



Research Paper

A kinetic process model for sewage sludge hydrothermal liquefaction in Aspen Plus: Model validation with pilot-plant data and scale up

Wahab Maqbool^a, Patrick Biller^{a,b}, Konstantinos Anastasakis^{a,b,*}

^a Department of Biological and Chemical Engineering, Aarhus University, Høngøvej 2, Aarhus 8200, Denmark

^b WATEC - Centre for Water Technology, Aarhus University, Ny Munkegade 120, Aarhus 8000, Denmark



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ABSTRACT

This study aims to develop a rigorous process simulation model for the hydrothermal liquefaction (HTL) of sewage sludge, allowing for more accurate predictions of product streams' yields, elemental recoveries, energy requirements and equipment dimensions under varying processing conditions and sewage sludge compositions. The model is based on lumped kinetics derived from lab-scale experiments and is implemented in Aspen Plus for a conceptual design of an upscaled HTL system integrated into a wastewater treatment facility. The model is first validated against experimental data and further validated against continuous-pilot-scale data. The developed process model showed satisfactory (at lower residence times - RTs) to very good (at higher RTs) predictions for all HTL product yields at two different temperatures (300 °C and 350 °C) when compared with lab-scale experimental data. Upon scaling up to the exact dimensions of the Aarhus University HTL pilot-plant, the model predicted an overall bio-crude yield of 31.4 wt% versus an experimentally derived yield of 29 wt% under varying residence times (8–14 min) and temperatures (300, 325 and 350 °C). The upscaled system, processing approximately 1.4 t/h of sewage sludge slurry with 20 wt% dry matter content at 325 °C, was designed for a total volume of 375L (reactor and heat exchanger), corresponding to 8.7 min of residence time in the heating zones. The model predicted bio-crude, residue, process water and gas yields of 32.2, 12.5, 43.3 and 12 wt%, respectively, in line with typical experimental yields. Carbon, nitrogen and ash distribution in the product streams as predicted by the model were also found in line with typical experimental distributions. A high EROI (Energy Return on Investment) of 11.8 was observed for HTL processing alone, while when factoring in the costs associated with treating the resulting process water in a conventional wastewater treatment plant, the EROI decreased significantly to 4.3. This highlights the critical need to explore alternative methods for the valorization or treatment of HTL process water. The proposed model serves as a solid framework for the integration, further optimization and analysis of industrial liquefaction processes.

1. Introduction

The proposed 'fit for 55' package by EU targets a 13 % reduction in the GHG intensity of transport fuels and a minimum target of 2.2 % for advanced biofuels share by 2030 [1]. Forecasted annual production growth of biofuels in the EU is only 0.5 % for 2019–2025, while an annual growth of 9 % between 2019 and 2030 is needed to reach the Sustainable Development Scenario (SDS), according to the International Energy Agency (IEA) [2]. Especially biofuels for aviation and shipping need to reach 31 and 15 Mtoe, respectively by 2030 (from 15 ktOE for aviation and close to zero for shipping in 2018), while the current global share of advanced biofuels is just 0.2 % [3].

Hydrothermal liquefaction (HTL) has been identified as one of the most promising technologies for converting organic material, from a plethora of sources, into bio-crude oil that can be further processed with adapted refinery technologies into drop-in fuels [4,5]. The process exploits liquid water properties at elevated temperatures and pressures as a reaction medium, to convert aqueous slurries to four product streams, bio-crude (which is the main desired product), solid residue, process water and gas. HTL over the last decades has mainly been in the research stage where batch reactors have been employed to examine product distribution under varying process conditions and different feedstock. More recently however, continuous HTL systems at various scales have emerged [6–8] in an attempt to evaluate process performance under

* Corresponding author at: Department of Biological and Chemical Engineering, Aarhus University, Høngøvej 2, DK-8200 Aarhus N, Denmark.
E-mail address: kanastasakis@bce.au.dk (K. Anastasakis).

conditions more relevant to industry.

For further deployment and commercialization of the technology, process models that can aid in understanding of the complex reaction schemes and product yields distribution for the industrial scale design and optimization of the entire HTL process chain are needed. Furthermore, the developed process models can be used for integration of HTL with downstream and upstream processes for mass and energy integration to maximize resource utilization in a biorefinery concept. Finally, overall system analysis, optimization and evaluation for different scales, scenarios and system boundaries can be performed, resulting in realistic data for subsequent techno-economic and (TEA) and life cycle assessments (LCA). The final aspects (TEA and LCA) are of paramount importance for decision-making regarding the direction of commercial growth.

To accomplish these objectives, it is necessary to develop robust models that can respond accurately to variations in process conditions. However, the non-conventional nature of biomass, the complex mixture of possibly thousands of individual components present in the bio-crude (with largest fraction still unknown) and therefore the lack of detailed reaction mechanism makes the development of rigorous process models a complicated task and often simplified approaches are followed. The most common approach for modeling HTL process, considers product yields for a certain feedstock and process conditions as determined experimentally (often from batch-scale experiments but also from continuous scale), which are then used as specifications for the outlet of the reactor (ASPEN Ryield) in process models [9–12]. This approach, although useful for describing HTL performance under specific process conditions and feedstock composition, clearly cannot predict product distribution under varying process conditions and changes in feedstock composition even for the same type of feedstock (e.g. varying elemental and/or biochemical composition) and depends on the availability of relevant experimental data. Despite the limitations of this modeling approach, Lozano et al. [10] used multi-objective optimization, for the representation of bio-crude with model compounds, subject to elemental and boiling point distribution constraints, based on experimental data. This approach, although non rigorous and dependent on the availability of experimental data, is useful for representing bio-crude composition which becomes important for integration with downstream processing (e.g., hydrotreating). A similar approach for representing bio-crude composition has been followed in the modeling work of Penke et al. [13] and Moser et al. [14]. They further improved the HTL modeling approach by representing biomass with model components and considering an extended reaction network (154 reactions) by specifying fractional conversions of these reactions according to elemental analysis and experimental product yields (ASPEN Rstoic).

Other HTL modeling approaches, include the extensive works from the research team at the Pacific Northwest National Laboratory (PNNL) [15–18], however details on process modeling are not provided. More recently, Shia and Yu [19] proposed a rigorous process model for HTL of microalgae. Through the creation of appropriate chemical pathways, regressed kinetic parameters, and thermodynamics, they developed a simulation scenario to describe the HTL system, by using 55 model compounds and 41 distinct reactions. The developed model was able to predict bio-crude yields within ± 10 wt% (for 75 % of the examined published studies) and bio-crude HHVs within ± 5 MJ/kg (for 72 % of the examined published studies). However, the kinetic model was not integrated in the process flowsheet. The reaction rates were calculated externally (in Matlab) and the respective calculated yields were returned to Aspen Plus through a yield reactor (Ryield) to maintain mass and energy balance. Hence, although this work represents the first attempt to rigorously model HTL process, the model cannot be applied for sizing the HTL reactor and heat exchanger according to different feed flow rates and desired products distribution.

Therefore, the present study aims to develop a rigorous process simulation model for HTL of sewage sludge. Sewage sludge is selected as the feedstock due to the potential advantages HTL technology can offer

compared to the state-of-the-art sewage sludge valorization technology of anaerobic digestion (AD). Briefly, HTL can produce renewable liquid fuels for hard to decarbonize transport sectors (aviation, marine, long haul transportation), can have higher carbon recovery in the bio-crude than methane in biogas, can eliminate micro-pollutants, microplastics, etc. due to high temperatures and pressures employed, can recover nutrients such as phosphorus in the solid residue, can significantly reduce processing time and land requirements for the valorization technology, among others [20,21]. Furthermore, in cases where the resultant digestate is incinerated, instead of applied in farmland, its high-water content (~ 70 %) presents a significant issue for incineration and its P content results in the incineration ash becoming unavailable for further use as fertilizer. The developed model will enable (a) accurate predictions of all product streams under varying operation conditions (temperature, residence time) and sewage sludge composition, (b) sufficient description of (main) elemental recoveries in the different product streams, (c) dimensioning of HTL reactor (length, diameter, number of tubes) and heat exchanger (heat transfer area) according to different feed flow rates, operation conditions and sewage sludge composition, and finally (d) the estimation of accurate mass and energy balances.

