



Nutrients

A collage of three photographs. On the left, a waterfall cascades down a rocky cliff. In the center, a scientist in a lab coat is looking through a microscope. On the right, a close-up of a person's hands holding a clear plastic test tube containing a small amount of liquid.

**FINAL
REPORT**

Genifuel Hydrothermal Processing Bench-Scale Technology Evaluation Project

Co-published by



LIFT6T14

GENIFUEL HYDROTHERMAL PROCESSING BENCH-SCALE TECHNOLOGY EVALUATION PROJECT

by:
Philip A. Marrone
Leidos, Inc.

2016



The Water Environment & Reuse Foundation (WE&RF) is a 501c3 charitable corporation seeking to identify, support, and disseminate research that enhances the quality and reliability of water for natural systems and communities with an integrated approach to resource recovery and reuse; while facilitating interaction among practitioners, educators, researchers, decision makers, and the public. WE&RF subscribers include municipal and regional water and water resource recovery facilities, industrial corporations, environmental engineering firms, and others that share a commitment to cost-effective water quality solutions. WE&RF is dedicated to advancing science and technology addressing water quality issues as they impact water resources, the atmosphere, the lands, and quality of life.

For more information, contact:

Water Environment & Reuse Foundation
1199 North Fairfax Street, 9th Floor
Alexandria, VA 22314
Tel: (571) 384-2100
www.werf.org
werf@werf.org

This report was co-published by the following organization.

IWA Publishing
Alliance House, 12 Caxton Street
London SW1H 0QS, United Kingdom
Tel: +44 (0) 20 7654 5500
Fax: +44 (0) 20 7654 5555
www.iwapublishing.com
publications@iwap.co.uk

© Copyright 2016 by the Water Environment & Reuse Foundation. All rights reserved. Permission to copy must be obtained from the Water Environment & Reuse Foundation.

Library of Congress Catalog Card Number: 2016931379
IWAP ISBN: 978-1-78040-840-8

This report was prepared by the organization(s) named below as an account of work sponsored by the Water Environment & Reuse Foundation (WE&RF). Neither WE&RF, members of WE&RF, the organization(s) named below, nor any person acting on their behalf: (a) makes any warranty, express or implied, with respect to the use of any information, apparatus, method, or process disclosed in this report or that such use may not infringe on privately owned rights; or (b) assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

Leidos, Inc.

The research on which this report is based was developed, in part, by the United States Environmental Protection Agency (EPA) through Cooperative Agreement No. CR-83419201-0 with the Water Environment Research Foundation (WERF). However, the views expressed in this document are not necessarily those of the EPA and EPA does not endorse any products or commercial services mentioned in this publication. This report is a publication of WE&RF, not EPA. Funds awarded under the Cooperative Agreement cited above were not used for editorial services, reproduction, printing, or distribution.

This document was reviewed by a panel of independent experts selected by WE&RF. Mention of trade names or commercial products or services does not constitute endorsement or recommendations for use. Similarly, omission of products or trade names indicates nothing concerning WE&RF's or EPA's positions regarding product effectiveness or applicability.

About WE&RF

The Water Environment & Reuse Foundation (WE&RF) is a 501c3 charitable corporation seeking to identify, support, and disseminate research that enhances the quality and reliability of water for natural systems and communities with an integrated approach to resource recovery and reuse; while facilitating interaction among practitioners, educators, researchers, decision makers, and the public. Our research represents a portfolio of more than \$200 million in water quality research.

WE&RF operates with funding from subscribers, donors, state agencies, and the federal government. Our supporters include wastewater treatment facilities, stormwater utilities, and regulatory agencies. Equipment companies, engineers, and environmental consultants also lend their support and expertise. WE&RF takes a progressive approach to research, stressing collaboration among teams of supporters, environmental professionals, scientists, and staff. All research is peer reviewed by leading experts.

For the most current updates on WE&RF research, sign up to receive Laterals, our bi-weekly electronic newsletter.

Learn more about the benefits of becoming a WE&RF supporter by visiting www.werf.org.

ACKNOWLEDGMENTS

The research team thanks Metro Vancouver for providing the wastewater sludge used in these hydrothermal processing tests. Paul Kadota, Mia Edbrooke, and the staff of Metro Vancouver provided advice on sludge types to test, spent a considerable amount of time collecting and dewatering the sludge to our specifications (particularly with secondary sludge), and patiently answered all of our questions.

