PNNL-34868

Development of a Sulfur Tolerant CHG Process (CRADA 442) Final Report

October 2022

Huamin Wang, Yuan Jiang, Todd Hart, Andrew Schmidt, Suh-Jane Lee

Pacific Northwest National Laboratory

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Cooperative Research and Development Agreement (CRADA) Final Report

Report Date: October 2022

In accordance with Requirements set forth in the terms of the CRADA, this document is the CRADA Final Report, including a list of Subject Inventions, to be provided to PNNL Information Release who will forward to the DOE Office of Scientific and Technical Information as part of the commitment to the public to demonstrate results of federally funded research.

Parties to the Agreement:

Southern California Gas (SoCalGas), 555 West Fifth St., Los Angeles, California 90013

Pacific Northwest National Laboratory (PNNL), 902 Battelle Blvd, Richland, Washington 99354

CRADA number: 442

CRADA Title: Development of a Sulfur Tolerant CHG Process

Responsible Technical Contact at DOE Lab: Huamin Wang

Name and Email Address of POC at Company: Flavio da Cruz, fdacruz@socalgas.com

DOE Program Office: N/A

Joint Work Statement Funding Table showing DOE funding commitment: N/A

Executive Summary

The Pacific Northwest Laboratory (PNNL) has developed the Catalytic Hydrothermal Gasification (CHG) technology, which can convert low-value organics dispersed in aqueous streams, such as the aqueous phase byproduct from hydrothermal liquefaction (HTL) of wet wastes, to a mixture of methane, H_2, and CO_2. The current CHG catalyst, ruthenium (Ru) on a graphite substrate, was selected for its effectiveness as a reducing catalyst. However, the target waste aqueous feedstock, the HTL aqueous phase from wet wastes, such as sewage sludge, contains a fair amount of sulfur in both organic and inorganic forms.

Like many other reduced metal catalysts, Ru is deactivated or poisoned by exposure to sulfur, among other contaminants. In general, a deactivated Ru catalyst cannot be reactivated or restored except by removing and returning it for remanufacturing. Therefore, there is an urgent need for a sulfur-resistant catalyst to enable CHG processing of the HTL aqueous waste stream. PNNL, with support from SoCalGas CRADA, has developed a sulfur resistant CHG catalyst and demonstrated a stable CHG process for converting HTL aqueous phases from wet wastes.

Here, we report the major accomplishments of the project:

- We have demonstrated that sulfided Ru based catalysts is stable during CHG of HTL aqueous waste stream, with a requirement of activity improvement.
- We have developed a new catalyst, with 0.5-2 wt.% Ru loading, showing better activity compared to the baseline 6.7 wt.% RuS_x/C catalyst.
- With the new catalysts, the single-pass COD reduction is approximately 60% and two-pass COD reduction can reach approximately 85%.
- The process is robust in terms of being effective across a wide range of organic species in the feedstock.
- Techno-economic analysis was conducted to evaluate the economic impact of catalyst advancement and identify further improvement requirements.

This type of catalyst shows great potential to be efficient and robust for CHG with low catalyst cost.

Summary of Research Results

1. Introduction

Southern California Gas Company (SoCalGas) is the nation's largest supplier of natural gas and is working with the State of California to achieve climate change goals with renewable natural gas and hydrogen as the key sources. The Pacific Northwest Laboratory (PNNL) has developed and licensed a Catalytic Hydrothermal Gasification (CHG) technology, which produces methane and/or H_2 from low-value organics dispersed in aqueous streams.[1,2,3,4] CHG process can break down organic matter contained in wastewater/biomass slurry, in a high-temperature high-pressure liquid phase, to gas products, such as methane, other hydrocarbons, and hydrogen. Hydrothermal gasification can be practiced at sub- or super-critical water conditions over a range of operating temperatures, pressures, and types of feedstocks. Using catalysts allows low-temperature operation while maintaining useful kinetics.

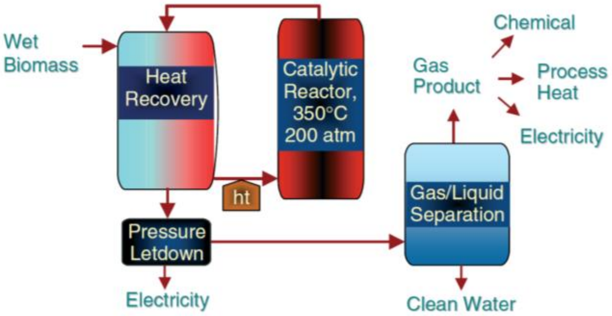


Figure 1. Catalytic hydrothermal gasification at subcritical conditions [1]

Specifically, CHG is suitable to treat the aqueous phase product from the Hydrothermal Liquefaction (HTL) of wet waste feedstocks such as wastewater sludge and food waste. The HTL stage converts approximately 60% of the organic matter in the feedstock (by carbon) into biocrude. There are around 25% of the carbon in the feedstock stays in the HTL aqueous product, which can be converted to gas by the CHG process. The goal of the CHG stage is to achieve high conversion (90%) of the remaining organic matter to gas, leaving the residual water sterile and recyclable to the headworks of a WRRF.

The current CHG catalyst is ruthenium (Ru) on a graphite substrate, selected for its effectiveness as a reducing catalyst.[1,2,3,4,5] However, the target waste aqueous feedstock, the HTL aqueous product from wet wastes, such as sewage sludge, contains a fair amount of sulfur in both organic and inorganic forms at concentrations of over 200 ppm. Like many other reduced metal catalysts, Ru is deactivated or poisoned by exposure to sulfur, among other contaminants. In general, deactivated Ru cannot be reactivated or restored except by removing and returning it for remanufacturing. Therefore, there is an urgent need for a sulfur-resistant catalyst to enable CHG processing of the HTL aqueous waste stream. In addition, the HTL aqueous products contain a wide range of oxygenates including carboxylic acids, phenols, alkanols, and aldehydes/ketones. The efficient conversion of all oxygenates is critical for the CHG catalyst.

PNNL, with support from SoCalGas CRADA, has been developing a sulfur-tolerant CHG process. *The goal of this project is to overcome catalyst sulfur poisoning to enable CHG processing of the*

HTL aqueous waste stream. Two primary focus areas to accomplish this goal are 1) the development of new sulfur-resistant CHG catalysts and 2) the development of new methods to effectively remove sulfur from the HTL aqueous stream prior to CHG processing. The primary thrust of the project is on focus area 1, to develop and demonstrate sulfur resistant Ru-based catalyst.