To achieve these, the lumped kinetic model for HTL of primary sewage sludge developed by Qian et al. [22], is evaluated and implemented in Aspen Plus, for a conceptual design of an upscaled HTL system integrated in a wastewater treatment (WWT) facility. The Aspen model is first validated against the experimental data [22] and is then used for further validation against continuous-pilot-scale experimental data at different temperatures and flow rates [20] by using the exact dimensions as in the Aarhus University HTL pilot-plant [8]. Following, the developed process model is upscaled for the valorization of sewage sludge generated by a 100 K person equivalent (PE) capacity WWT facility. The main parts of the HTL system (heat exchanger, reactor) are sized according to the given flowrate, desired conversion and product distribution. A mass balance, including main elemental distribution in the product streams, and an energy balance, including energy costs for process water treatment, of the process are presented. The proposed model presents the basis for further model improvements to predict biocrude yields from the same feedstock but with different elemental composition, to investigate the complex HTL reaction network and to deliver accurate mass and energy balances under varying process conditions for further system analysis in the form of process integration, life cycle analysis (LCA) and techno-economic analysis (TEA).

2. Methodology

2.1. Global assumptions

Three models were developed: a) a batch-scale kinetic model which was validated against lab-scale experimental data, (b) a pilot-scale continuous kinetic model to match the exact dimensions of the Aarhus University (AU) pilot-scale HTL reactor which was validated against pilot-scale experimental data, and (c) an upscaled system to represent a base case scenario of implementing HTL in a WWT facility.

The process models were built in Aspen Plus v12, and the following assumptions are valid for all models (global):

- The processes are simulated in steady-state mode.
- The property method and free-water methods are Soave-Redlich-Kwong ('SRK') equation of state (EOS) and 'STEAMNBS', respectively, unless otherwise stated.
- The stream class is defined as mixed conventional and non-conventional components ('MIXNC').
- HTL feed (sewage sludge) and products (bio-crude, process-water, residue, and gaseous products) are all represented as non-conventional compounds.

- The physical and chemical properties of non-conventional compounds (biomass feed and HTL products) are estimated by 'HCOALGEN' and 'DCOALIGT' enthalpy and density models, respectively.
- The employed kinetics are assumed to be the same for processing slurries of primary and secondary sewage sludge.

Enthalpy and density models employed ('HCOALGEN' and 'DCOALIGT'), require proximate ('PROXANAL') ultimate (ULTANAL) and heat of combustion (HHV) data to calculate required properties for the selected non-conventional compounds. Table 1 shows the respective data for HTL products employed for all process models in the present study. Bio-crude elemental composition, and ash contents were taken from the work of Silva Thomsen et al. [20] while volatile matter (VM) and fixed carbon (FC) composition were taken from Nazari et al. [23]. For the process water, VM, FC, ash content and elemental composition were determined experimentally after water evaporation at 30 °C of process water produced from pilot-scale HTL processing of sewage sludge at 325 °C at the Aarhus University (AU) HTL pilot plant (described in detail in [8]). Similarly, proximate and ultimate analysis of the residue was performed in-house at AU from the solids produced during the same pilot-scale processing campaign. Gaseous elemental composition was calculated from the experimental characterization of gas product of sewage sludge HTL as reported in Do et al. [24], and its heat of combustion was directly calculated from the weighted summation of individual components heating values. The heat of combustion (HHV) for the remaining non-conventional compounds was calculated with the Channiwala and Parikh correlation [25] according to their elemental and ash contents.

Composition of HTL products (proximate, ultimate, etc.) differs upon processing at different process conditions (mainly at different temperatures and residence times). As an indication, Qian et al. 2020 [22] reported bio-crude CHNSO composition (wt.%) of 72.1, 9.7, 2.8, 0.6, 14.7 and of 71.8, 9.9, 2.5, 0.5, 15.2, after HTL of sewage sludge at 300 °C & 60 min RT and 350 °C & 4 min RT, respectively. Similarly, Silva Thomsen et al. reported bio-crude CHNSO composition (wt.%) of 71.5, 8.6, 3.2, 0.5, 15 and of 72.8, 8.9, 3.1, 0.4, 12.7, after continuous HTL processing of sewage sludge at 325 °C & 20 min RT and 350 °C & 20 min RT, respectively, while Biller et al. [26] reported 74.6, 10.1, 2.5, 0.7, 12.2 after batch HTL processing of sewage sludge at 340 °C & 20 min RT. Even though there are differences in the composition of bio-crudes obtained from different processing conditions, these differences are relatively minor. Therefore, similar to bio-crude composition, the composition of all HTL products was assumed to remain constant for the different models in the present study.

The HTL reactor models developed in the present study are based on the kinetics recently developed by Qin et al. [22] for the reactions

Table 1

Proximate ('PROXANAL'), ultimate (ULTANAL) and heat of combustion (HHV) data for representation of non-conventional HTL products in Aspen Plus.

Composition, wt.%	Bio-crude	Process Water	Gaseous	Residue
<i>PROXANAL Composition</i> ^a				
Fixed carbon (FC)	9.7	9.1	–	10.0
Volatile matter (VM)	89.3	83.8	–	25.0
Ash	1.0	7.1	–	65.0
<i>ULTANAL Composition</i> ^a				
Carbon (C)	71.6	43.6	32.0	23.0
Hydrogen (H)	8.6	7.5	1.6	2.3
Nitrogen (N)	3.2	6.3	–	1.3
Oxygen (O)	15.0	35.1 ^b	66.4	7.8
Sulfur (S)	0.5	0.4	–	0.6
HHV ^c (MJ/kg)	33.6	20.2	4.5	8.6
References	[20]	This work	[24]	This work

^a PROXANAL and ULTANAL compositions are given on dry basis.

^b Calculated by difference; ^c calculated by Channiwala and Parikh formula [25].

involved in sewage sludge HTL.

In the present study, the Arrhenius parameters for the HTL reaction scheme as determined in the original study [22] were input into Aspen Plus, in the form of power-law kinetic reaction set, in both RBATCH and RPLUG blocks. These kinetics were derived from experimental results in both subcritical and supercritical regions, where the remarkable decrease in density of water in the supercritical region can affect the estimated values of kinetic constants. The reported data included just two sets of yields in subcritical conditions, hindering the estimation of kinetics just in this region. Hence, the activation energies and pre-exponential factors were adjusted within the reported deviations [22] to better describe the predicted yields in the subcritical region. Table 2 summarizes the adjusted kinetic parameters for processing sewage sludge slurry with 2.2 wt% DM content as input in Aspen Plus. Volatiles fraction was assumed to be the same as the aqueous phase fraction and were lumped together as 'process water' in the present study. Sewage sludge slurries with different DM content (2.2-20 wt% DM) were assumed to follow the same kinetics. However, the pre-exponential constants in the Arrhenius expressions were normalized for higher DM content slurries as explained analytically in section 2.3.

2.2. Lab-scale kinetic model

The small batch reactors employed in the kinetic study by Qian and co-workers [22] were represented by a 'RBATCH' reactor in Aspen Plus. The 'RBATCH' block had a single input and output stream with the sewage sludge slurry and the HTL products, respectively. The same conditions as in the original kinetic study were used for validating the model. Sewage slurry with 2.2 wt% DM content (rest being pure water) and CHNSO and ash composition (wt.%, dry) of 46.5, 7, 33.3, 2.1, 0.6, 33.3 and 10.3, respectively, comprised the input (feed) stream. Since further information on fixed carbon and volatile matter contents of sewage sludge were not given in the original study, they were assumed as 15 wt% and 85 wt% of the dry ash free fraction of biomass, respectively, according to analysis of sewage sludge feedstocks in Phyllis database [27]. The 'RBATCH' reactor was operated at 400 bar and different temperatures (300 °C and 350 °C) and residence times (RT) (1–60 min). The six aforementioned first-order Arrhenius type kinetics were input as a reaction set. 'Volatile' and 'aqueous' fractions in the product stream were lumped together as 'process water' for expressing the results. The Mean Absolute Error (MAE) (eq. (1)) was applied to investigate the fitting of the model predicted HTL product yields to experimental data.

$$MAE = \frac{1}{N} \sum_{i=1}^N |Y_{i, \text{exp}} - Y_{i, \text{mod}}| \quad (1)$$

where $Y_{i, \text{exp}}$ is the respective product yield as determined experimentally in the original study, $Y_{i, \text{mod}}$ is the corresponding product yield as predicted by the present Aspen model and N is the number of experimental observations.

Table 2

Adjusted Arrhenius parameters from the reaction network proposed by Qian et al. [22] as input in Aspen Plus for processing sewage sludge slurry with 2.2 wt% dry matter.