The team would also thank Peter Kistenmacher and staff at Silicon Valley Clean Water for funding the collection and analysis of product gas samples for siloxanes and arranging for the laboratory that they utilize (Atmospheric Analysis & Consulting, Inc.) to perform these analyses.

Thanks also go to Dr. Tryg Lundquist and Braden Crowe of the California Polytechnic State University in San Luis Obispo, CA, for performing proximate analyses on samples of each sludge feed type.

The team is grateful to all members of the Project Subcommittee and Steering Committee for their interest in this project, for providing various data related to sludge handling and disposal, and for their insightful comments and suggestions on the Quality Assurance Project Plan and this Test Report. The team thanks the U.S. Department of Energy for generously providing funds for Pacific Northwest National Laboratory (PNNL) staff to work on this project and the equipment used to perform these tests. Thanks are also extended to the U.S. Environmental Protection Agency and to the wastewater utilities represented on the Project Steering Committee for direct funding of this work. Finally, the team thanks the WE&RF staff, and particularly Program Manager Jeff Moeller, for coordinating this project and for making this investigation of hydrothermal technology possible.

Research Team

Principal Investigator:

Philip A. Marrone, Ph.D.
Leidos, Inc.

Project Team:

Douglas C. Elliott
Todd R. Hart
Andrew J. Schmidt
Pacific Northwest National Laboratory

Jesse A. Margolin
Margaret A. Randel
Leidos, Inc.

James R. Oyler
Genifuel Corporation

Project Subcommittee

Mohammad Abu-Orf, Ph.D.
AECOM

Bob Forbes, M.Sc., P.E
CH2M

Angela M. Hintz, PE, CEM, CEA, ENV SP
ARCADIS US

Bryan Jenkins, Ph.D.
University of California – Davis

Patricia A. Scanlan, PE, BCEE
Black & Veatch

Jefferson William Tester, Ph.D.
Cornell University

Project Steering Committee

John B. Barber, Ph.D.
Eastman Chemical Company

Ken Baxter
Melbourne Water Corporation

Deborah Beatty
Toho Water Authority

Mia Edbrooke
Metro Vancouver

Victor J. Godlewski, P.E.
City of Orlando, FL

Paul Kadota
Metro Vancouver

Zachary Kay
City of Santa Rosa, CA

Kim Hackett
Silicon Valley Clean Water

Morris Liu
Carlos Vargas
City of Calgary, Alberta

Amanda Roa
Delta Diablo

Department of Energy (DOE) Liaison

Mark Philbrick, Ph.D.
Department of Energy

Innovative Infrastructure Research Committee (IIRC)

Stephen P. Allbee
Retired

Traci Case
Water Research Foundation

Peter Gaewski, MS, P.E. (Retired)
Tata & Howard, Inc.

Kevin Hadden (SAM IAT)
Orange County Sanitation District, CA

David Hughes, P.E.
American Water

Kendall M. Jacob, P.E. (SAM IAT)
Cobb County, GA

Jeff Leighton
City of Portland, OR, Water Bureau

Daniel Murray
U.S. Environmental Protection Agency

Michael Royer
U.S. Environmental Protection Agency

Steve Whipp
Water Innovation Consultant

Research Council Liaisons

Rajendra P. Bhattacharai, P.E., BCEE
City of Austin, TX

Terry Johnson, Ph.D., PE, BCEE
(Retired Black & Veatch Corporation)
Water Consulting, LLC

Water Environment & Reuse Foundation Staff

Director of Research: Amit Pramanik, Ph.D., BCEEM

Director of Water Technologies/Project Manager: Jeff Moeller, P.E.

Program Director: Walter Graf

Additional Interested WE&RF LIFT Working Group Participants

Robert Harris, Jr., P.E.

Gwinnett County Department of Water Resources, GA

Sean Stephan

Alexandria Renew Enterprises

Mark Capron, PE

City of Thousand Oaks, CA

ABSTRACT AND BENEFITS

Abstract:

Hydrothermal Liquefaction (HTL) and Catalytic Hydrothermal Gasification (CHG) proof-of-concept bench-scale tests were performed to assess the potential of the Genifuel hydrothermal process technology for handling municipal wastewater sludge. HTL tests were conducted at 300-350°C and 2900 psig on three different feeds: primary sludge (11.9 wt% solids), secondary sludge (9.7 wt% solids), and post-digester sludge (also referred to as digested solids) (16.0 wt% solids). Corresponding CHG tests were conducted at 350°C and 2900 psig on the HTL aqueous phase product using a ruthenium based catalyst. A comprehensive analysis of all feed and effluent phases was also performed. Total mass and carbon balances closed to within $\pm 15\%$ in all but one case. Biocrude yields from HTL tests were 37%, 25%, and 34% for primary sludge, secondary sludge, and digested solids feeds, respectively. The biocrude yields accounted for 59%, 39%, and 49% of the carbon in the feed for primary sludge, secondary sludge, and digested solids feeds, respectively. It should be noted that HTL test results for secondary sludge may have been affected by equipment problems. Biocrude composition and quality were comparable to that seen with biocrudes generated from algae feeds. CHG product gas consisted primarily of methane, with methane yields (relative to CHG input) on a carbon basis of 47%, 61%, and 64% for aqueous feeds that were the product of HTL tests with primary sludge, secondary sludge, and digested solids, respectively. Siloxane concentrations in the CHG product gas were below the detection limit and well below fuel input composition limits set by several engine manufacturers. Relative to that of the sludge feeds, the HTL-CHG process resulted in a reduction in chemical oxygen demand (COD) of greater than 99.9% and a reduction in residual solids for disposal of 94-99%. The test results, as a whole, support further long-term testing in a larger-scale integrated system that is representative of what would be installed at a water resource recovery facility (WRRF) in order to fully assess the technical and economic viability of this technology for wastewater sludge treatment.

Benefits:

- ◆ Demonstrates that biocrude can be generated from HTL of all three major types of wastewater sludge (primary, secondary, and digested solids) at reasonable yields (i.e., 25-37%) and of comparable quality to that of other biocrudes generated from other high water content biomass feeds.
- ◆ Demonstrates that secondary sludge is more difficult to dewater than either primary sludge or digested solids, and results in a biocrude that may be difficult to recover, though the latter may have been at least partially a result of test equipment problems.
- ◆ Demonstrates that CHG gas product is capable of meeting siloxane limits for use as an internal combustion engine fuel, and CHG aqueous product is capable of meeting water discharge requirements except for nitrogen for some wastewater treatment facilities.
- ◆ Provides a fully characterized set of feed and effluent data for each sludge feed type tested.

Keywords: Liquefaction, catalytic gasification, wastewater sludge, biocrude.

TABLE OF CONTENTS

Acknowledgments.....	iv
Abstract and Benefits	viii
List of Tables	xi
List of Figures	xiii
List of Acronyms	xvi
Executive Summary	ES-1
1.0 Background and Purpose	1-1
2.0 Objectives.....	2-1
3.0 Sludge Feed identification and Preparation	3-1
3.1 Sludge Types.....	3-1
3.2 Sludge Feed Requirements.....	3-1
3.3 Selection of Sludge Feed Supplier	3-2
3.4 Sludge Feed Collection and Preparation.....	3-5
3.4.1 Digested Solids	3-5
3.4.2 Primary Sludge.....	3-6
3.4.3 Secondary Sludge.....	3-11
3.5 Lessons Learned from Sludge Preparation Efforts	3-16
4.0 Hydrothermal Processing Tests.....	4-1
4.1 Test Location.....	4-1
4.2 Equipment and Process Descriptions	4-2
4.2.1 Hydrothermal Liquefaction.....	4-2
4.2.2 Catalytic Hydrothermal Gasification	4-9
4.3 Feed Preparation at PNNL	4-13
4.3.1 Digested Solids	4-13
4.3.2 Primary Sludge.....	4-15
4.3.3 Secondary Sludge.....	4-16
4.4 Tests Performed	4-18
4.4.1 Digested Solids	4-20
4.4.2 Primary Sludge.....	4-29
4.4.3 Secondary Sludge.....	4-36
4.5 Process Monitoring Data.....	4-43
5.0 Sampling and Analytical Results	5-1
5.1 HTL Sampling Strategy and Procedures.....	5-1
5.2 CHG Sampling Procedures	5-2
5.3 Analytical Data	5-3
5.3.1 HTL Feedstock Characterization	5-3
5.3.2 Biocrude Characterization.....	5-4
5.3.3 HTL Aqueous Product Characterization.....	5-5
5.3.4 HTL Solid Product Characterization	5-7
5.3.5 HTL Gas Product Characterization.....	5-8
5.3.6 CHG Feed: Pre- and Post-Ion Exchange	5-9
5.3.7 CHG Aqueous Product Characterization	5-10

