Effect of heterogeneous zeolite catalyst on hydrothermal liquefaction of pulp and paper mill mixed sludge

Teo Virta [1], *Orlando* Salcedo[1*], *Ekaterina* Sermyagina [2], *Rama* Layek [2], *Kristian* Melin [2]

[1]Department of Separation Science, LUT University, Lappeenranta, Finland
[2]Department of Separation Science, LUT University, Lahti, Finland

Abstract. Pulp and paper mill sludge (PPMS) is a major biogenic waste stream whose valorization is limited by its high moisture and inorganic content. Among thermochemical routes suitable for wet feedstocks, hydrothermal liquefaction (HTL) enables conversion of biomass into energy-dense bio-oil without prior drying. This study evaluates the effect of a low-cost heterogeneous protonated zeolite (PZ) catalyst on HTL performance of PPMS. Experiments assessed the influence of temperature (255–285 °C), residence time (22.5–47.5 min), solids loading (5–10 wt.%), and catalyst loading (2.5–7.5 wt.% of dry solids) on product yields and bio-oil quality. The zeolite enhanced bio-oil yield and heating value under mild HTL conditions. At 255 °C and short residence time, increasing catalyst loading to 7.5 wt.% resulted in bio-oil yield (dry ash free) up to 10 wt.%. In contrast, at higher temperatures, higher catalyst loading promoted gasification and char formation, reducing bio-oil yields from 17.6 wt.% (low catalyst loading) to 6.2 wt.% under otherwise identical conditions. These results indicate that protonated zeolite shows limited effectiveness under higher-temperature HTL conditions, suggesting alternative catalysts may provide improved performance. The study contributes experimental evidence for catalyst screening in HTL and supports development of more efficient valorization pathways for PPMS.

1 Introduction

The pulp and paper industry generates large quantities of sludge from wastewater treatment, typically comprising a mixture of primary fibrous sludge and secondary biological sludge. Due to high moisture content, ash-forming elements, and potential heavy metal contamination, conventional utilization routes such as anaerobic digestion, land application or combustion are technically and environmentally constrained [1].

Hydrothermal liquefaction (HTL) is a thermochemical conversion process operating in hot compressed water (250–370 °C, 10–25 MPa) that enables direct conversion of wet biomass into bio-crude, aqueous organics, gases, and solid residues [1]. HTL is particularly attractive for sludge-type feedstocks, as it eliminates the need for energy-intensive drying

* Corresponding author: orlando.salcedo.puerto@outlook.com

and tolerates elevated inorganic contents. The primary objective of HTL is to recover carbon and hydrogen from biomass into the bio-oil phase, while minimizing heteroatoms (N, O, S) and separating inorganic ash from the liquid product. HTL product distributions are strongly dependent on feedstock composition. The carbon content of HTL bio-oils is typically around 70 wt.% on a dry ash free basis (daf). Lignocellulosic biomass yields bio-oils with higher oxygen content (~20 wt.% daf) and lower nitrogen (~4 wt.% daf), whereas algal biomass produces oils with lower oxygen (~10 wt.% daf) and higher nitrogen (~7 wt.% daf) [2]. Mixed sludge typically produces 10–35 wt.% (daf) bio-oil [3].

The use of catalysts capable of directly improving bio-crude yield and quality during the reaction is of fundamental importance for increasing the overall process efficiency. Zeolites are widely applied as solid acid catalysts in petrochemical and biomass upgrading processes due to their strong Brønsted acidity, shape selectivity, and thermal stability [4]. In HTL systems, heterogeneous zeolites have been proposed to promote cracking, dehydration, and oligomerization reactions, potentially enhancing bio-oil yield and quality [5]. Nevertheless, catalyst deactivation, mass transfer limitations, and interactions with ash components remain critical challenges. This work evaluates the feasibility of a protonated zeolite catalyst for HTL of mixed pulp and paper mill sludge under mild subcritical conditions, aiming to clarify its influence on product yields and bio-oil properties.

2 Materials

Mixed pulp and paper mill sludge (PPMS) was obtained from a wastewater treatment facility of the integrated kraft pulp and paper mill in Finland. The feedstock consisted of mechanically dewatered primary and secondary sludge blended at the mill. Prior to HTL experiments, the sludge was homogenized and characterized for moisture content, ash content, and elemental composition (CHNSO). The dry matter content of the as-received sludge was approximately 3 wt.%, and the ash fraction was significant due to process-derived inorganics. Prior to HTL experiments, the sludge was conditioned to the required solids content as described in Section 3.1.