Pathway	Ea (kJ/mol)	Log(A) (s ⁻¹)
Solids → Biocrude	60	3.9
Solids → Aqueous	55	3.7
Solids → Gas	91	6.2
Biocrude → Aqueous	132	7.6
Aqueous → volatiles	88	5.4
Aqueous → Gas	106	6.6

2.3. Pilot-scale kinetic model

The developed kinetic model was scaled up to the exact dimensions/specifications of the AU pilot-HTL reactor to check how the model predictions fit with continuous operation data. The predictions of the numerical simulations were validated against the experimental results of Silva Thomsen et al. [20] for HTL processing of primary sewage sludge in three different temperatures (300, 325 and 350 °C) and residence times. The AU pilot-HTL reactor, which has been designed in a way that enables direct scaling up, is described in detail in [8,28]. Briefly, it consists of a lengthy tubular system (126.5 m excluding the product cooler) at constant diameter (ID 14.2 mm), divided in several convolutions, enabling turbulent flow [28] with an estimated overall Reynolds number in the range of 15000. The developed flowsheet is shown in Fig. 1. A 16 wt% DM slurry of primary sewage sludge ('SLURRY') is pressurized and pumped to the cold side of the heat exchanger (HEX) at 220 bar. Primary sewage sludge was modeled according to its CHNSO and ash composition of 45.3, 7.8, 3, 0.3, 36.5 and 7 (wt.%, dry), respectively, in agreement with [20], while the same assumptions as above were made for volatile and fixed carbon. The pressurized slurry ('COLD-IN') is preheated in the cold side of the heat exchanger by the reaction products stream ('HOT-IN') before entering ('COLD-OUT') a plug flow reactor ('PFR').

The pilot HTL reactor system consists of a heat exchanger, a trim heater and a plug flow reactor with an internal diameter of 14.2 mm throughout the overall length of the tubular system [8]. The same diameter was used for the simulations. The heat exchanger is operating counter-currently and consists of two pipe line systems (2 × 24m, cold & hot sides of heat exchanger) which are thermally connected with cast iron clamps (average distance between each clamp of 30 mm) which act as the heat transfer medium [8,28]. Considering the length of one side of the heat exchanger, its diameter and the average distance between the heat clamps, it gives an effective heat exchanger area of 0.78 m². This calculated exchanger area was used for the simulations along with an overall heat transfer coefficient (U) of 600 W/m²K. An 'RPlug' block was used for the rigorous simulation of the reactor and trim heater, with a total length of 102.2 m and diameter of 14.2 mm. The same six first order reactions, as in the case of the lab-scale model, were implemented as a reaction set in 'RPLUG'. The kinetics were assumed to be the same for higher DM content slurries. However, since Aspen considers the water content of the feed slurry in rate calculations, the pre-exponential constants in the Arrhenius expressions were normalized for higher DM content slurries, by factoring the ratio of biomass to water in the original kinetic study (2.2/97.8) and the present case (16/84). The length of the

'RPlug' block incorporates the combined lengths of the cold side of the heat exchanger, trim heater and plug flow reactor of the AU pilot-HTL reactor system (total length of 102.2 m). The HTL reactions already start at the cold side of the heat exchanger and continue throughout the trim heater and reactor. However, since there is no option for incorporating kinetics in heat exchanger blocks in Aspen Plus, it was decided to include the combined length of the heated zones as the total length of the PFR reactor, where the HTL reactions are implemented. The 'RPlug' block was modeled as a non-isothermal reactor with specified temperature profile according to the respective lengths and heating rates of the cold side of the heat exchanger (24 % of the modeled PFR) and the trim heater. Reaction temperature was considered to have been reached at the exit of the trim heater which corresponds at the point of 36 % of the length of the modeled PFR.

The HTL products at the exit of the PFR ('PFRPROD') are directed to an 'RYield' block which simply serves for the conversion of the modeled non-conventional gaseous compound to the conventional composition of the gaseous phase (CO₂, CO, CH₄, C₂H₄, C₂H₆ and C₃H₈) according to [24]. The rest of the HTL products (bio-crude, solid residue and process water) remain to be represented as non-conventional components. The product stream is subsequently directed to the cold side of the heat exchanger ('HOT-IN') where it cools by exchanging heat with the feed slurry, before the final cooling at 40 °C in a simple heater block ('COOLER'). No further separation of the products was considered at this stage since this was included in the upscaled design flowsheet.

Three different thermodynamic property methods were investigated to examine the accuracy of the estimations (product yields, duties, heat recovery, etc.) and their dependence on the selected method. Since the system under investigation involves non-conventional components (bio-crude, residue, process water, gas), polar components (water), non-polar components (water at high temperature and pressure), light gases (CO₂, CO, etc.) and high pressures (220 bar), EOSs (equations of state) are more suitable for the calculations. Peng Robinson (PENG-ROB), Predictive Soave-Redlich-Kwong (PSRK) and Soave-Redlich-Kwong (SRK) EOSs were selected for the investigation. Both PENG-ROB and SRK yield accurate results for non-polar components at elevated pressures, while the PSRK is an extension of the SRK EOS to handle supercritical components, capture non-ideal interactions and predict properties of pseudo-components by incorporating the UNIFAC method for calculating mixture parameters [29].

2.4. Upscaled design

Following validation of the developed kinetic process model with lab

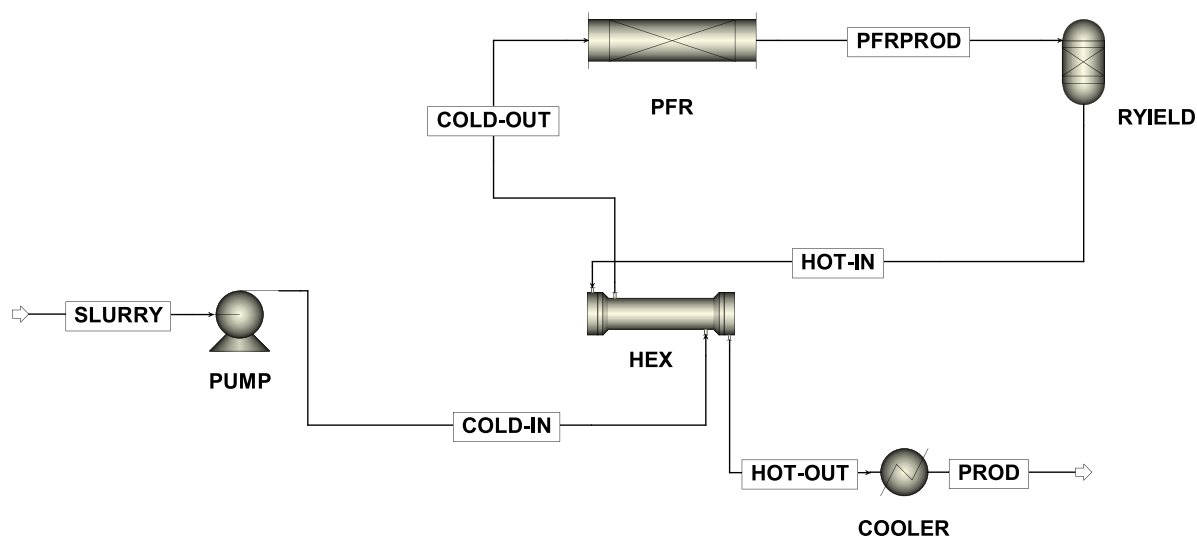


Fig. 1. Process flowsheet of the AU pilot-scale HTL reactor in Aspen Plus (v12).

and pilot scale data, it was then used as the basis for upscaling. The upscaled design considered a WWT plant size of 100,000 PE and the proposed HTL system was considered as an addition to an existing WWT facility. 300 L/day-PE was chosen as the design wastewater production with 0.025 wt% as the wastewater influent total solids content [30–32]. Typical primary and secondary sludge dry matter (DM) production of 0.15 and 0.08 kg/m³ of wastewater, respectively, were considered [31]. The DM contents of the resultant sludges were considered as 4 wt% and 0.9 wt% for primary and secondary sludge, respectively [20,31]. Both sludges were modeled according to their CHNSO, ash, VM and FC composition as reported by Skaggs et al., 2018 [33]. More specifically, the respective composition for primary sludge was 47.8, 6.5, 3.6, 0.5, 33.6, 8, 82.2 and 9.8 wt% on dry basis and 43.6, 6.6, 7.9, 0.7, 29, 12.2, 65, 22.8 wt% for secondary sludge.