2. Development of sulfur-tolerant CHG catalyst

2.1 Approach

Catalyst with different metal identities (and loading was synthesized by using conventional wet impregnation methods. The catalyst has been reduced and sulfided in the reactor prior to CHG testing.

CHG test was conducted by using lab-scale continuous CHG test systems. All the tests have at least 80 hours time on stream (TOS) to ensure steady-state water and gas samples can be collected. The liquid samples have been analyzed by chemical oxygen demand (COD) measurement, HPLC, ICP, and CHN elemental analysis. The performance of the catalyst has been primarily determined by COD conversion [$(COD_{feed} - COD_{product})/COD_{feed} \times 100\%$]. The spent catalysts have been analyzed by ICP (for metal loading and possible inorganic contamination) and other characterization techniques.

The HTL aqueous products used as feed for the test are derived from the HTL of sewage sludge. Some properties of the HTL aqueous product include:

- COD: 55,000 – 65,000 mg O/L
- Total carbon: 1.65-1.80 wt.%
- Sulfur: 110-140 ppm
- Nitrogen: ~0.5 wt.%
- Major organic compounds:
  - Carboxylic acids (1.09 wt.%): acetic acid (0.60 wt.%), propanoic acid (0.23 wt.%), butanoic acid (0.22 wt.%).
  - Phenolics (0.13 wt.%): phenol (0.05 wt.%), cresol (0.08 wt.%
  - Alkanols (0.18 wt.%): ethanol (0.09 wt.%), propanol (0.08 wt.%), butanol (0.01wt.%)
  - Aldehydes and ketones (0.08 wt.%): furfural (0.01 wt.%), butanone (0.02 wt.%), pentanone (0.02 wt.%), hexanone (0.01 wt.%).
- Major inorganic species: Si (~200 ppm), K (~200 ppm), Na (~100 ppm)

2.2 Stability of RuS_x/C catalyst for CHG

The previous study by PNNL has identified that the Ru catalyst, such as 6.7 wt.% Ru/C, in reduced form, has excellent CHG activity (>95% COD reduction), but it suffers fast catalyst deactivation by sulfur poisoning. Figure 2 showed the COD conversion of a supported Ru catalyst, pretreated by reduction, and the catalyst presented a high initial activity (100% COD reduction), but rapidly deactivated to near the background activity (measured by using carbon support without Ru loading) within 100 hours. It suggests the rapid deactivation of the catalyst in reduced form. As identified previously, such deactivation is because of sulfur poisoning.

Ru in sulfide form can also catalyze a similar reaction and is essentially sulfur resistant. As shown in Figure 2, the supported Ru catalyst was sulfided under a high H_2S/H_2 ratio condition to ensure

RuS_x formation and then tested under the same conditions. This catalyst also experienced an initial deactivation but reached a steady state after 60 hours of TOS at a COD conversion of around 50%. The results suggested that the Ru sulfide catalyst is much more stable than the reduced Ru catalyst for CHG because it is sulfur resistant and Ru sulfide had better activity than sulfur-deactivated reduced Ru catalyst.

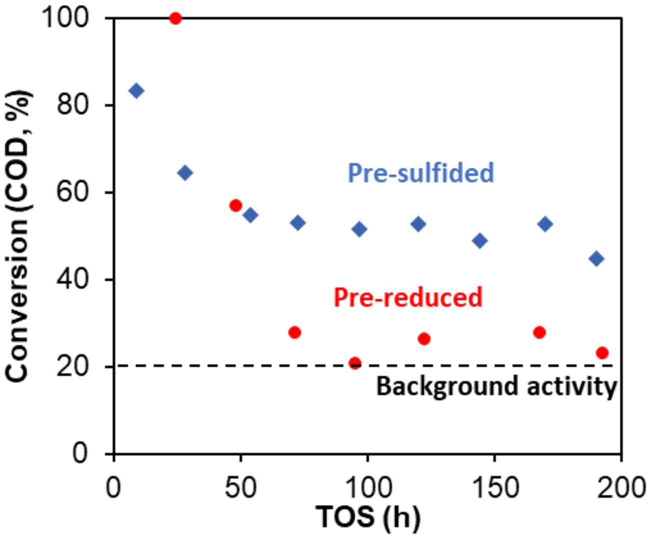


Figure 2. COD conversion of a supported Ru catalyst with different pretreatment. (Reaction conditions: 350 °C, LHSV of 0.54 h^{-1}, 2750 psi)

A 7 wt.% Ru/C catalyst, which is identified by our previous study and used as a baseline catalyst, was then also tested in its sulfide form. As shown in Figure 3, almost 500 hours test was conducted, and the catalyst showed a stable performance under different conditions. Adding sulfur (by blending di-tert-butyl disulfide) in the feed did not influence the activity and stability. A higher reaction temperature (370 °C compared to 350 °C) led to a much-increased COD reduction (from ~40 to 60%). The produced gas contains 30-35 % CH_4, 15-30 % H_2, 10-25 % C2+ alkanes, and 20-30 % CO_2.

