A systems approach to model nonconventional streams applied to biocrude production from hydrothermal liquefaction

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# Abstract

This work proposes a systems approach to model and characterize non–conventional streams, applied to the Hydrothermal Liquefaction (HTL) of sewage sludge towards biocrude. Biocrudes are complex mixtures involving a great many number of compounds, and this introduces challenges in their characterization and the HTL process modelling. For the development of suitable representations and property models for the HTL input/output streams, we create a mathematical model, and solve it using four different optimization algorithms. The optimization is based on experimental data found in the literature, mapping the quantitative and qualitative characteristics of different feedstocks and product streams (organic substrate, reactor inlet and biocrude) and byproducts. Results reveal the most efficient models in terms of their prediction accuracy and convergence speed.

**Keywords**: Hydrothermal Liquefaction, biocrude, sewage sludge, property modelling, nonconventional stream characterization, optimization

# Introduction

Fuels derived from biomass are efficient, sustainable and cost-effective alternatives to fossil fuels and they are increasingly used to reduce the carbon emissions (Liu et al., 2021). Biofuels typically originate from nonconventional feedstocks processed through nonconventional processes. Their production involves advanced thermochemical or biochemical processing, e.g. transesterification, gasification, pyrolysis, fermentation etc. (Lin & Lu, 2021). There are several challenges in the design, efficiency and operation of these process, since it is particularly hard to characterize such highly heterogeneous mixtures of chemicals of diversified composition and origin. The thermodynamic, physical and transport properties depend on the feedstock, and it is required to carry out expensive experiments for the selection of the best process conditions, and apply heuristics e.g. for process integration. Due to lack of accurate simulation models it is impossible to scale up these processes and create commercial and business promise for novel biofuel production technologies.

This work considers the HTL of sewage sludge towards biocrude and proposes a systems approach to address the above challenges. HTL (or hydrous pyrolysis) is among the processes that can be used to convert wet biomass into biofuels. It operates at high pressure (10–25 MPa) and moderate temperature (280 °C–370 °C), and uses the water as the reaction medium and catalyst. HTL can accommodate diversity of organic substrates as potential feedstocks; process feedstocks with high humidity or water content; wide range of process conditions and organic content in product streams; and potential to upgrade locally or centrally. After upgrade, the resulting biocrude can be used as a liquid fuel alternative. The total processing cost of the HTL and the upgrade processes is very competitive, but depends strongly on the process performance (Pedersen et al., 2018).

The HTL process has been widely investigated to understand the mechanism and kinetics at different batch scales of operation. Different types of mathematical models are used to predict product yields and compositions for different biomass and waste feedstocks (Kumar, 2022). However, the biomass feedstock and the resulting biocrudes are complex mixtures involving hundreds or thousands of chemicals. This introduces challenges in their characterization and prediction of basic physical and thermodynamic properties, the available process simulation and optimization technology can be extremely poor, the mass and energy balances are done empirically etc. Therefore, despite the high readiness level of HTL technologies, it is impossible to monitor the process efficiently and adjust the operating conditions according to the processed stream.

The compositions of the processed streams are oftentimes obtained by analytical methods, since the chemical content is critical to predict the stream properties. Gas Chromatography – Mass Spectrometry (GC-MS) is one of the most popular method to obtain data on the presence and the quantity of different organic compounds. Zhu et al. (2017) relied on GC–MS data to predict the composition of the bioliquid outlet stream, and validated their model using elemental balances. Taghipour et al. (2022) used biocrude GC–MS data combined with fractional distillation data and applied multi-objective optimization to improve the prediction accuracy of the density and the Boiling Point Temperature (BPT) curve. Yu et al. (2023) considered the HTL of municipal solid waste and analyzed the effect of operating conditions and waste to water ratio on the mass and energy yield. Machine learning has recently gained attention for accurate and efficient biofuel process modelling (Jeon et al., 2023), and Gopirajan et al. (2021) applied ML-based optimization to improve the process-specific yield and the quality of the product.