The process scheme employed in the present simulation study is shown in Fig. 2 including primary and secondary (activated) sludge dewatering, HTL and products separations. Primary ('PSLURRY') and secondary (or activated) ('ASLURRY') sludge slurries are mixed ('MIX') at their respective production rates and DM contents. The combined sludge slurry ('FEED') is then pumped ('PUMP1') at 2 bar to a dewatering station ('DEWATER') represented by a 'Filter' block. The DM content of the combined sludges slurry is increased from 1.8 wt% to 20 wt% in the dewatering step. Dewatered feed ('DEW-FEED') is then pumped ('PUMP2') at high pressure of 220 bar ('COLD-IN') in the cold side of the heat exchanger ('HEX'), represented by a countercurrent flow 'HeatX' block, to recover energy from the hot product stream ('HOT-IN') of the plug flow reactor ('PFR'). The pre-heated stream ('COLD-OUT') is then directed to the PFR reactor ('PFR') represented by an 'RPlug' block. The PFR reactor was modeled as a non-isothermal reactor, according to the previously described procedure (section 2.3) by incorporating the size of the cold-side of the heat exchanger. The feed slurry was assumed to be pre-heated to 85 % of the target temperature in the heat exchanger as explained analytically in section 3.2. In the absence of kinetic data for secondary sludges, both primary and secondary sludge were assumed to follow the same kinetics, which were implemented in the 'RPlug' block by factoring the ratio of biomass to water for the upscaled design (1:4). The size and operation temperature of the PFR were selected according to the procedure explained analytically in section 3.3. The HTL products ('PROD-1') are then directed to two theoretical blocks ('RYIELD1' and 'RYIELD2') before passing through the hot-side of the heat exchanger for heat recovery as described earlier. The first RYIELD block serves for the conversion of the remaining unreacted sludge DM to residue, while the second RYIELD block serves for the conversion of the modeled non-conventional gaseous compound to the conventional composition of the gaseous phase, as explained in section 2.3. After the heat exchanger, the product mixture ('HOT-OUT') passes through a filter ('FILTER') to remove HTL solids as 'RESIDUE'. It was assumed that 1 wt% of liquid and gaseous products each ('HOT-OUT') are being lost during operation of the filter along with 'RESIDUE', to account for losses during actual operation as explained in more detail in section 3.2. Solids-free product mixture ('PROD-3') is then cooled down

to 60 °C in 'COOLER' and is depressurized across valve 'V1', from 220 bar pressure down to ambient pressure (1 bar). Depressurized mixture ('PROD') gets phase separated into 'LIQUID' and 'GAS' streams in a flash operation ('FLASH'). A DECANTER unit then separates the 'LIQUID' stream into bio-crude (BC-1) and process water ('PW-1') streams, where the process water stream contains water along with dissolved organics and inorganics. Finally, an 'FSplit' block ('SPLIT') is used to include a specific amount of process water into bio-crude for a 95 wt% final product purity, the rest 5 wt% being process water. This final step serves in a more realistic representation of the bio-crude product with some typical moisture content after actual operation.

3. Results & discussion

3.1. Kinetic process model validation with lab-scale experimental data

The Aspen Plus kinetic model was first validated by comparing the predicted HTL product yields against the experimental results of Qian et al. [22]. Fig. 3 shows the HTL product yields as predicted by the model (solid lines) against the experimental ones (data points) for RT between 1 and 60 min at 300 °C (Fig. 3-a) and 350 °C (Fig. 3-b), while the corresponding error analysis through MAE is summarized in Table 3. Visual observation of Fig. 3 indicates satisfactory predictions of HTL product yields at both temperatures examined. MAE analysis revealed better prediction at reaction temperature of 300 °C for all product yields, apart of the residue and gas, for the residence times examined. The overall MAE for the yields of bio-crude, process water, gas and residue ranged from 2 to 6. However, as is apparent from Fig. 3, the reactions proceed in a high rate during the first three minutes (more notable at 350 °C, Fig. 3-b) and the model was not able to have a high correlation with the experimental data in this region. When this region in time is passed, the model results in significant better agreement with the experimental data.

The model gave sufficient to very good predictions for bio-crude yields, which is the main desired product in HTL, for both temperatures examined. When excluding the first three minutes of reaction time, MAE for bio-crude yield was 1.8 and 1.7, at 300 °C and 350 °C, respectively. In general, the model gave better predictions for all product yields at higher than three minutes of RTs. The highest deviations were observed in bio-crude and process water yields at 350 °C and less than 3 min of RT (MAE of 9.3 and 13.7, respectively). Notably, the developed model is able to predict both the steady increase in bio-crude yield with increasing RT at lower temperatures (Fig. 3-a) and the slight decrease in bio-crude yield at prolonged RT at higher temperatures (Fig. 3-b). Overall, the developed kinetic model showed satisfactory (at lower RTs) to very good (at higher RTs) predictions for all HTL product yields. It was therefore selected for further validation with pilot-scale HTL data before used for the design of the upscaled continuous HTL system.

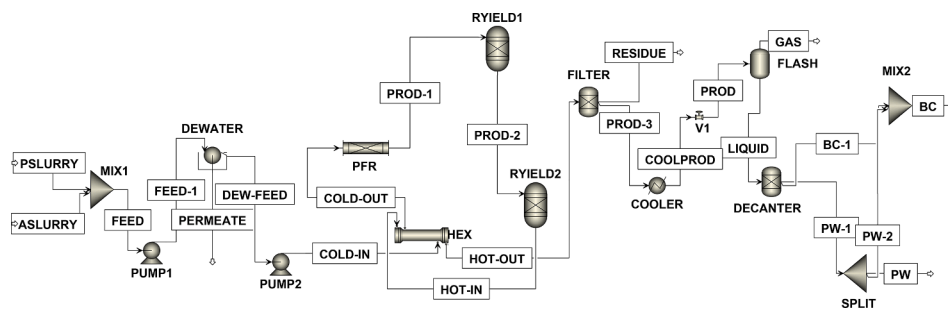


Fig. 2. Flowsheet for the Aspen Plus simulation of the upscaled HTL system including primary and secondary (activated) sludge dewatering, HTL and products separations.

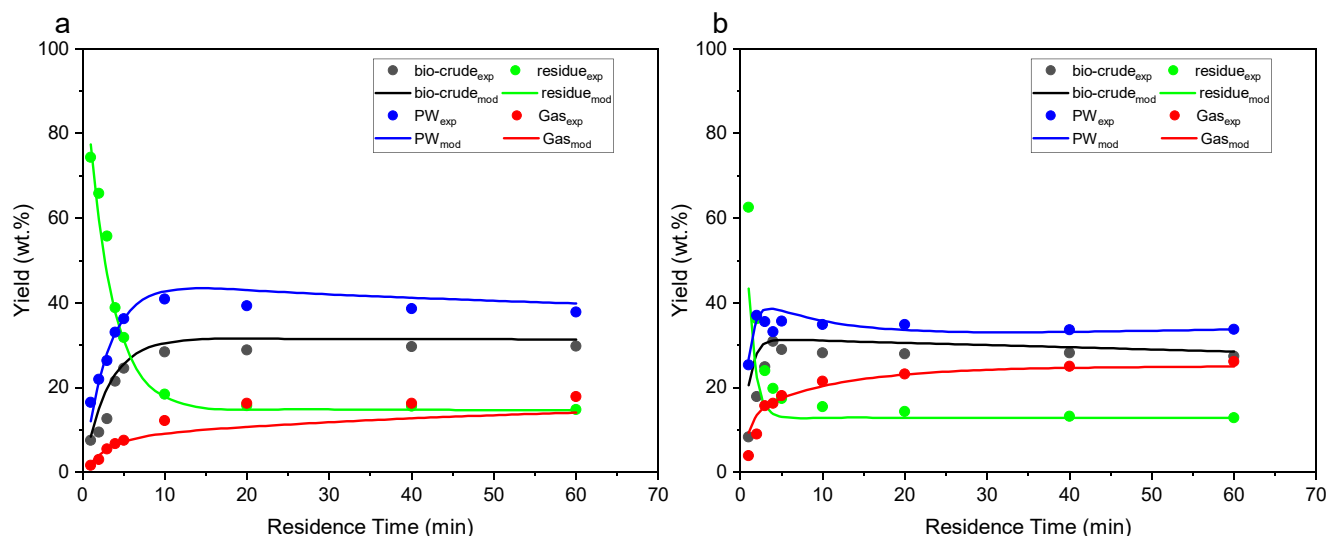


Fig. 3. Model predicted (solid lines) versus experimental [22] (data points) product yields from hydrothermal liquefaction of sewage sludge at (a) 300 °C and (b) 350 °C and different residence times (1–60 min) at 400 bar.

Table 3

Mean Absolute Error (MAE) calculated for model predicted HTL product yields at reaction temperature of 300 °C and 350 °C.

	Bio-crude	Process water	Gas	Residue
300 °C				
MAE	2.7	2.5	1.9	2.0
MAE for RT > 3 min	1.8	0.7	1.7	0.3
MAE for RT ≤ 3 min	4.5	6.1	2.3	5.5
350 °C				
MAE	4.3	6.2	1.8	1.5
MAE for RT > 3 min	1.7	2.5	1.8	0.6
MAE for RT ≤ 3 min	9.3	13.7	1.8	3.4

3.2. Kinetic process model validation with pilot-scale experimental data

Having validated the model with experimental batch-scale HTL results, it was of interest to compare its predictions against experimental results from continuous flow HTL, which represents more realistic conditions expected in industrial HTL plants. The model was built to match the AU-HTL pilot plant and experimental conditions used by Silva Thomsen et al. [20], where primary sewage sludge was processed at three different temperatures (300 °C, 325 °C and 350 °C) and flow rates (39–94 kg/h).