A zeolite catalyst was prepared from commercial low-silica zeolite 13X (Sigma Aldrich 96096) and protonated through acid dealumination. A total of 50 g of zeolite was added to 750 ml of a 0.1N citric acid solution (VWR GPR Rectapur, 99.5% purity) and heated to 75 °C for 3 hours under continuous mixing. After treatment, the material was filtered, washed with deionized water and dried at 110 °C for 12 h. The dried material was subsequently calcined at 400 °C for 3 h, after which a sample was collected from the drying crucibles. The catalyst was used in powdered form and added directly to the HTL slurry prior to sealing the reactor. The crystal structure of the modified zeolite was verified using X-ray diffraction analysis, confirming that the dealumination treatment did not alter the zeolite framework structure.

3 Methodology

3.1 Slurry preparation

Fresh sludge samples had an initial solids content of approximately 3 wt.% and were therefore dewatered by centrifugation at 4560 rpm for 5 minutes prior to the experiments. The decanted liquid was collected and reused for slurry preparation. HTL batches were prepared by calculating the required amount of sludge solids and adding the decanted process water to achieve the target solids loading of 5–10 wt.% in the slurry. The sludge was thoroughly mixed prior to each experiment to ensure homogeneity.

3.2 HTL experimental setup

HTL experiments were conducted in a stainless-steel Parr 4523 1 L autoclave reactor equipped with temperature and pressure control and mechanical stirring (Figure 1). The reactor was purged three times with nitrogen and pressurized to 20 bar N_2 prior to heating. The operating conditions evaluated in this study, temperature (255–285 °C), residence time (22.5–47.5 min), solids loading (5–10 wt.% of slurry), and catalyst loading (2.5–7.5 wt.% relative to dry solids), were selected based on the literature, where these four factors are consistently identified as the most relevant to bio-oil yield and quality [6].

Residence time was defined as the period during which the reactor contents were maintained at the target temperature. Once the desired temperature was reached, the reactor was held at this temperature for the specified time before rapid cooling.

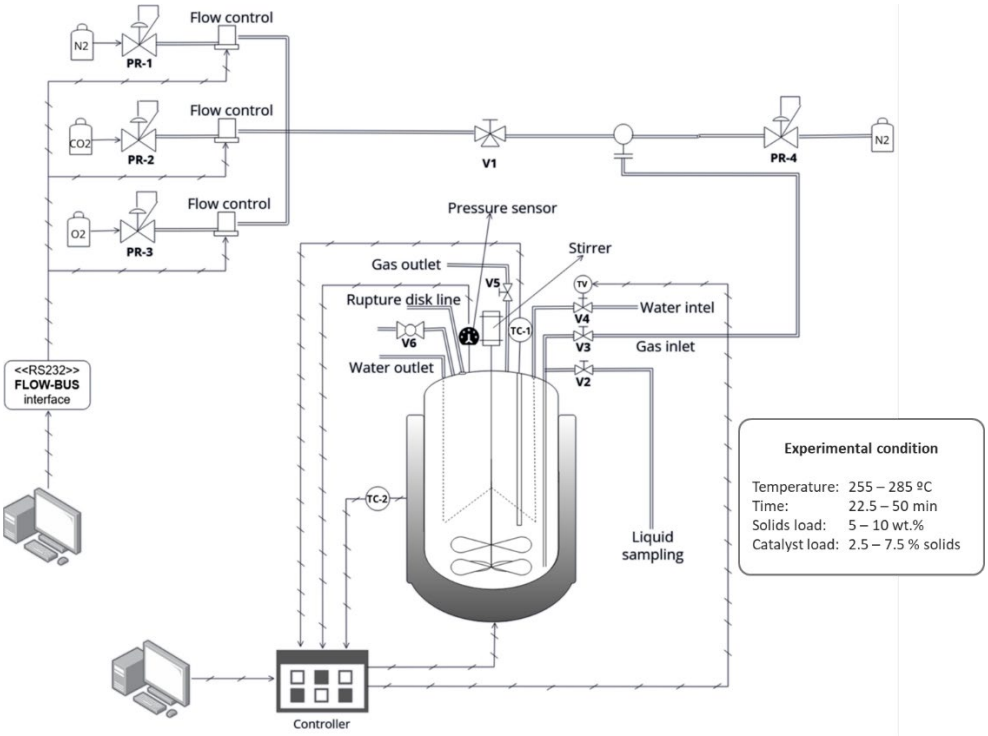

Figure 1. Hydrothermal batch reactor setup. Schematic of the Parr 4520 autoclave and HTL experimental conditions.