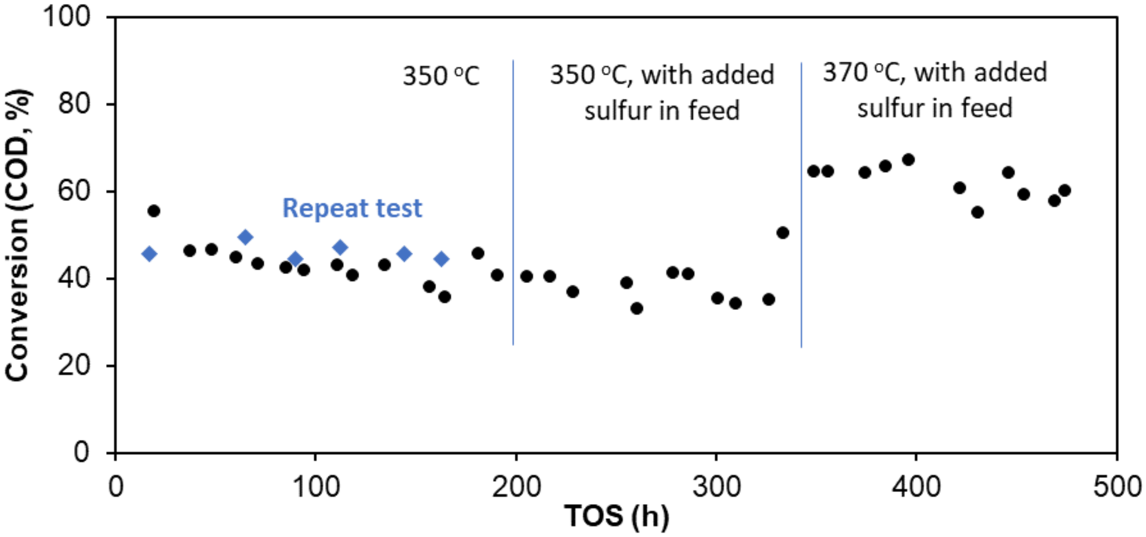


Figure 3. COD conversion of the sulfided RuS_x/C catalyst at different conditions. (Reaction conditions: 350-370 °C, LHSV of 0.54 h^{-1}, 2750 psi)

More tests were conducted using similar supported Ru catalysts and similar results were observed. In general, the Ru in sulfide form (RuS_x), prepared by *in situ* sulfidation, showed stable CHG activity. However, RuS_x/C shows lower activity compared to a reduced Ru/C at the initial less contaminated stage. The best COD conversion for supported RuS_x catalyst is around 50% at 350 ^oC and 60 % at 370 ^oC. As elaborated in section 3 about TEA, the catalyst cost (Ru loading) and by-product credits are key cost drivers. This requires an improved CHG catalyst/process with reduced Ru usage and a high COD reduction, which is the goal of the research described in section 2.3. In addition, the analysis of spent catalysts after the 500-hour TOS CHG test suggested accumulation of inorganics over catalysts could be an issue for a longer-term operation.

2.3 New catalyst with reduced Ru loading

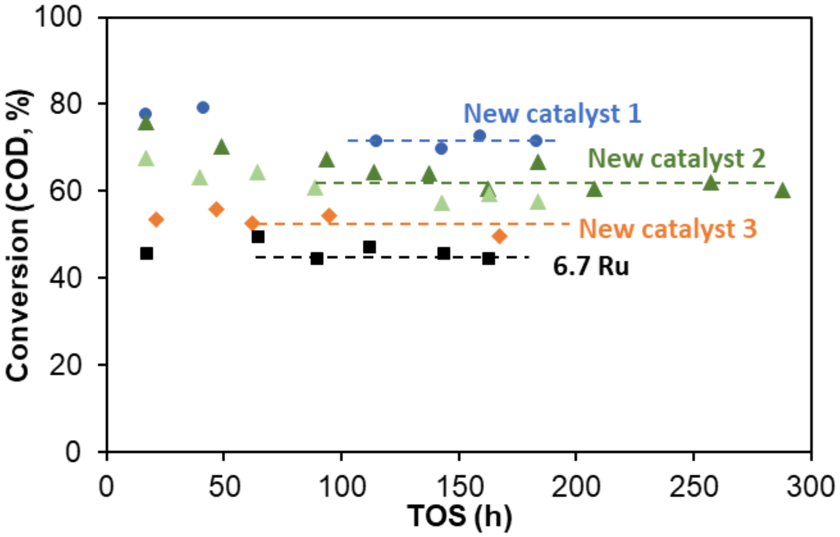


Figure 4. COD conversion of the new catalysts and its comparison to sulfided RuS_x/C catalyst. (Reaction conditions: 350 ^oC, LHSV of 0.54 h^{-1}, 2750 psi)

This project has extensively evaluated different types of Ru-based catalysts for CHG and successfully developed a much-improved catalyst. As shown in Figure 4, new Ru based catalysts with a much-reduced Ru loading (0.5-2 wt.%) showed higher activity than the baseline RuS_x/C catalyst (6.7 wt.%). This type of catalyst was also stable, as demonstrated by more than 300 hours of TOS testing. Higher activity was achieved with a higher Ru loading.

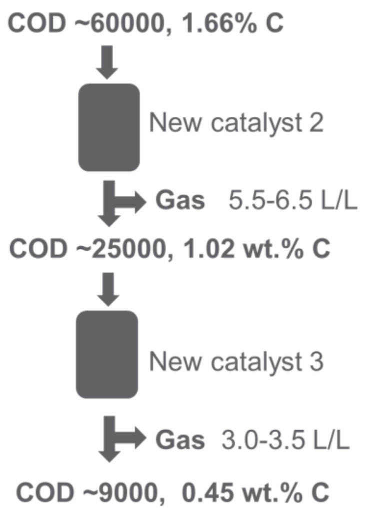


Figure 5. Two-pass CHG using the new catalyst. (Reaction conditions: 350 °C, LHSV of 0.54 h^{-1}, 2750 psi)

The best sulfide catalyst we developed can reach a 70% COD reduction at 350 °C and LHSV of 0.54 h^{-1}. A higher reaction temperature could lead to a higher conversion with the challenges of maintaining condensed phase operation. A lower space velocity did not result in a much higher COD conversion and also brought challenges in lower reactor throughput. In order to achieve a higher COD conversion (>90%), we conducted the reaction in two passes, which included the collection of water produced from the first pass and feeding them to a second reactor. As shown in Figure 5, the single-pass COD reduction is ~60% and two-pass COD reduction can reach ~85%, by using the new catalyst. Total gas production was 8.5-10 L gas per L feed. The gas product contains 40-45% methane, 5-10% H_2, 10-15 % C2+ alkanes, and 30-40% CO_2. ICP analysis of the spent catalyst did not show a noticeable loss of metal components. The synthesis and testing of these catalysts have been repeated by different researchers.

All of these results indicate that the newly developed catalysts, with a much-reduced Ru loading, are stable and active for CHG and, together with process optimization, a high COD reduction can be achieved.