The yields of all predicted HTL products are depicted in Fig. 4, while the estimated residence times and bio-crude yields, along with the respective experimental values, are shown in Table 4. The yields of all products apart of solid residue were lower at 300 °C because of the higher flow rate employed at this temperature (94 kg/h), in line with the experimental conditions, resulting in a significant lower residence time. The RT estimated by the different thermodynamic property methods ranged between 6.4 and 7.9 min, compared to 7.9 min calculated during pilot-scale processing at this temperature and flow rate. The predicted product yields were not influenced by the different thermodynamic property methods employed, exhibiting only minimal differences. At these conditions, predicted product yields through the developed model were 27.3, 26.2, 39.1 and 7.4 wt% for bio-crude, solid residue, process water and gas, respectively. The predicted bio-crude yield was significantly higher than the one experimentally determined during pilot-scale processing at these conditions (27.3 vs 17.7 wt%), while no information on the rest product yields were given in the pilot-scale study. At higher reaction temperatures (325 °C and 350 °C) the employed flow rates were similar (43 and 39 kg/h, respectively) and approximately half of the

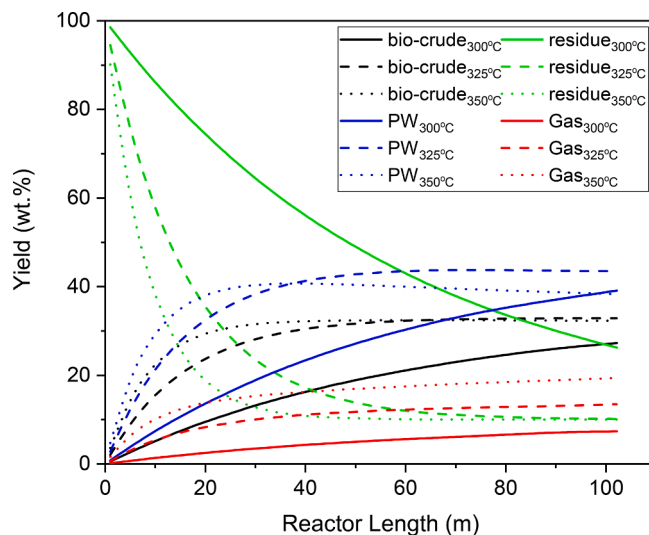


Fig. 4. Model predicted product yields from hydrothermal liquefaction of sewage sludge (16 wt% DM slurry) at 220 bar and temperatures of 300 °C (solid lines), 325 °C (dashed lines) and 350 °C (dotted lines) as a function of reactor length.

flow rate at 300 °C, resulting in sufficient residence time for the complete evolution of the reaction products at each temperature. Even though the decomposition is faster at 350 °C, as indicated by the steeper decline in the slope of the solid residue, bio-crude yield at 350 °C was slightly lower than at 325 °C at the exit of the reactor. At both temperatures the solid residue reached a yield of approximately 10 wt% indicating complete decomposition at the given reactor dimensions and hence RT. However, gas yield was significantly higher at 350 °C, mainly at the expense of lower PW yield, in line with the kinetic mechanism adopted.

Overall, the developed model predicted significantly higher at 300 °C (27.2 vs 17.7 wt%), slightly higher at 350 °C (32.3 vs 31.8 wt%) and lower at 325 °C (32.9 vs 40.8 wt%) bio-crude yields than the ones experimentally determined during pilot-scale processing at the same conditions. However, the aggregated bio-crude yield when considering the feedstock consumed and total bio-crude recovered, during the overall pilot-scale experimental campaign at different temperatures and

Table 4
Comparison of different thermodynamic (property) methods predictions vs experimental data (experimental data from [20]).

	RT (min)	T, COLD- OUT (°C)	HEX duty (kW)	External Duty (kW)	Bio-crude yield (wt.%)
<i>300 °C – 94 kg/h</i>					
PENG-ROB	7.9	254.4	26.1	13.1	27.2
PSRK	6.4	258.2	24.1	12.1	27.4
SRK	7.5	250.9	26.7	13.7	27.3
Experimental	7.9	214.6	–	9.2 ± 0.6	17.7
<i>325 °C – 43 kg/h</i>					
PENG-ROB	16.4	301.5	15	5	32.9
PSRK	13.1	304.1	13.8	4.7	32.9
SRK	15.2	299.4	15.3	5.2	32.9
Experimental	13.9	237.1	–	7.5 ± 0.6	40.8
<i>350 °C – 39 kg/h</i>					
PENG-ROB	16.8	330	15.5	4.1	32.3
PSRK	13.3	330	14.2	4	32.3
SRK	15.3	327.4	15.8	4.3	32.3
Experimental	13.8	251.1	–	11.6 ± 2.5	31.8

residence times, was 29 wt% while when considering the predicted bio-crude yields for the same feedstock consumption and the same conditions, an aggregated bio-crude yield of 31.4 wt% is reached. These discrepancies (especially at lower temperature) are believed to be due to the accumulation of bio-crude in the HTL reactor for the first hours of operation (as was the case for the experimental campaign at 300 °C in [20]), reducing the bio-crude outflow and hence lowering the experimentally calculated yields. During pilot-scale processing on the AU HTL system, it has been observed a sudden increase in bio-crude outflow after several hours of operation due to the gradual buildup of viscous bio-crude in the system, followed by an abrupt release after a certain time interval as explained and shown by Anastasakis et al. [8]. These, along with the unavoidable losses during products separation, bio-crude recovery, residual bio-crude remaining in the long tubular system of the HTL reactor at the end of the experimental campaign, etc., can explain the differences between the modeling and experimental aggregated bio-crude yields. Eventually, process simulations capture ideal cases under steady state operation and minimal losses unlike pilot-scale processing. However, some sources of these losses can also be considered when developing process models, which has been implemented in the case of the scaled-up design in the present study. Furthermore, inherent modeling uncertainties may also contribute to the deviation between the measured and the estimated by the model yields. Generally, despite some deviations, the predicted by the developed kinetic process model bio-crude yields were in sufficiently good agreement with the ones achieved during pilot-scale processing.

Another crucial aspect on modeling and upscaling of hydrothermal systems is the heat exchanger design and the achieved heat recovery to reduce the energy input in the system. The same heat exchanger design as the one used in the AU pilot-scale HTL reactor has been considered in the present study with an effective exchanger area of 0.78 m² as described previously in section 2.3. The temperatures at the exit of the cold side of the heat exchanger (COLD-OUT) and the additionally required external duty to reach the reaction temperature, as predicted by the different thermodynamic property methods along with the respective pilot-scale processing data, at the specified process conditions, as presented in Table 4. The pilot-scale data, used for the comparisons, were averages during the last hour of operation at the given temperature (approximately 4 h of operation at each temperature), as they are more indicative of steady state conditions. Achieving steady state operation of the AU HTL pilot-plant has been shown to take several hours [34]. In general, SRK and PENG-ROB methods resulted in similar predictions for the attained heat recovery, external duty requirements and residence times, while PSRK had higher predictions for the heat recovery and lower predictions for the external duty and residence time than the other two methods. In addition, SRK method gave more

reasonable prediction for the heat recovery at 350 °C, since it was the only of the selected methods to give lower temperature, than the applied constraint of 20 °C as the minimum temperature approach, for the stream at the exit of the cold side of the heat exchanger. For these reasons SRK was chosen as the thermodynamic property method during process synthesis of the upscaled design.

When comparing with experimental data, the model predicted significantly higher heat recoveries for the same exchanger area as in the AU HTL pilot plant. More specifically, feed slurry was predicted to be preheated to 83.6 %, 92 % and 93.5 % of the set point temperature (300 °C, 325 °C and 350 °C, respectively) at the given flow rates, while the respective pilot-scale preheating was 71.5 %, 73 % and 71.8 %. There are several reasons for these deviations from the pilot-scale data. The first is related to the non-ideal thermal insulation in the pilot-plant. The second is related to the limited operation time of 3–8 h at steady state conditions for the given pilot-scale campaigns. Heat recoveries > 80 % have been achieved with prolonged operation (>10 h) at steady state conditions at the AU HTL pilot plant [34]. Lastly, a closer observation of the thermal profiles in the pilot-scale reactor, as presented in Silva Thomsen et al. [20], shows that lower than the set temperatures were reached in many parts of the pilot HTL system. For example, the set temperature of 350 °C was not reached in most parts of the HTL system e.g., 342 °C was reached at the exit of the trim heater and was only reached towards the exit of the reactor. Therefore, in a larger-size, commercial HTL system, the heat recovery is expected to be higher than 85 % due to prolonged operation and better insulation. Hence, a conservative approach for heat recovery of 85 % was assumed as the base case during process synthesis of the upscaled design. The higher heat recoveries, calculated by the model, resulted in lower external heat requirements than the calculated ones from the pilot-scale data, as expected. However, when the heat exchanger is modeled according to the temperature profiles obtained from the pilot-plant heat exchanger ($T_{cold, in}$ and $T_{cold, out}$) and not according to its actual size, then the external required duties estimated by the model are within the range of the reported ones during pilot-scale processing (e.g., 9 and 9.3 kW at 325 °C and 350 °C). This shows that the estimated required duty in case of improved thermal insulation and prolonged operation is reasonably accurate.