In view of the difficulty to apply conventional systems methods, this work proposes data modelling and optimization to predict the quantitative and qualitative composition of the biomass inlet, the biocrude and the upgraded biocrude streams. Section 2 presents the proposed models, section 3 reports the obtained results for HTL of sewage sludge towards biocrude and discusses the potential of the models, and section 4 concludes this work.

# Methodology

This work integrates diversified sets of experiments, and combines them with first-principle based models to produce reliable representation of the involved input-output streams. For a systems description of the problem, we consider that given are the:

* Experimental data
* Process operations: reaction, downstream separation
* Feedstock/product streams: substrate, reactor inlet, biocrude, byproducts
* Background data (first-principle based)
* Set of compounds, conventional thermodynamics, unit operations

and we need to optimally determine:

* Chemical representation: minimum set of suitable components and composition: discrete variables
* Surrogate models: suitable adjustments to existing models

The above problem is formulated as a discrete-continuous optimization model:

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| --- | --- |
| $$\min\_{N,x\_{n},y\_{n,k}}f=\sum\_{n}^{N}\sum\_{k}^{K}\left(\frac{\hat{y}\_{n,k}-y\_{n,k}}{\hat{y}\_{n,k}}\right)^{2}$$ | (1) |

Where *N* is the set of measuremens, with *n* in *N*, *K* is the set of properties, $\hat{y}\_{n,k}$ denote the experimental data, $y\_{n,k}$ are the first-principle based data: $y\_{n,k}=g(x\_{n},p\_{k})$, $x\_{n}$ is the mass fraction of *n*, and $p\_{k}$ denotes the value of property *k*.

For the processing of sewage sludge using HTL, the model is configured for each one of the following streams: the biomass inlet, the biocrude and the upgraded biocrude. Each of these streams is expected to contain a different set of compounds. The model parameters and the model constraints differ between streams, but they can be easily adjusted to address any similar problem. Each stream is associated with a subset of properties and different contraints apply. The properties in the *K* set generally include:

* biochemical composition of proteins, lipids, carbohydrates, lignin, etc.: $bc={\sum\_{n}^{N\_{bc}}x\_{bc\_{n}}}/{\sum\_{n}^{N}x\_{n}}$, $\sum\_{n}^{N}x\_{n}=a, 0\leq x\_{n}\leq 1$, where *α* is the total organic content of the feedstock ($a=1$ for biomass)
* elemental composition of C, H, O, N, P, etc. $ec=\sum\_{n}^{N}\left({\left(Ar\_{i}∙N\_{n,i}\right)}/{\left(MW\_{n}∙N\right)}\right)$, where *Ari* is the atomic weight of the respective element *i*, *MWn* is the molecular weight of compound *n*.

Additional constraints apply for the boiling point (*BP*) temperature distribution {bpd} of the biocdude streams:

* compositions per BP fraction: $\sum\_{n}^{N\_{i}}x\_{n}\leq a\_{i},∀N\_{i}=\left\{nϵN:BP\_{n}\leq T\_{i}\right\}$ , where $a\_{i}$ is the sum of compositions in fraction *I*, *BPn* is the BP temperature of component *n*, and *Ti* is the cut point temperature of fraction *i.*

The resulting mixed-integer nonlinear programming (MINLP) problem is solved using four open-source algorithms: two evolutionary (firefly algorithm (FA) and particle swarm optimization (PSO)) and two deterministic algorithms (sequential quadratic programming (SQP) and least squares optimization (LS)).

# Model comparison results and discussion

The prediction model of section 2 is applied here to the biomass input, the biocrude and the upgraded biocrude steams. The problem considered here for sewage sludge invloves 165 component candidates, BP range: 20-750 °C and MW range: 45-700. Since the composition of sewage sludge can radically differ depending on its origin, we create an extensive dataset of experimental literature data, to map the diversity of quantitative and qualitative characteristics of different feedstocks, product streams and byproducts.