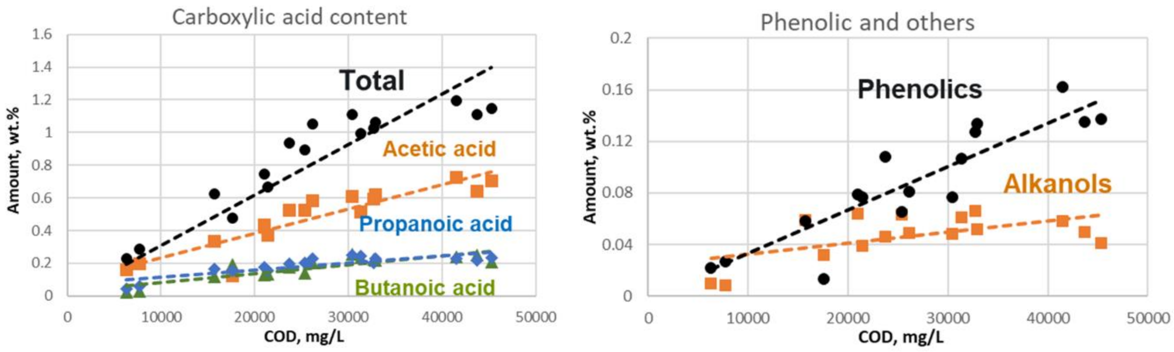


Figure 6. Content of different compounds in processed water products at different COD levels (therefore COD conversion)

The water produced after CHG has been analyzed by HPLC and other techniques. Figure 6 summarizes the content of major compounds found in the feed and produced water after CHG as a function of COD. The major organic compounds found in these samples include carboxylic acids (acetic acid, propanoic acid, butanoic acid), phenolics (phenol, cresol), alkanols (ethanol, propanol, butanol), and aldehydes/ketones (acetone, butanone, cyclopentenone, furfural). The linear dependence of their content with COD (therefore COD conversion) indicates the simultaneous reduction of test organic compounds, suggesting that the process is robust concerning being effective across a large range of organic species in the feedstock.

2.4 Other catalysts

Besides the RuS_x/C and the new catalysts, we have also evaluated other catalysts including doped RuS_x/C catalyst, RuSx over other supports, and non-Ru-based metal catalysts. The major conclusion is listed below and detailed results are available upon request.

- A certain oxide supported Ru catalyst showed slightly better activity than a carbon-supported catalyst at similar Ru loading. However, the oxide support brings concerns about its hydrothermal stability.
- CoMo and NiMo sulfide catalysts were much less active than Ru catalysts. Unsupported NiMoSx was also much less active and required improvement in strength to avoid structure collapse.

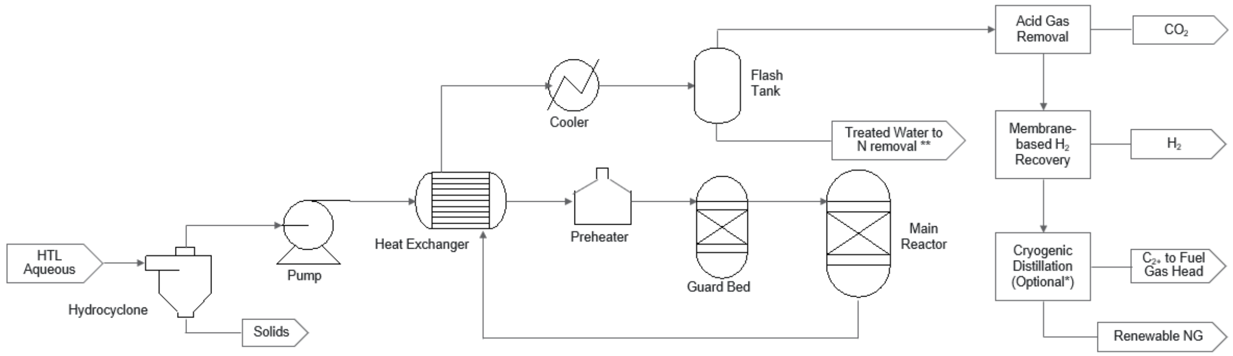
3. Techno-economic Analysis of CHG with Sulfur Tolerant Catalyst for HTL Aqueous Phase Treatment

To support the development of a sulfur tolerant catalytic hydrothermal gasification (CHG) catalyst for treating the aqueous phase waste stream produced from wet waste hydrothermal liquefaction (HTL), techno-economic analysis (TEA) was conducted for six CHG cases with different catalyst designs and operating conditions. This work was done before the new catalyst was developed. Therefore, the CHG cases using the new low Ru loading catalyst are not available.

Process models were developed in Aspen Plus V10 for the wet waste HTL process integrated with CHG for aqueous phase treatment and gas separation unit for producing renewable natural gas (RNG). Experimental data, as well as the projected performance of CHG catalysts, were used as the basis to model the six cases. Minimum biocrude selling price (MBSP) and aqueous phase treatment cost were considered as the key economic measures for catalyst performance evaluation and comparison. The results indicate that catalyst cost, capital investment, and RNG credits are the top three contributors to the economic measures. From the catalyst performance perspective, the impacts on economic measures rank as catalyst life > liquid hour space velocity (LHSV) > CH_4 selectivity > conversion.

3.1 Process Configuration

Details about the wet waste HTL process can be found in our previous reports.[6] Figure 7 gives the process configuration of the CHG unit for HTL aqueous phase treatment. In the CHG unit, the aqueous phase waste stream from the HTL unit is sent to a hydrocyclone for solid removal, pumped to the required pressure for the CHG reactor (210 bar), and heated to about 350 °C before entering the reactors. The main reactor is packed with a Ru-based catalyst to reduce the COD of the aqueous phase and convert organics into light gases (mainly CH_4, CO_2, H_2, and C_{2+}). A guard bed is used to protect the catalyst bed in the main reactor from metals in the aqueous phase waste stream.



*Not required if the fraction of C_{2+} can satisfy the pipeline specification.
**NH_3 stripping + Ammonia sulfate production (if COD reduction > 90%) or THROX for NH_3 destruction.

Figure. 7. Process configuration of CHG unit with gas separation.

The product stream from the main reactor is used to preheat the feed stream, then cooled and sent to a flash tank for phase separation. The liquid phase is the treated water containing a significant amount of NH_3. If a COD reduction above 90% is achieved in the CHG reactor, a high-purity NH_3 stream can be recovered by NH_3 stripping and then used for ammonia sulfate production. If not, thermal oxidation (THROX) technology is used for NH_3 destruction. If RNG is considered as a by-product, the vapor phase from the flash tank will be sent to a series of gas separation units, acid gas removal, H_2 recovery, and cryogenic distillation, as shown in Figures 8 and 9. If RNG is not desired as a by-product, the entire vapor phase product from the flash tank will be used as a utility to support the heat required in other unit operations.