The developed process model predicted slightly higher bio-crude yields at HTL temperature of 325 °C, in line with recent experimental observations during lab and pilot scale processing of sewage sludge [20,21]. Furthermore, lower reaction temperatures require less external duty when the same heat recovery (i.e., 85 %) is assumed. Hence, 325 °C was selected as the operation temperature for the design of the upscaled HTL system.

3.3. Reactor sizing for upscaled design

One of the advantages of developing kinetic models, instead of shortcut or ‘black box’ models, for the simulation of chemical processes is that they can react accurately to changes in process conditions, enabling their further optimization. The PFR used to model the HTL reactor and the cold side of the heat exchanger, was initially designed with an ID of 40 mm, which as approximately 3 times the ID of the AU-HTL pilot plant, tube length of 10 m and 10 tubes in total. A sensitivity analysis was performed, by varying the length of each tube, to examine the influence of residence time in the conversion, and more specifically on bio-crude yields. Since RT is directly proportional to the volume of the reactor, at a given flow rate and process conditions, the overall volume of the reactor at each residence time was also calculated. The results of this sensitivity analysis are depicted in Fig. 5. As it can be appreciated from the figure, bio-crude yields increase with tube length and overall volume of the reactor (and therefore residence time) until reaching a plateau, followed by a minor decrease for larger volumes. Maximum bio-crude yield of 32.7 wt% was obtained at tube length of 45 m, corresponding to an overall reactor volume of approximately 565L

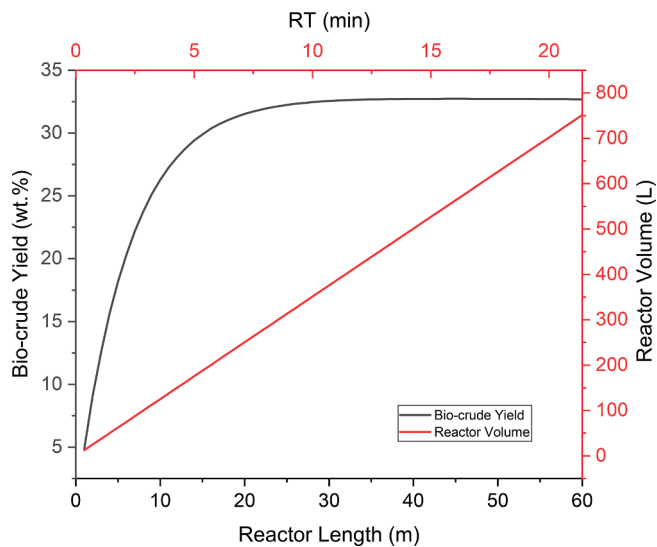


Fig. 5. Bio-crude yield as a function of reactor and cold side heat exchanger length, volume, and residence time at 325 °C ($D = 40$ mm, number of tubes = 10).

and RT of 16 min. For larger reactor volumes (up to 735L corresponding to 21.5 min of RT, shown in Fig. 5) the reduction in bio-crude yield was just 0.1 wt% in absolute values, however for even larger volumes the yield reduction becomes more apparent. Although bio-crude yield reached its maximum at a reactor volume of 565L, it had already reached significant yield at lower volumes. The ratio of bio-crude increase over reactor volume increase, at each different interval examined, becomes less than 0.1 for reactor volumes greater than approximately 290L. Indeed, bio-crude yield at reactor volume of 290L (corresponding to 8.3 min RT) was 32 wt% compared to the maximum yield of 32.7 wt% obtained at 565L reactor volume. Therefore, by also considering design margins, it was decided to set the desired overall reactor volume at 110 % of design basis (320 ± 20 L) for further optimization of the reactor size.

According to the analysis in Fig. 5, a desired volume of 325 L is reached by using 10 tubes of 26 m Length and 0.04 m of Diameter, each. However, to avoid using excessively long tubes, it was decided to increase the number of tubes in the reactor to 24 and perform a sensitivity analysis on how different lengths and diameters influence the overall volume and surface area of the reactor. The same reactor volume can be obtained with various geometries (L, D) and number of tubes, resulting in different overall mass of stainless steel used and surface area. As described previously in sections 2.3 & 2.4, the present design of the PFR includes the combined volumes of the heat exchanger and the reactor, used in an HTL system, to account for the conversion already occurring in the heat exchanger. Therefore, the objective can be to minimize the surface area, if the overall system is sized as a heat exchanger, or to minimize the mass of stainless steel used per tube, if the overall system is designed with the same diameter. It was decided to minimize the steel mass per tube, since this is directly related to the cost of the overall system, while achieving high bio-crude yields (overall reactor volume equal to 320 ± 20 L), subject to certain constraints. Total number of tubes was fixed at 24, length of each tube between 5 and 15 m and internal diameter between 20 and 100 mm were chosen as the constraints to evaluate the designs that give the lowest steel mass per tube with an overall reactor volume of 320 ± 20 L.

Stainless steel mass per tube was calculated by equation (2):

$$Mass = \pi \times D \times L \times t_w \times \rho \quad (2)$$

where D is the diameter of the tube (m), L the length of the tube (m), t_w the wall thickness (m) and ρ the density of SS 304 (8000 kg/m^3). The

wall thickness of the tube was calculated by equation (3):

$$t_w = \frac{P \times D}{2 \times S \times E - 1.2 \times P} \quad (3)$$

where P is the design pressure taken 10 % above the operation pressure (Pa), D the diameter of the tube (m), S the max allowable stress (taken as 80.7 N/mm^2 for SS304 at 371 °C and E the welded joint efficiency (taken as 0.85).

The analysis indicated that a minimum tube mass of 90 kg, corresponding to an overall volume of 302 L is achieved by using 24 tubes of 10 m Length and 0.04 m of Diameter. This tube mass and volume correspond to the combined sizes of the reactor and the cold side of the heat exchanger. The cold side of the heat exchanger occupies 24 % of that volume (72.5L) while the rest 230L correspond to the reactor. Hence, the total volume of both the overall heat exchanger (both cold and hot sides) and the reactor will be 375L. These dimensions were selected as the base case scenario for further analysis in the present study. However, the dimensions can be adjusted in case of a different desired product distribution (e.g., less concentrated process water, higher solids yield, etc.).

3.4. Mass balance for the upscaled design

The upscaled HTL system (Fig. 2), designed to process primary and secondary sludge generated from a 100 K PE WWT plant, resulted in 1437.5 kg/h of slurry input flow rate after dewatering to 20 wt% DM. The kinetic model using 325 °C and 8.7 min of residence time, predicted bio-crude, residue, PW and gas yields of 32.2, 12.5, 43.3 and 12 wt%, respectively (Fig. 6). The relatively low residue yield, considering the ash contents of primary and secondary sewage sludge (8 and 12.2 wt%, respectively), indicates complete conversion of the feed DM. The gaseous phase consisted mainly of CO_2 (10.6 wt% of input DM) with the remaining 1.4 wt% consisting of combustible hydrocarbons (CO , CH_4 , C_2H_4). As discussed previously in sections 3.2 & 2.4, certain sources of product losses were introduced in the upscaled design to account for losses during actual operation of an industrial HTL plant. These losses resulted in final bio-crude product recovery ('BC' stream in Fig. 2) of 31.8 wt% on dry feed basis, with 5.4 wt% moisture (process water)

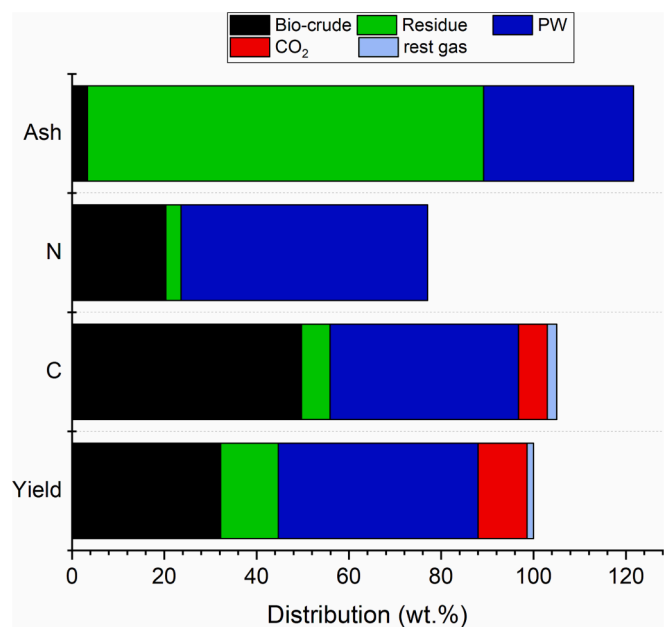


Fig. 6. Product yields and elemental (C, N, Ash) distribution in product streams during HTL of sewage sludge at 325 °C and 1.4 t/h Input flow rate (20 wt% DM) as predicted by the model.

content. Solid residue ('RESIDUE' stream in Fig. 2) is recovered with 26.5 wt% moisture (process water) content, while 1 wt% of the produced gas is also lost during operation of the filter. The recovered process water ('PW' stream in Fig. 2) has a 9.8 wt% concentration of dissolved organics and inorganics while 18 wt% of the produced CO₂ was also found to be dissolved in process water under the separation conditions.