3.3 Product analysis

The solid, liquid, and gaseous products obtained from the HTL experiments were quantified and characterized. Hydrochar and feedstock samples were analyzed for solids content and ash according to SFS-EN 12880 and SFS-EN 12879 standards. Elemental composition (CHNS) was determined using a LECO 628 analyzer. Higher heating values (HHV) were measured using a Parr 6400 calorimeter.

Bio-oil samples were diluted in acetone prior to analysis and dried at 50 °C to remove solvent before elemental and calorific value measurements. Gas production was estimated from the pressure difference measured before and after the reaction at 40 °C using the ideal

gas law (Eq. 1), assuming CO_2 as the representative gaseous species, as HTL gas products are typically dominated by CO_2.

$$m(CO_2) = M(CO_2) * \frac{(P_2 - P_1) * V_{empty}}{R * T} \quad (1)$$

where M is CO_2 molar mass (44.01, g/mo; P_1 and P_2 (Pa) are the pressures at 40°C before and after HTL; R is the ideal gas constant (8.31451 Pa.m^3/mol.K); T is the temperature (313.15 K); and V_{empty} is the empty reactor volume (0.0006, m^3). The empty volume was estimated at 0.6 L, considering a sludge feed of 400 g in a 1 L reactor.

The carbon content of the hydrochar samples was corrected to account for inorganic carbon associated with the high ash content of both the raw sample and the resulting hydrochars. In ash-rich materials, part of the measured carbon may occur as carbonates (e.g., $CaCO_3$) rather than organic carbon. Therefore, carbonate-derived carbon was estimated from the measured Ca concentration assuming Ca was present as $CaCO_3$ and subtracted from the measured carbon content according to Eq. (2). Based on sludge volatile solids analysis (67.9%), a fixed carbon content of approximately 5% was estimated, which is reasonably consistent with the correction assuming ~3% of the carbon is present as carbonate.

$$C_{corr} = \frac{m_{hc}C_{hc} - m_{raw}Ca_{raw}(\frac{M_C}{M_{Ca}})}{m_{hc}} \quad (2)$$

where m_{hc} is mass of hydrochar; m_{sludge} is mass of raw sludge; C_{hc} is measured carbon fraction in hydrochar; Ca_{raw} is the calcium fraction in the raw sludge; M_C is the molecular weight of carbon (12.01 g/mol); and $M_{Ca}$is the molecular weight of calcium (40.08 g/mol).

3.4 Experimental design

Since three-way interactions among these factors are unlikely in hydrothermal systems, a fractional factorial design was selected. A full 2^4 factorial would require 16 runs without replicates, providing no internal error estimate, whereas a half-fraction design reduces the number of experiments to eight and it is therefore appropriate for screening purposes. Temperature and residence time are consistently reported as the dominant parameters in hydrothermal treatments, and solids loading has shown additional effects in some studies [7].

Solids loading was therefore included here mainly to assess interaction effects with catalyst loading. Two center points were added to detect curvature, known to be significant in certain HTL studies, and to provide an estimate of experimental error within the limited degrees of freedom of a single replicate fractional design [7].

The factorial experiments are denoted as runs R1–R8, while the center point experiments are labelled C1 and C2 throughout the manuscript. The final design matrix is presented in Table 1.

Table 1. Experimental design matrix for HTL experiments and corresponding factor levels.

Run ID	Standard order	Run Order	Temp. [°C]	Time [min]	Solids load [%]	Catalyst load [%]
R1	1	6	285	47.5	10	7.5
R2	2	4	285	22.5	5	7.5
R3	3	1	285	22.5	10	2.5
R4	4	2	285	47.5	5	2.5
R5	5	7	255	47.5	5	7.5
R6	6	8	255	22.5	10	7.5
R7	7	3	255	22.5	5	2.5
R8	8	5	255	47.5	10	2.5
CP1	-	9	270	35	7.5	5
CP2	-	10	270	35	7.5	5

R1–R8 correspond to the fractional factorial design; CP1–CP2 denote center point experiments.

4 Results and Discussion

The statistical significance of the experimental factors was evaluated using analysis of variance (ANOVA). The corresponding p-values for the main factors and interaction effects influencing bio-oil yield are reported in Table 2. ANOVA results confirmed temperature as the dominant factor influencing product distribution, with a significant quadratic effect indicating an optimal operating window for bio-oil formation at moderate severity conditions.