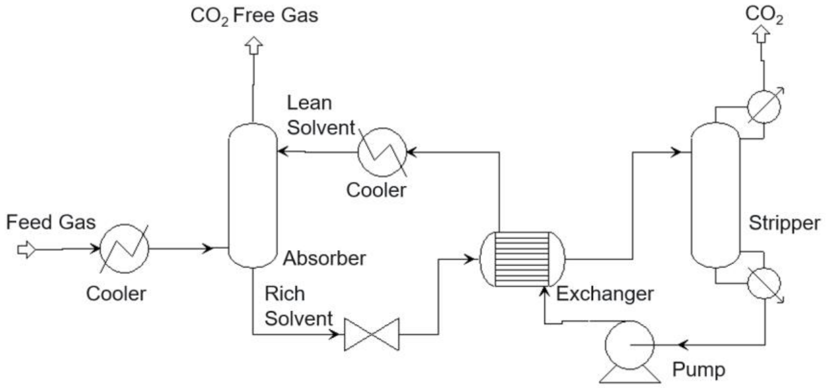


Figure 8. Process configuration of the acid gas removal unit.

In the acid gas removal unit, as shown in Figure 8, CO_2 is removed by chemical absorption using aqueous amine (15 wt% diethanolamine (DEA) and 28 wt% methyl-diethanolamine (MDEA)) as solvent. Here, DEA/MDEA mixture was selected as it has been widely used in the natural gas processing plant for acid gas removal at high pressure.[7] The feed gas and CO_2 lean solvent are cooled before being fed to the absorber in a countercurrent at about 80 bar. The CO_2-free gas leaves the absorber at its top, while the CO_2-rich solvent leaves the absorber at its bottom. Then the rich solvent is depressurized to 2 bar and sent to the stripper to separate CO_2 from the rich solvent and regenerate lean solvent to be used in the absorber. The hot lean solvent at about 112 °C from the stripper's bottom is used to preheat the rich solvent before it enters the stripper.

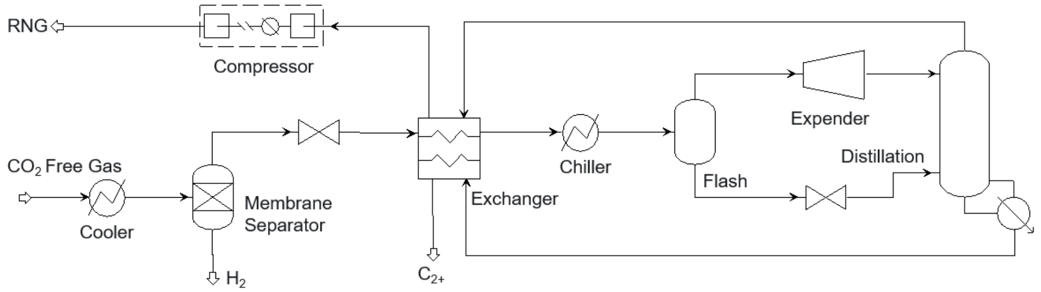


Figure 9. Process configuration of H_2 recovery and cryogenic distillation units.

As shown in Figure 9, the CO_2-free gas is then sent to a membrane separation unit to recover H_2 from light hydrocarbons. The retentate stream from the membrane separator is then depressurized to 62 bar and chilled to -56 °C before being sent to a flash drum for phase separation. The vapor phase from the flash drum is depressurized to 14 bar in an expender to create a low-temperature (-107 °C) vapor stream to be fed to the cryogenic distillation column for CH_4/C_{2+} separation. The liquid phase from the flash drum is also depressurized to create a low temperature. The RNG stream from the top of the distillation column, containing 96 mol% CH_4, 1 mol% CO_2, 2 mol% H_2 and < 3 mol% C_{2+}, is then compressed to 29 bar to satisfy pipeline specification.

3.2 Process Modeling

In this work, process models were developed in Aspen Plus V10 for the HTL process integrated with CHG and gas separation units, as shown in Figure 7. The performance and detailed modeling approach of the HTL process can be found in our 2021 state-of-technology (SOT) report,[6] while this report focuses on the CHG and gas separation units. For the CHG unit, the main reactor was modeled as a yield reactor in Aspen Plus given the conversion rate and product selectivity measured experimentally. Here, six cases as summarized in Table 1 were studied to evaluate the potential impacts from catalyst development and operating conditions. Note that Case 'Ru/C R 0.54 RNG' represented a reduced CHG catalyst developed in the previous project, which did not have good stability and sulfur tolerance. In this case, the catalyst life is expected to be very low even with frequent catalyst regeneration. Ru/C S and Ru/C-2 S are sulfided CHG catalysts with better stability and sulfur tolerance but slightly lower COD reduction. Ru/C-2 S catalysts were tested at two liquid hour space velocities (LHSV) to understand the economic trade-offs between reactor size and conversion. In addition, Case 'Target RNG' represented a performance target with higher COD reduction and more economic benefits, that will need additional catalyst R&D. In this case, the gas selectivity was assumed to be the same as the experimental measures. The COD reduction was assumed to be 90%, allowing high-purity NH_3 production in the NH_3 stripper, which can be converted to high-value by-product $(NH_4)_2SO_4$.

Table 1. Summary of CHG technology options.