The developed kinetic process model is able to predict the overall mass balance, however, individual elemental balances depend on the availability and accuracy of characterization data for the different products. It was hence of interest to examine the distribution of certain elements in the different product streams under the assumed proximate and ultimate analysis for the feed and HTL products (section 2) and the HTL product yields as predicted by the model. Specifically, the fate and distribution of carbon, nitrogen and ash in the product streams influence the quality of the products. The majority of carbon, representing combustible matter, is desired to speciate in the bio-crude phase while the least nitrogen and ash in the bio-crude will result in less challenges in downstream processing (e.g. through hydrotreatment). Fig. 6 shows the distribution of carbon, nitrogen and ash in the HTL products. Overall carbon balance resulted in remarkably accurate closure of 105 wt% among the product streams. The majority of carbon present in the feed speciates in the bio-crude (49.7 wt%), followed by process water (40.8 wt%), gas (8.4 wt% of which 6.3 wt% as CO₂) and residue (6.2 wt%). Contrary to the carbon balance, overall nitrogen and ash balances in the product streams were under- (77.1 wt%) and over- (121.7 wt%) predicted, respectively. Nonetheless, nitrogen is speciated mostly in process water (53.5 wt%) and bio-crude (20.4 wt%) with only 3.2 wt% in the solid residue. On the other hand, ash appears mostly in the residue (85.8 wt%) followed by process water (32.5 wt%) with just 3.4 wt% of ash content in the feed ending up in the bio-crude.

The predicted elemental balance closures are similar to typical experimental balances. Silva Thomsen et al., 2023 [21] found carbon and nitrogen recoveries in the HTL products between 82 wt% and 110 wt% and 72–102 wt%, respectively, during batch HTL of different WWT sludges and their mixtures. Similarly, Matayeva et al., 2022 found carbon recoveries between 75 and 105 wt% and nitrogen recoveries between 72 and 125 wt% in the HTL products resulting from different waste feedstock, including sewage sludge [35]. Hence, the developed process model in addition of predicting HTL product yields with reasonable accuracy, is also capable of sufficiently describing elemental recoveries in the different product streams.

The main reason for the mismatch in the overall elemental recoveries (not closing to 100 %) is believed to stem from the characterization data used to model process water. PW is usually analyzed for its TOC (total organic carbon), TN (total nitrogen) and NH₄⁺ concentrations. However, in the present study the organic content in PW was modeled as a non-conventional component according to its ultimate and proximate composition. Since literature data on CHNSO analysis of PW is not available, PW resulting from HTL of sewage sludge in the AU pilot HTL plant, was dried at low temperature and subsequently analyzed for its elemental and proximate composition (section 2). A significant part of nitrogen present in PW, often more than 50 %, is in the form of ammonium ions (NH₄⁺) [21]. During the drying process, it is believed that a significant part of dissolved NH₄⁺ is released as gaseous ammonia. In this case, N content of PW as determined by elemental analysis would be underestimated and at the same time the rest of the elemental composition (C, H, etc.) including ash would be overestimated. Therefore, the initial assumed elemental composition of PW was adjusted in order to achieve complete (100 %) overall elemental balances for C, N and ash. The results of the adjusted composition compared to the initial assumed composition of PW are shown in Table 5. Indeed, nitrogen content should be significantly higher (9 vs 6.3 wt%), while ash content should be significantly lower (2.4 vs 7.1 wt%) and carbon slightly lower (38.9 vs 43.6 wt%) than the ones initially assumed. This adjusted PW composition can be used as input for future applications of the

Table 5

Initial and adjusted elemental composition of process water to maintain elemental (C, N and ash) balance.

Composition, wt.%	Initial	Adjusted
Carbon (C)	43.6	38.3
Hydrogen (H)	7.5	7.5
Nitrogen (N)	6.3	9.0
Oxygen (O)	35.1 ^a	42.4 ^a
Sulfur (S)	0.4	0.4
Ash	7.1	2.4

^a calculated by difference.

developed model in the absence of more accurate PW yields and analysis.

3.5. Energy balance for the upscaled design

The main power requirements for HTL comprise of the electricity requirements for pumping and dewatering the slurries as well as the heating after the heat exchanger to reach the target HTL temperature. In addition, significant power is required for the downstream treatment of the resulting process water, an aspect that is often neglected when estimating energy requirements and energy efficiency of HTL process. As shown previously (section 3.4) approximately 40 % of the carbon and more than 50 % of the nitrogen present in sewage sludge speciate in HTL process water.

Table 6 shows the calculated power requirements, as estimated by the model, for processing a mixture of primary and secondary sewage sludge (1.4 t/h, 20 wt% DM) at 325 °C by HTL. Dewatering of the mixture from ~ 2 wt% DM to 20 wt% DM requires 2.8 kW for pumping and dewatering in a rotary drum filter. The main, high-pressure HTL pump has an electricity requirement of 9.7 kW while the HTL reactor requires 60 kW to raise the temperature of the feed slurry from 276 °C at the exit of the heat exchanger ('COLD-OUT') to 325 °C. The overall energy requirements when considering a standalone HTL process were estimated as 72.5 kW.

However, when the power requirements for treating the resulting process water in a WWT plant are also considered, the overall power requirements increase substantially. It is envisioned that the HTL plant is installed in the premises of a WWT facility where it can directly process the generated sludges and it is assumed that the resulting PW is returned to the conventional activated sludge (CAS) process or to the primary treatment for further handling. By taking into account the adjusted carbon composition of the DM present in PW (Table 5) and its volumetric flow rate (1328 L/h), a total organic carbon (TOC) content of 35.4 g/L is estimated. Silva Thomsen et al. [21] found COD/TOC ratios between 2.6 and 3.3 in HTL-PW by processing sewage sludges (both primary and secondary) and their mixtures from various WWT plants. An average COD/TOC ratio of 3, results in 106.2 g/L of COD present in the PW while the limit for effluent discharge after secondary treatment (CAS process) is just 0.125 g/L of COD in EU [36]. Considering this

Table 6

Power requirements for HTL processing of primary and secondary sewage sludge (1.4 t/h, 20 wt% DM) at 325 °C.

Block	Description	Power (kW)
PUMP1	Pumping primary and secondary sewage sludge slurries to rotary drum filter for mechanical dewatering	0.6
DEWATER	Rotary drum filter for dewatering slurries to 20 wt% DM	2.2
PUMP2	High pressure pump for HTL	9.7
PFR	HTL reactor	60
Total (HTL)		72.5
-	Treatment of process water in WWT facility	125.3
Total	Including process water treatment in WWT facility	197.8

substantial required reduction in the COD content of HTL-PW and the energy consumption in CAS process (0.9 kWh/kg COD removed) [37], the overall power requirement for treating PW is estimated as 125.3 kW. This is ~ 175 % higher than the energy requirements for sludges dewatering & HTL processing (Table 6).