The prediction model is trained and tested on this dataset, using the four optimization algorithms of section 2. The performance of the four resulting models depends on their capacity to predict the stream compositions and properties. Table 1 reports the results obtained from the four algorithms for each stream, and their relative deviations (green) from the experimental values (blue). The experimental values shown on the table include the stream elemental and biochemical (shown here as component groups) compositions, and property values. HHV denotes the Higher Heating Value of the fuel, which increases from biomass, to biocrude and to upgraded biocrude, as expected. SSRD denotes the sum of the squares of the relative deviations likewise to the objective function of Eq. (1). The table also reports the overall statistics for each stream and the total SSRD per algorithm. Note that, the upgraded biocrude contains 60 % fuel and has density 1048 kg/m3. An important assumption to be reconsidered in the future is that biocrude is not solid-free.



According to the results, there is particularly good match between the experimental data and the predicted biocrude compositions/properties for SQP, LS and PSO. For all algorithms, the majority of observed deviations lie around 3-4 % and is generally below 10 %. Only in the case of FA on upgraded biocrude we observe high deviations on the predicted values for most of the components, elements and HHV, and unacceptably high deviations in the compositions of O and especially N (these account for 0.8 % of the mixture). The average error per parameter is 6.06 %, 6.56 %, 7.49 % and 59.01 % for SQP, LS, PSO and FA, respectively. Looking at the total SSRDs for all algorithms and each stream, SQP is the best option to model the biomass and upgraded biocrude, and LS is the best for biocrude.

Another critical metric beyond compositions is the fit of the obtained BP curves to the experimental data for biocrude. Figure 1 shows the curves for biocrude without (up) and with (down) upgrade. Note that, the quality of the upgraded product is superior since it has higher HHV. Again, we observe excellent match of experimental data for the deterministic methods and PSO, and a good amount of desired fractional cuts.





Figure 1: Experimental data and predicted biocrude (without / with upgrade) BP curves

The developed models allow us to explore changes in the operation as a function of variations, investigate process and energy integration opportunities, and improve process performance and energy efficiency. The convergence speed is also very important for real-time process control. SQP is the fastest for upgraded biocrude with execution time 9.1 s, followed by 40 s for PSO and over 67 s for LS and FA. This particularly low convergence speed indicates that SQP might also be a very good candidate for real-time applications. Therefore, based on its overall performance, SQP is found to be the most accurate, reliable and fast optimization option for this case study.

The predicted stream compositions and properties can be used as input to simulation software within a complete simulation package that will be validated on existing HTL pilots. Accurate simulations will certainly facilitate the development of reliable scale-up/down models for HTL and other novel processes, the assessment of uncertainties, and the conduction of techno-economic analyses for different business cases with potential lower cost for efficient resource utilization and biofuel production.

# Conclusions and future work

Biocrude can be produced from a variety of resources and unless properly characterized, this valuable product stream would be unable to enter conventional refineries either as a drop-in fuel or, alternatively, as an intermediate feedstock to upgrade.

This work proposes a systems approach to model and characterize non–conventional streams, applied to the HTL of sewage sludge towards biocrude. For the development of suitable representations and property models for the process input/output streams, we build an MINLP model and solve it with four different optimization algorithms (SQP, PSO, FA and LS). The objective function is expressed as the sum of squares of relative differences between the known data and the model predictions. The modeling of physical processes (e.g. distillation) relies on the physical properties of the input streams (e.g. the BP temperatures of the stream components), and data quality is important to obtain reliable models. The proposed approach is generic and systematic; therefore, it can be suitable to represent and characterize a wide range of nonconventional streams typically encountered in biomass/biofuel processes.

Preliminary results for the biomass inlet and the biocrude (with and without upgrade) using the SQP, PSO and LS algorithms appear very promising. The prediction accuracy is very good (0.3-11 % for SQP), while the predicted chemical compositions are reasonable and consistent with literature data. Additionally, the SQP execution time is adequately low to consider online implementation for real-time process control.

Future work involves the reconsideration of assumptions, and the expansion of the components dataset to extend the model applicability. We also wish to investigate improvements in terms of the algorithm implementation, to increase accuracy and speed, and generally extend the capabilities of the implemented tools. Our work will enable more accurate process simulations, therefore a more efficient and reliable study of HTL and other novel processes to improve biofuel production.

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