Table 2. ANOVA results for bio-oil yield, response transformation, model statistics, and model actual factor coefficients.

Factors	SS	Dof	MS	F-value	p-value	Coefficients
Model	1.14	5	0.2283	99.99	0.0016	-20.92463
A-Temperature	0.1867	1	0.1867	81.78	0.0029	0.07055
B-Time	0.0905	1	0.0905	39.65	0.0081	0.14524
D-Catalyst	0.0372	1	0.0372	16.31	0.0273	215.61918
AB	0.0912	1	0.0912	39.95	0.008	-0.00057
AD	0.7357	1	0.7357	322.26	0.0004	-0.80870
Curvature	0.1963	1	0.1963	85.98	0.0027	
Residual	0.0068	3	0.0023			
Lack of Fit	0.0065	2	0.0032	8.16	0.2403	
Pure Error	0.0004	1	0.0004			
Cor Total	1.34	9				
Fit Statistics						
R^2	0.99					
Adjusted R^2	0.98					
Predicted R^2	0.91					
Adeq Precision	29.25					

SS: sum of squares; Dof: degrees of freedom; MS: mean square; F-value: Fisher's F statistic; p-value: probability value; Coefficients: regression coefficients of the fitted model.

The addition of protonated zeolite showed a clear temperature-dependent effect. Increasing catalyst loading had a positive effect on bio-oil yield at lower temperatures. More specifically, bio-oil yields ranged from 6.1 to 17.6 wt.% dry ash free (daf) basis, with the highest yield obtained in run R3 (17.6 wt.% daf) at 285 °C, 22.5 min, 10 wt.% solids and 2.5

wt.% catalyst. At the lower temperature (255 °C), increasing catalyst loading from 2.5 to 7.5 wt.% increased oil yields from 6.1 to 10.0 wt.% (daf) at shorter residence time (runs R7 and R6, respectively) and from 6.5 to 9.5 wt.% (daf) at longer residence time (runs R8 and R5), as shown in Figure 2. This trend indicates a positive catalytic effect under mild HTL conditions.

In contrast, at higher temperatures, the catalytic system exhibited decreased bio-oil yields, from 17.6 to 8.7 wt.% (daf) at 22.5 min (runs R3 and R2) and from 11.6 to 6.2 wt.% (daf) at 47.5 min (runs R4 and R1). This reduction was accompanied by increased gas formation and hydrochar production. For instance, when comparing runs R3 and R2, hydrochar and gas yields increased by approximately 2% and 37%, respectively, suggesting that secondary cracking and gasification reactions were promoted by the acidic catalyst under more severe conditions. The formation of non-condensable gases (CO_2, light hydrocarbons) indicates enhanced fragmentation of intermediate liquid compounds, reducing their retention in the oil phase.

Oil energy yields followed similar trends, ranging from 6.3 to 28.4%, with the maximum energy recovery in the bio-oil phase observed at 285 °C and low catalyst loading (run R3). Total energy recovery (bio-oil + hydrochar) remained relatively high and stable (up to 65.0%), indicating that energy was largely retained in the solid fraction when oil yields decreased. Hydrochar yields were high (40.8–51.8 wt.%) and decreased with increasing temperature, reflecting enhanced devolatilization and conversion of organics into liquid products.

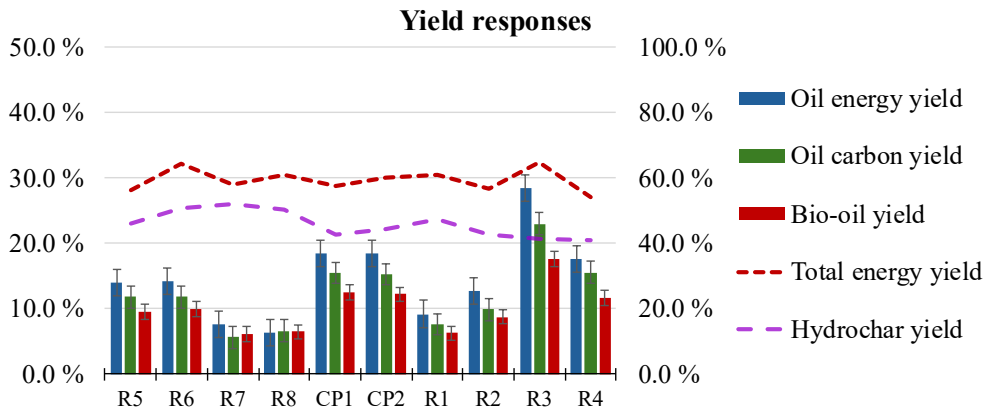

Figure 2. Product yields obtained in HTL experiments R1–R8 and CP1–CP2. Bars represent bio-oil and hydrochar yields (left axis), while lines indicate gas yield (right axis). The experimental conditions corresponding to each run are listed in Table 1.