Based on the above estimations for power requirements, the overall efficiency of the process was calculated considering two system boundaries, by including and excluding energy costs for PW treatment. Thermal efficiency (η_{th}), total efficiency (η_{tot}) and energy return on investment (EROI) were calculated by the procedure explained previously [8] and the results for the two cases are shown in Fig. 7. Thermal efficiency of the system is 52.5 % for both cases as it simply represents the ratio of the energy content of the main product (bio-crude) over the energy content of the feedstock, without considering any external energy requirements for operation. When considering however the external energy requirements to operate the process, total efficiency reduces from 50.3 % to 46.8 % and more substantially, EROI reduces from 11.8 to 4.3 when the energy requirements for PW treatment are also included. EROI is defined as the ratio of the energy content of the bio-crude over the external energy requirements and as shown in Table 6 total energy requirements increase approximately 2.7 times when energy requirements for PW treatment are included. Even though obtaining 4.3 times more energy in the bio-crude than the energy invested for operating the process is still better than other biomass derived fuels (e.g. 1.3 EROI for biodiesel, 0.8–1.6 for corn-based ethanol [38]), it needs to be highlighted that bio-crude is an intermediate rather than a final product. Its high viscosity and heteroatom content (O, N) makes hydrotreatment necessary before it can be blended with petroleum crude oil in a refinery for final fuel applications. The energy requirements of this additional step are expected to further decrease the EROI of the final fuels.

Therefore, appropriate handling (valorization/treatment) of HTL-PW is of paramount importance for increasing the overall efficiency of HTL process and the net-amount of energy that is made available for other (societal) purpose. Various technologies for further energetic valorization of the significant organic content of HTL-PW have been proposed, including anaerobic digestion (AD), microbial fuel cells (MFC), hydrothermal gasification (HTG), etc. [39]. More recently, wet oxidation (WO) [40] has been shown to significantly reduce the COD content of HTL-PW (up to 75 % reduction with 15 min residence time), hence substantially reducing the energy cost for final post-WO PW

treatment in CAS process. In addition, WO, due to the exothermic nature of the reactions, has the potential to be operated autothermally with the only external energy requirements being associated with oxygen/air compression [41]. Thus, there is the potential of decreasing the energy cost for treating HTL-PW in a WWT facility and hence increasing the overall HTL energy efficiency.

3.6. General discussion

The developed kinetic process model showed how kinetic data from controlled lab-scale experiments can be used to scale up HTL process with reasonable accurate predictions of the resulting product yields. The model was shown to adjust for different feedstock composition and predict with certain degree of confidence HTL product yields and at the same time can sufficiently describe the elemental recoveries in the different product streams. However, since the different sewage sludges used in the different cases (lab-scale, pilot-scale and upscaled design) had similar composition (e.g., ash content between 7 and 12.2 wt%), further validation with more diverse feedstock compositions is needed to show the versatile applications of the model.

The development of such rigorous process model allows more informed dimensioning of the HTL reactor (length, diameter, number of tubes) and heat exchanger (heat transfer area) according to different feed flowrates, desired conversion and products distribution. In the present study the upscaled reactor was designed according to max bio-crude yield at reasonable residence time. However, as shown in section 3.5 treatment of the resulting PW in a WWT facility has a high energy cost. It might therefore be preferred to operate HTL at higher temperature (e.g., 350 °C) and prolonged residence times to have less organics present in PW (and therefore reduce the energy requirements for its treatment), mainly at the expense of higher gas yield and slightly lower bio-crude yield as shown in Fig. 4. Certainly, a more holistic assessment of this is needed, since the final decision is going to be based on tradeoffs between overall capital and operational expenses as well as on the respective environmental emissions. Another preference could be to obtain higher solid residue yield mainly at the expense of bio-crude. HTL solid residue appears as a valuable by-product since it contains most of the phosphorous present in the feedstock [35]. A higher residue yield would result in more carbon distributed in the solid phase and could improve the overall environmental indexes by carbon sequestration in a scenario that solids are directly applied in land for fertilizing purposes. A

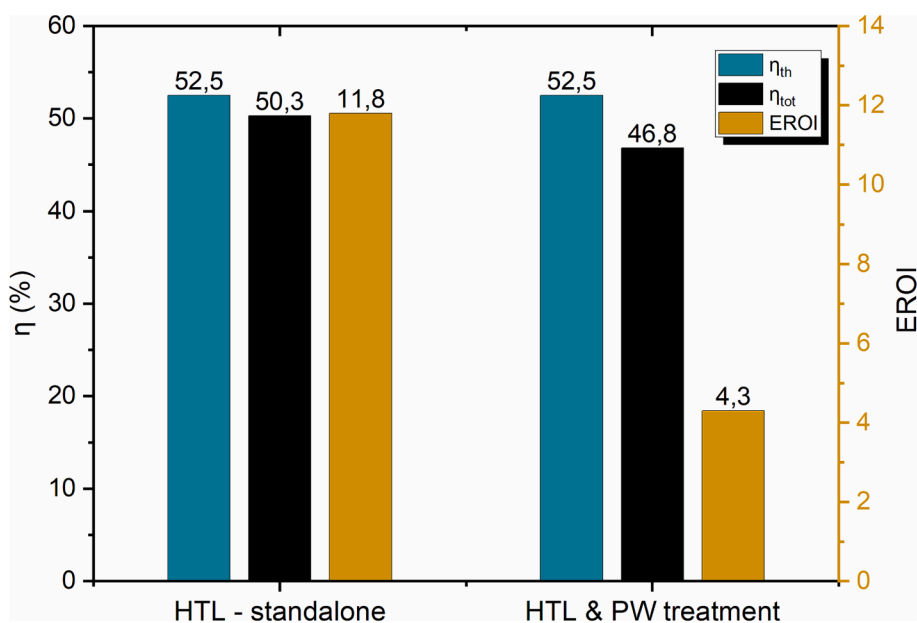


Fig. 7. Energy efficiency (thermal, total and EROI) of HTL process as standalone and by considering process water treatment.

higher carbon content in the solid residue would also result in more material available in a scenario where it is further valorized to renewable adsorbents after P extraction [42]. The developed model can react accurately to changes in process conditions according to the different needs and can therefore provide the necessary data for more accurate subsequent techno-economic (TEA) and life-cycle assessments (LCA) of different scenarios and integration with other technologies.

Nevertheless, despite the versatile applications of the developed process model, it also poses a significant limitation. This lies in its inability to fully describe the composition of the generated products under varying process conditions. Even though the elemental distribution in the different product streams as predicted by the model (Fig. 6) was found similar to typical distributions determined experimentally, the model assumes constant products' composition since they were defined as non-conventional components according to their ultimate and proximate analysis. This can lead to inaccuracies in products' quality under different process conditions and feedstock composition. It would therefore be of interest to experimentally establish empirical correlations between processing conditions and products quality/composition for different feedstock, for potential integration in process models. Especially HTL gas, is the product stream that has received less attention with gas composition data being scarce in literature.

In addition, to further proceed with the development of rigorous and representative process models as the one showcased in the present study, kinetic data are needed. The present study used kinetics for HTL of primary sewage sludge developed by Qian et al. [22] and assumed that secondary sewage sludge follows the same kinetics due to absence of relevant kinetic data. Even though HTL of a diverse range of feedstock (lignocellulosic, marine, waste biomasses, polymers, etc.) has been subject of extensive research, most studies focus on examining the effect of a limited set of process conditions (usually temperature and residence time) on product yields (mainly aiming to maximize bio-crude yield), without providing a complete set of data that would enable kinetics determination. Indeed, out of the rich experimental HTL research only a handful of studies provide kinetic data for primary sewage sludge [22], certain microalgae strains [43–49], and biomass model components [50–53].

4. Conclusions

This study presented a kinetic process simulation model for hydrothermal liquefaction (HTL) of sewage sludge, in Aspen Plus. The developed model predicts with reasonable accuracy the resulting product yields and main elemental recoveries in the different product streams as a function of reaction conditions and sewage sludge composition. The predictions were found to be in good agreement both with lab-scale and pilot-scale HTL product yields. A distinctive feature of the developed model is its ability to size the HTL reactor and heat exchanger according to the desired product distribution. These attributes were used for scaling up to an industrial relevant size HTL plant (1.4 t/h of 20 wt% DM slurry input) integrated in a wastewater treatment facility. The energetic analysis revealed a high EROI of 11.8 when considering only the HTL system, which reduced to 4.3 upon including the energy requirements to treat the resulting HTL process water in the wastewater treatment facility. This highlights the importance for a holistic assessment of HTL technology that combines integration with downstream processes such as hydrotreatment of biocrude, treatment/valorization of process water and solids application, to develop combined economic and environmental analysis. The proposed model can be a key tool for this endeavor. Overall, the predictive approach of the developed model and its ability for dimensioning, provides a robust foundation for quicker and more reliable systems integration, thermodynamic-, economic-, environmental-analysis and design of industrial-scale HTL processes for sewage sludge.

CRedit authorship contribution statement

Wahab Maqbool: Investigation, Methodology, Software, Writing – review & editing. **Patrick Biller:** Funding acquisition, Investigation, Supervision, Writing – review & editing. **Konstantinos Anastasakis:** Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing – original draft, Writing – review & editing.

Declaration of competing interest

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

Data availability

Data will be made available on request.

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