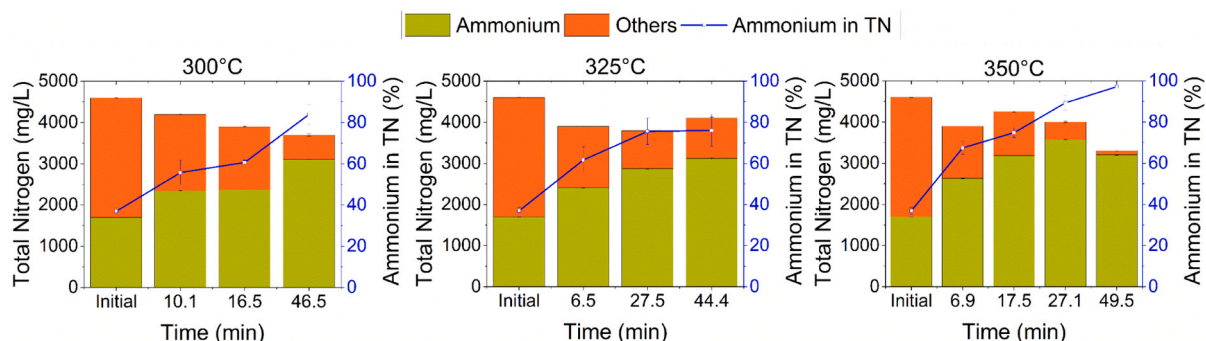


Fig. 8. Total Nitrogen and ammonium proportion during the WAO process.

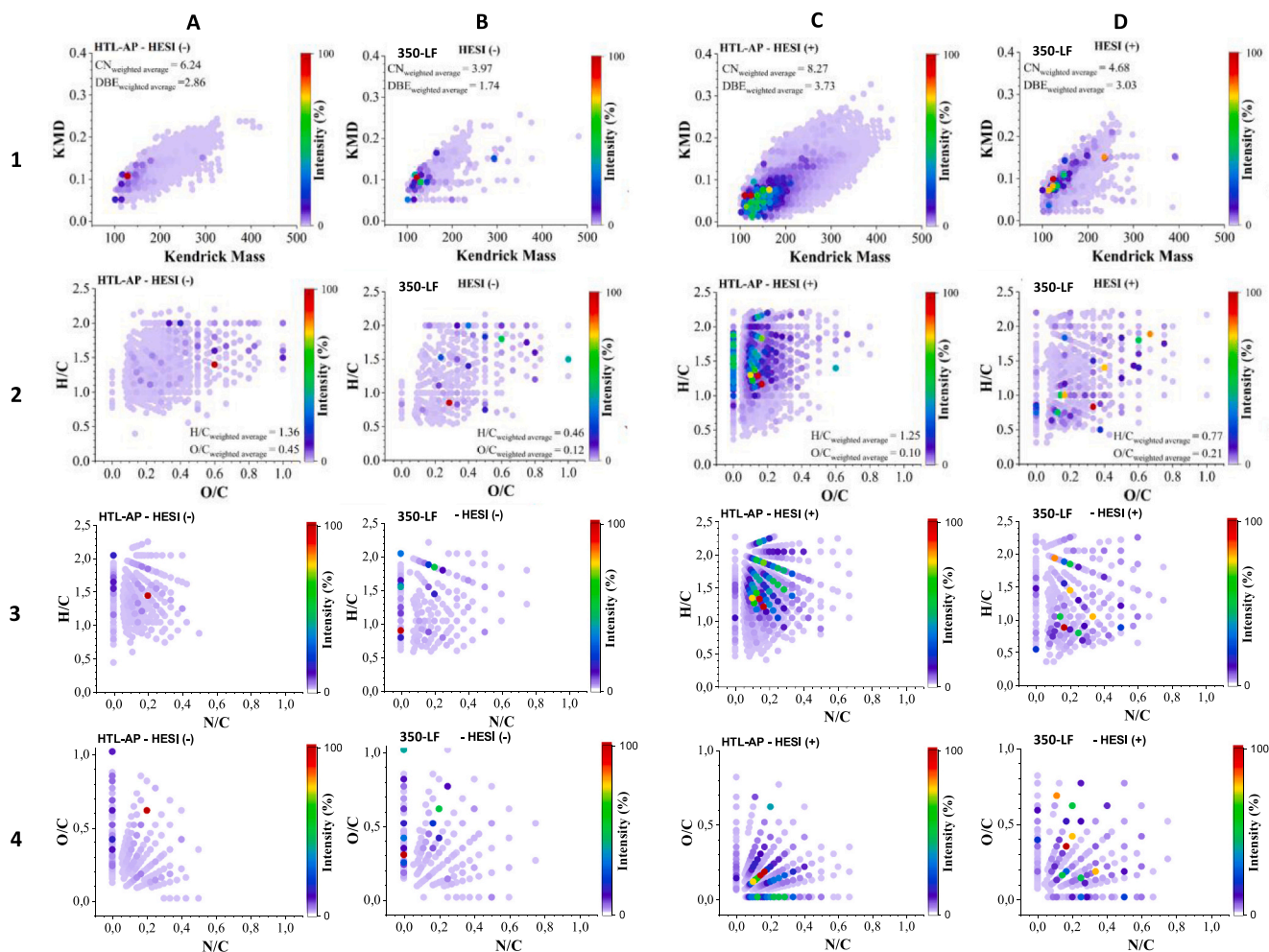


Fig. 9. Kendrick and van Krevelen diagrams of HTL-AP and 350-LF WAO.

degradation of the N_1O_1 class, and indicates that these classes are most recalcitrant for degradation (Figure S12).

4. Conclusion

This study demonstrates that continuous wet air oxidation using a tubular reactor can achieve a high reduction of the TOC and COD of HTL-AP at temperatures and residence times similar to the HTL process. The increase in temperature and residence time increases the removal rates, reaching values up to 95.3 and 91.8 % removal of COD and TOC, respectively, at 350 °C after 49.5 min. The energy consumption during WAO was up to 40 % lower due to exothermic reactions. Autothermal operation was not achieved, requiring improvements in the reactor design.

The WAO process increased the concentration of VFAs, mainly acetic acid while reducing the concentration of organic pollutants. The high concentration of acetic acid and reduced recalcitrant compounds in the post-WO process water improves its opportunity for valorisation by biological processes. Almost complete decomposition of organonitrogen compounds was achieved at the harshest operational condition investigated, which generates high levels of ammonium, creating the possibility of nutrient recovery via different routes. FT-Orbitrap MS promoted a comprehensive overview of the impact of WAO at molecular level of HTL-AP constituents. The speciation corroborates with the total nitrogen reduction showing that the most affected compounds are from N_1 and N_2 classes as well as the increase of O_3 and O_4 caused by the WAO. N_1O_2 and N_1O_3 classes are revealed as more recalcitrant than N_1O_1 .

CRedit authorship contribution statement

Jhonattas de Carvalho Carregosa: Writing – review & editing, Visualization, Investigation, Formal analysis, Data curation. **Alberto Wisniewski:** Writing – review & editing, Supervision, Resources. **Konstantinos Anastasakis:** Writing – review & editing, Supervision, Resources, Conceptualization. **Patrick Biller:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Funding acquisition, Conceptualization. **Lars Bjørn Silva Thomsen:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation, Conceptualization.

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.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jece.2024.112672.

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