Bio-oil quality improved with increasing temperature and, under mild conditions, with higher catalyst loading (Figure 3). The carbon contents increased from 48.8 wt.% (daf) in run R7 (255 °C, 2.5 wt.% catalyst) to values as high as 71.0 wt.% (daf) in run R3 (285 °C, 2.5 wt.% catalyst), while oxygen content decreased from 39.2 to 16.3 wt.% (daf), resulting in a substantial increase in higher heating value (HHV). The highest HHV, 31.7 MJ/kg, was obtained in run R3 whereas the lowest value, 19.1 MJ/kg, was observed in run R8, reflecting the strong influence of temperature on bio-oil upgrading.

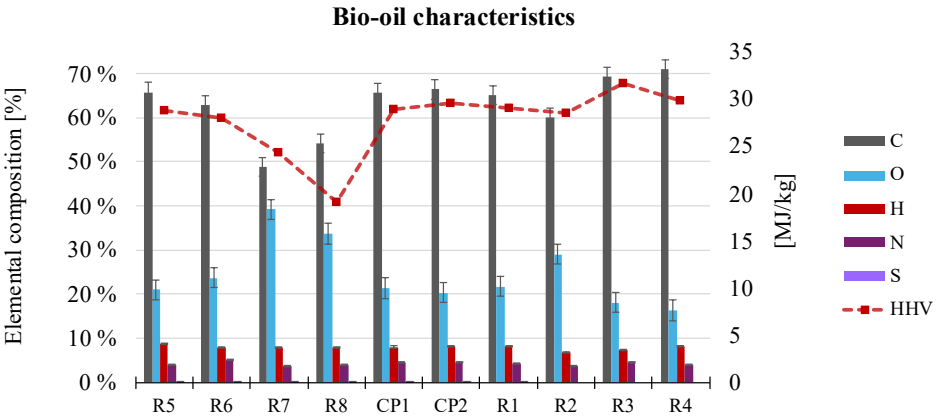

Figure 3. Elemental composition (C, O, H, N, S) and higher heating value (HHV) of HTL bio-oil for runs R1–R8 and C1–C2. The experimental conditions corresponding to each run are listed in Table 1.

Hydrochar (HC) yields were high under the evaluated HTL conditions, confirming that a substantial fraction of feedstock carbon and inorganics remains in the solid phase (Figure 4). Under the mildest conditions (run R7), hydrochar yields reached 51.8 wt.% dry base (db), while under the most severe conditions (run R1) the yield decreased to 40.8 wt.% (db), corresponding to an approximate 23% relative reduction in solid yield. This trend is consistent with previous studies conducted under comparable subcritical HTL conditions, which reported that increasing temperature reduced solid yields by approximately 10 wt.% while gas yields increased by about 10 wt.% [8]. These shifts indicate that increasing reaction severity enhances sludge conversion by transforming organic solids and dissolved organics into biocrude and gaseous products, thereby improving overall carbon conversion efficiency.

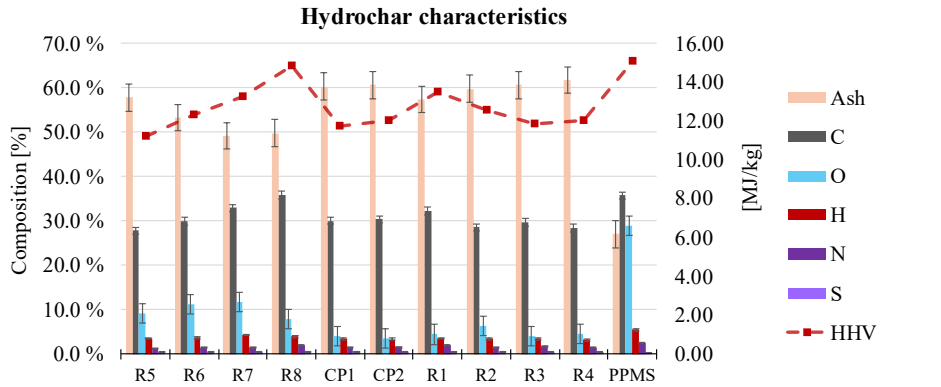

Figure 4. Elemental composition, ash content, and higher heating value (HHV) of HTL hydrochar for runs R1–R8 and C1–C2. The experimental conditions corresponding to each run are listed in Table 1.