Options	Ru/C R 0.54 RNG (1)	Ru/C S 0.54 RNG	Ru/C-2 S 0.54 RNG	Ru/C-2 S 0.54 Utility	Ru/C-2 S 0.25 RNG	Target RNG (2)
Technology						
Catalyst (3)	Ru/C R	Ru/C S	Ru/C-2 S	Ru/C-2 S	Ru/C-2 S	Ru/C-2 S
LHSV, hr^{-1}	0.54	0.54	0.54	0.54	0.25	0.54
Catalyst life, yr	0.25	1	1	1	1	1

Regeneration frequency	5 days (acetone/H_2)	0.25 yr (weak acid)	0.25 yr (weak acid)	0.25 yr (weak acid)	0.25 yr (weak acid)	0.25 yr (weak acid)
Gas product usage	RNG	RNG	RNG	Utility	RNG	RNG
NH_3 treatment	$(NH_4)_2SO_4$ production	THROX	THROX	THROX	THROX	$(NH_4)_2SO_4$ production
Experimental data						
COD reduction, %	>99	55	65	65	72	90 (2)
C reduction, %		48	63	63	68	
S reduction, %		0	18	18	28	
Gas selectivity						
CH_4, mol%	72	35	28	28	40	28 (2)
CO_2, mol%	21	31	27	27	23	27 (2)
H_2, mol%	2	28	17	17	15	17 (2)
C_{2+}, mol%		7	28	28	22	28 (2)

(1) Reduced CHG catalyst developed in the previous project
(2) Targeted performance for future catalyst R&D
(3) R = Reduced, S = Sulfided

For the acid gas removal unit, the ELECNRTL model was used as the property package for process simulation, with property parameters available in the Aspen Plus database.[8] Both the absorber and the stripper were modeled as rate-based columns in Aspen Plus with chemistry and reaction kinetics. The lean, rich loadings were set to 0.04 and 0.24 mol CO_2/mol solvent, respectively. A design spec was set up to achieve a CO_2 concentration lower than 1 mol% in the CO_2-free gas by adjusting the solvent circulation rate. For H_2 recovery, the membrane unit was modeled as a component separator with a hydrogen recovery rate of 97%. Hydrogen permeance of 1E-6 mol/s/m^2/Pa was used for membrane sizing and capital cost estimation.[9] For the cryogenic distillation unit, RK-SOAVE was used as the property package in Aspen Plus. A design spec was set up to achieve a CH_{2+} concentration lower than 3 mol% in the RNG stream by adjusting the distillate-to-feed ratio in the distillation column.

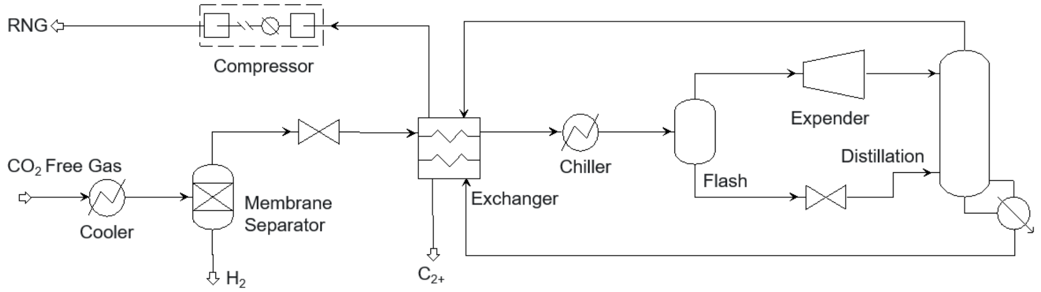


Figure 10. Process configuration of H_2 recovery and cryogenic distillation units.

3.3 Economic Analysis

The mass and energy balance from the process model was sent to the Excel-based economic model to conduct discounted cash flow analysis. Key economic measures, minimum biocrude selling price (MBSP), and aqueous phase treatment cost were estimated in 2016 pricing basis for the HTL process integrated with CHG. Capital costs of key equipment were estimated from vendor cost, Aspen Process Economic Analyzer, or open literature. Tables 2 and 3 lists the key economic assumptions and prices of raw materials, chemicals, and utilities. Here MBSP is the selling price of biocrude that meets a 10% internal rate of return when the net present value is equal to zero. Aqueous phase treatment cost is the estimate of the revenue required to recover annual operating and capital investment of the aqueous phase treatment units (CHG, gas separation, NH_3 stripping, and treatment) considering by-product credits. As the Ruthenium price and carbon credits vary significantly in the past few years, a sensitivity study was conducted to understand their influence on the key economic measures. A more detailed economic analysis approach can be found in our previous publication.[10]

Table 2. Prices of raw material, chemicals, by-products, and utilities (in 2016 U.S. dollars)

Variable	Value	Variable	Value
Wet waste, \$/dry metric ton	0	Electricity, ¢/kwh	6.53
Natural gas, \$/1000 scf	3.51	RIN credits (1), \$/MMBtu	27.1
Quicklime, \$/metric ton	117.1	LCFS credits (1), \$/MMBtu	9.1
Sulfuric acid, \$/short ton	89.3	Ammonium sulfate, \$/short ton	293.7
CHG catalyst (2), \$/lb	57.5		

(1) Equivalent to \$2.5/RIN, and \$190/ton CO_2 avoided, respectively
(2) Strongly depend on the price of Ruthenium

Table 3. Key economic assumptions

Assumption	Value	Assumption	Value
Plant capacity (tpd, daf wet waste) (1)	110	Cost year of analysis	2016
Project contingency (%)	10	Plant life (yr)	30
Indirect cost factor (% of TIC)	60	Construction period (yr)	3
Direct cost factor (% of TIC)	18.5	Maintenance/overhead (% of labor & supervision)	90
Working capital (% of FCI)	5	Start-up time (yr)	0.5
Depreciation period (yr)	7	Stream factor (%)	90
Equity financing (%)	40	Internal rate of return (%)	10
Loan rate (%)	8	Income tax rate (%)	21

(1) tpd = short ton per day, daf = dry ash free.

3.4 Results and Discussion

Table 4 summarized the key modeling results from Aspen Plus. As shown in Table 4, the modeled COD reduction and S reduction agree with experimental measures, while the deviations in C reduction range from 2-8 %. This suggests the Aspen Plus model can adequately represent the performance of different CHG cases and is sufficient for a preliminary techno-economic analysis. The carbon selectivity to RNG and production rates of all by-products are also provided in Table 4. As shown in Table 4, Ru/C S catalyst can offer the highest RNG yield but the lowest COD reduction. On the other hand, Ru/C-2 S catalyst can offer higher COD reduction, but lower RNG selectivity.