Moreover, the HC exhibited very high ash contents (49–62 wt.% db), significantly higher than the original mixed sludge (27 wt.% db), indicating strong concentration of inorganics in the solid phase. Despite $CaCO_3$-corrected carbon contents of 28–36 wt.% (daf), hydrochar HHV remained low (11.2–14.8 MJ/kg), limiting its suitability as a solid biofuel. These results suggest that HC valorization would require alternative pathways (e.g., material applications or controlled disposal) rather than direct energy use.

Overall, these findings suggest that the zeolite catalyst may not be selective towards bio-oil compounds but still enable reaction pathways that are otherwise limited at lower temperatures. In conventional HTL systems, polymerization reactions are often partially suppressed by use of homogenous base catalyst, as dehydration reactions are favored under acidic conditions. However, when the objective is to lower the reactor operating temperature, the use of modified zeolites may offer a viable strategy to enhance conversion despite these trade-offs [9].

Despite localized improvements in bio-oil quality, overall yields remained modest across the design space, and catalyst addition did not result in a substantial net enhancement of energy recovery. The catalytic performance was likely further constrained by fouling from inorganic species present in the sludge, limiting the effectiveness of protonated zeolite under the studied conditions. From a practical perspective, these results indicate that protonated zeolite is not a robust catalyst for HTL of ash-rich pulp and paper mill sludge under mild subcritical conditions.

5 Conclusions

This study assessed the influence of a heterogeneous protonated zeolite catalyst on the hydrothermal liquefaction of mixed pulp and paper mill sludge using a statistically designed experimental approach. The catalyst improved bio-oil yield and quality at lower reaction temperatures but promoted gasification and char formation at higher temperatures. Overall product yield remained low, indicating limited catalytic benefits within the operating window investigated. The findings suggest that zeolite-based catalysts are not optimal for the HTL of inorganic-rich sludge under mild catalytic systems. Future work should therefore focus on alternative catalytic systems, higher reaction severities, or integrated upgrading strategies. The results provide practical guidance for catalyst screening in HTL of industrial wet residues and support the development of more efficient sludge valorization pathways.

References

1. O.E. Salcedo Puerto, Valorization of agricultural and industrial side streams: energy potential and environmental assessment, LUT University (2025)
2. J. Mozas Santhose Kumar, R. Prakash, P. Panneerselvam, Hydrothermal liquefaction − A sustainable technique for present biofuel generation: Opportunities, challenges and future prospects, Fuel, **385,** 134141 (2025)
3. J. Cheikhwafa, K. Glińska, E. Torrens, C. Bengoa, Effect of temperature on hydrothermal liquefaction of high lipids and carbohydrates content municipal primary sludge, Heliyon, **10**, 3, e24731 (2024).
4. Y. Li, L. Li, J. Yu, Applications of Zeolites in Sustainable Chemistry, Chem, **3**, 928–949 (2017)
5. M. Scarsella, B. de Caprariis, M. Damizia, P. De Filippis, Heterogeneous catalysts for hydrothermal liquefaction of lignocellulosic biomass: A review, Biomass Bioenergy, **140**, 105662 (2020).
6. Z. Wang, X. Li , H. Liu, C.S. Lin, Q. Wang, Hydrothermal liquefaction of sewage sludge: A comprehensive review of biocrude oil production, byproducts valorization, and future perspectives, Renew Sust Energy Rev, **224**, 116086 (2025).
7. L. Nazari, Z. Yuan, M.B. Ray, C. (Charles) Xu, Co-conversion of waste activated sludge and sawdust through hydrothermal liquefaction: Optimization of reaction parameters using response surface methodology, Appl. Energy, **203**, 1–10 (2017).

8. D. Xu, G. Lin, L. Liu, Y. Wang, Z. Jing, S. Wang, Comprehensive evaluation on product characteristics of fast hydrothermal liquefaction of sewage sludge at different temperatures, Energy, **159**, 686–695 (2018)
9. Y. Chen, Y. Wu, D. Hua, C. Li, M.P. Harold, J. Wang, M. Yang, Thermochemical conversion of low-lipid microalgae for the production of liquid fuels: challenges and opportunities, RSC Adv., **5**, 18673–18701 (2015)