Table 4. Summary of Aspen Plus modeling results

Options	Ru/C R 0.54 RNG (1)	Ru/C S 0.54 RNG	Ru/C-2 S 0.54 RNG	Ru/C-2 S 0.54 Utility	Ru/C-2 S 0.25 RNG	Target RNG (2)
Aqueous phase						
COD reduction, %	99.8	50	65	65	72	90
C reduction, %	>99	56	69	69	75	92
S reduction, %	100	0	18	18	28	18
Organic N to NH_3, %	100	32	54	54	63	89
C to CH_4, %	77.4	42.7	21.9	21.9	33.6	21.9
By-products, per gge biocrude						
RNG, MMBtu	0.027	0.010	0.006		0.009	0.008
H_2, MMBtu		0.002	0.001		0.001	0.001
$(NH_4)_2SO_4$, lb	2.28					2.13

The key economic measures are presented in Table 5 and Figures 11-13. Figure 11 presents the MBSP (black dots) and detailed cost breakdown (bars) of the HTL process with CHG and gas separation. Here, the first column represents the original 2021 SOT without CHG unit for aqueous phase treatment. In 2021 SOT, it is assumed that the aqueous phase product from the HTL reactor can be directly recycled to the wastewater treatment and water resource recovery facility after NH_3 stripping. However, the significant COD remaining in the aqueous phase stream could potentially impact the biological operation of wastewater treatment and water resource recovery facilities. Therefore, it is important to explore other treatment options. As shown in Figure 11, adding a CHG unit will increase the MBSP of the HTL process even with the consideration of by-product credits from RNG, hydrogen, and $(NH_4)_2SO_4$. The catalyst cost (marked in yellow bar) is the key contributor to the increase in MBSP, as the catalyst formula contains the precious metal Ru. Therefore, because of the low catalyst life, even with the greatest by-product credits, the MBSP of Case ‘Ru/C R RNG’ is still higher than most of the other cases. The comparison between Case ‘Ru/C-2 S 0.54 RNG’ and Case ‘Ru/C-2 S 0.54 Utility’ suggests that with the same catalyst performance, adding gas separation units for RNG production is more economic than using all gas products from CHG as plant utility. The comparison between Case ‘Ru/C-2 S 0.54 RNG’ and Case ‘Ru/C-2 S 0.25 RNG’ suggests that because of the high price of CHG catalyst, it is not very economical to increase COD reduction by reducing LHSV. The comparison between Case ‘Ru/C S 0.54 RNG’ and Case ‘Ru/C-2 S 0.54 RNG’ suggests that the CH_4 selectivity in the CHG gas-phase product is also critical to the economic measures. Case ‘Target RNG’ suggests that with more catalyst R&D, the increase in MBSP caused by adding a CHG unit can be minimized by enabling high COD reduction and production of $(NH_4)_2SO_4$ as a by-product. The MBSP with CHG can be as low as $2.63/gge, 10% lower than the current best case (Ru/C S 0.54 RNG). The aqueous phase treatment cost can be as low as $0.21/tonne of treated water, about 36% lower than the current best case.

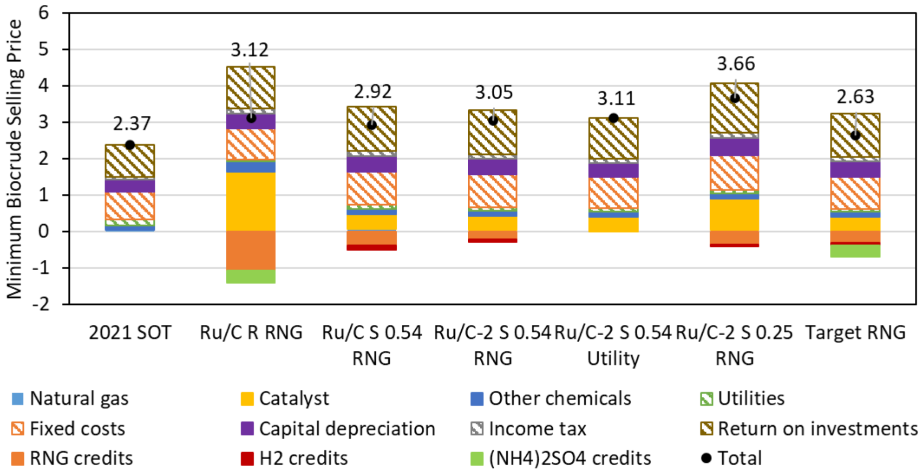


Figure 11. MBSP of HTL process with different CHG designs.

Table 5 summarizes the economic measures of the aqueous phase treatment system. In general, it follows the same trend as Figure 11, because all cases have the same design for HTL and balance of plant. To summarize, the impacts on MBSP and aqueous phase treatment rank as catalyst life > LHSV > CH_4 selectivity > CHG gas yield. In addition, Figure 12 provides a detailed capital cost breakdown for all aqueous phase treatment units. It suggests that CHG unit, cryogenic distillation, and NH_3 treatment are the top three capital cost contributors to the aqueous phase treatment. The capital cost of the CHG unit increases with decreasing LHSV. The capital cost of THROX unit is higher than that of $(NH_4)_2SO_4$ production unit.

Table 5. Aqueous phase treatment cost of different CHG designs.

Options	Ru/C R 0.54 RNG (1)	Ru/C S 0.54 RNG	Ru/C-2 S 0.54 RNG	Ru/C-2 S 0.54 Utility	Ru/C-2 S 0.25 RNG	Target RNG (2)
MBSP increase, \$/gge	0.751	0.549	0.682	0.745	1.286	0.265
Total installed cost of aqueous treatment, MM\$	7.64	9.67	9.35	7.12	12.14	8.88
Treatment cost, \$/tonne aqueous treated	0.495	0.332	0.443	0.568	0.675	0.210
Revenue, MM\$/yr						
RNG	0.315	0.113	0.066		0.104	0.087
H_2		0.131	0.059		0.059	0.077
RIN & LCFS for RNG	3.734	1.228	0.780		1.233	1.035
RIN & LCFS for H_2		0.326	0.148		0.148	0.192

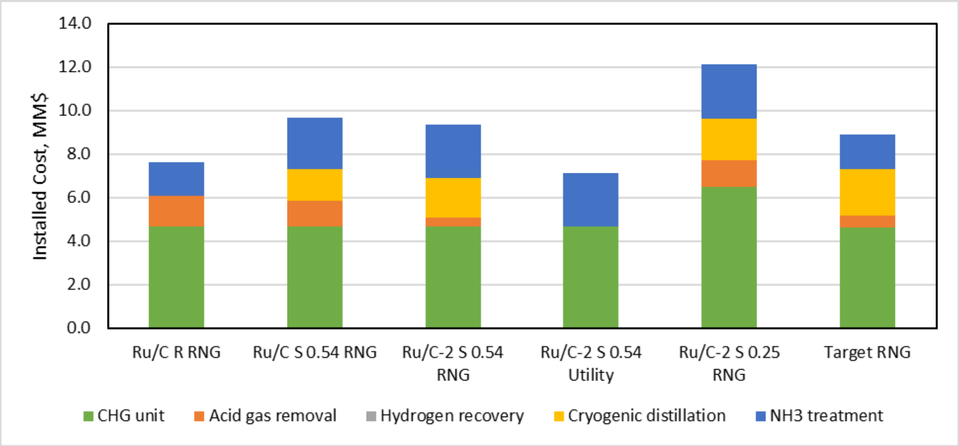


Figure 12. Capital cost breakdown of aqueous phase treatment units.

As shown in Figure 11 and Table 6, both catalyst costs and by-product credits can significantly impact the key economic measures of the HTL process integrated with CHG-based aqueous phase treatment. As Ru price and carbon credits vary significantly in the past few years, a sensitivity study was conducted for Case 'Ru/C-2 S 0.54' and Case 'Ru/C-2 S 0.25' by varying catalyst lifetime from 0.25 to 2 years, with catalyst cost from $29 to $145 per pound, and RIN/LCFS credits +/-50% from the baseline. Figure 13 suggests that the MBSP and aqueous phase treatment cost will increase significantly with a catalyst lifetime lower than 1 year. The key economic measures will increase linearly with an increasing catalyst cost and decreasing carbon credits. The impact of catalyst cost on key economic measures is greater than that of carbon credits.

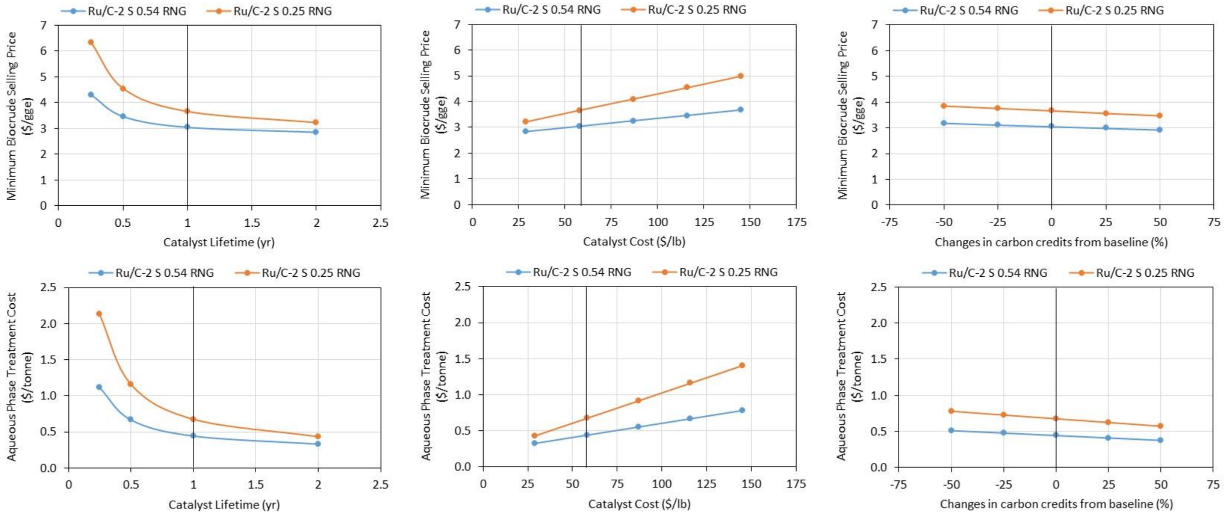


Figure 13. Sensitivity study regarding catalyst price, catalyst lifetime, and carbon credits.

4.0 Development of new methods to effectively remove sulfur from the HTL aqueous stream

PNNL has investigated several approaches for removing organic and inorganic sulfur from aqueous waste streams with only marginal success. For CHG with a reduced Ru/C catalyst, a target of < 10 ppm of sulfur has been suggested to make a stream amenable to CHG; however, to prevent long-term deactivation, the real target should probably be < 1 ppm. Prior approaches investigated include: the use of a Raney Nickel guard bed, precipitation (to form calcium salts), anion exchange, contact with granular activated carbon (GAC), and use of iron and zinc oxide sponges. Of these approaches, only anion exchangers and GAC have removed sulfur species to near target levels; however, the anion exchangers and sorbents are not highly selective and remove more than 50% of the organics in the aqueous stream. Also, after loading the anion exchanger and GAC, attempts at regeneration have failed.

Under this project, we also conduct screening tests to investigate two novel sulfur removal technologies: adsorption using Metal-Organic Framework (MOF) and a reversible electrochemical method. However, the performance of the two technologies has not achieved the sulfur reduction goal and their development was discontinued after phase 1.

For the desulfurization using Nanoporous Materials in Metal-Organic Frameworks (MOF), the objective was to evaluate the adsorptive desulfurization technology using MOFs. Previous work at PNNL on the development of various sorbents for advanced sorption/separation systems has established a unique database for various guest molecules including sulfur-containing moieties. Under this project, a series of nanoporous materials were tested for screening of desulfurization of HTL aqueous stream. Certain MOFs showed sorption performance towards desulfurization. However, the sulfur reduction was <30%, and the loss of oxygenates was not clear.

For the desulfurization using an electrochemical approach, the objective was to identify an electrochemical process for their ability to selectively absorb and desorb both organic sulfur and sulfate from the HTL aqueous stream. Previous work at PNNL has demonstrated the ability to electrochemically remove a great portion of sulfur from HTL biocrude (not the aqueous stream) on a Pt electrode. The results obtained for this project showed that sulfur was converted but not removed (nor adsorbed); N was both converted (into NO_3^{-1}) and removed; C was converted (into short-chain carboxylic acids) and removed as volatile HC (ethane, ethylene, etc); and H_2 is simultaneously produced during S conversion and N and C (conversion + removal).

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6.0 Products developed under the CRADA

One patent application has resulted from this work.

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