5.3.8	CHG Gas Product Characterization	5-11
5.3.9	CHG Sulfur Removal and Catalyst.....	5-11
5.4	QA Review.....	5-12
5.4.1	Ammonia	5-12
5.4.2	Anions	5-13
5.4.3	Chemical Oxygen Demand	5-13
5.4.4	Density and Kinematic Viscosity	5-14
5.4.5	Dissolved Organics	5-14
5.4.6	Elemental Analysis	5-14
5.4.7	Gravimetric Analyses	5-15
5.4.8	Light Hydrocarbons and Permanent Gases	5-16
5.4.9	Metals.....	5-16
5.4.10	Moisture	5-18
5.4.11	pH.....	5-18
5.4.12	Siloxanes	5-18
5.4.13	Total Acid Number	5-19
5.4.14	Total Organic Carbon.....	5-19
6.0	HTP Technical Analysis	6-1
6.1	Sludge Feed Characteristics and Performance	6-1
6.2	Biocrude and Methane (CHG Gas) Yields	6-3
6.3	Mass Balances.....	6-8
6.4	Effluent Quality.....	6-13
6.4.1	CHG aqueous Phase Product	6-13
6.4.2	Siloxane Analysis of the CHG Gas Phase	6-18
6.4.3	HTL Solids	6-19
6.4.4	HTL Effluent Gas Product	6-24
6.5	CHG Catalyst Performance.....	6-24
6.6	System Performance	6-25
7.0	Economic Potential	7-1
7.1	Implications from Test Results	7-1
7.2	WRRF Sludge Disposal	7-6
8.0	HTP Lessons Learned.....	8-1
9.0	Summary and Conclusions.....	9-1
10.0	Recommendations	10-1
Appendix A:	Primary Sludge Feedstock Analytical Data	A-1
Appendix B:	Secondary Sludge Feedstock Analytical Data.....	B-1
Appendix C:	Digested Solids Feedstock Analytical Data	C-1
Appendix D:	Fresh Catalyst and Raney Nickel Metals Analysis Data.....	D-1
Appendix E:	Feedstock Proximate Analysis Data	E-1
References	R-1	

LIST OF TABLES

ES-1	HTL Test Matrix and Process Conditions	ES-5
ES-2	CHG Test Matrix and Process Conditions	ES-5
ES-3	Summary of Test Results	ES-6
1-1	Types of Hydrothermal Processing	1-1
3-1	WRRF Candidates for Providing Sludge	3-3
3-2	Summary of Wastewater Sludge Provided by Metro Vancouver for Testing	3-5
3-3	Comparison of Pre- and Post-Autoclave Samples of Dewatered Primary Sludge	3-9
3-4	Sludge Preparation Data.....	3-10
3-5	Lab-Scale Centrifuge Results with Secondary Sludge	3-13
3-6	Comparison of Pre- and Post-Autoclave Samples of Dewatered Secondary Sludge	3-16
4-1	Sludge Preparation Work at PNNL.....	4-13
4-2	Tests Performed	4-18
4-3	HTL Test Matrix	4-19
4-4	CHG Test Matrix	4-19
4-5	CHG Effluent Samples.....	4-19
4-6	HTL Process Monitoring Data	4-44
4-7	CHG Process Monitoring Data	4-45
5-1	HTL Sampling Strategy	5-2
5-2	CHG Sampling Strategy	5-2
5-3	HTL Sludge Feedstock Characterization	5-3
5-4	Biocrude Oil Characterization	5-4
5-5	HTL Aqueous Product Characterization.....	5-5
5-6	HTL Solid Product Characterization.....	5-7
5-7	HTL Gas Product Characterization.....	5-8
5-8	CHG Feed – Pre- and Post-Ion Exchange.....	5-9
5-9	CHG Aqueous Product Characterization	5-10
5-10	CHG Gas Product Characterization	5-11
5-11	Raney Nickel Sulfur Removal/Ruthenium on Graphite Characterization	5-12
6-1	Key Sludge Feed Data.....	6-2
6-2	Key Biocrude Data.....	6-3
6-3	Biocrude Yield Values	6-5
6-4	CHG Gas Product Data	6-6
6-5	Calculated High Heating Values of HTL Biocrude and CHG Product Gas	6-8
6-6	HTL Flow Rates and Total Mass Balance	6-9
6-7	HTL Carbon Flow Rates and Carbon Balance	6-9
6-8	CHG Flow Rates and Total Mass Balance	6-10
6-9	CHG Carbon Flow Rates and Carbon Balance	6-11
6-10	Pseudo-Combined HTL-CHG Process Total Mass Balance	6-12

6-11	Pseudo-Combined HTL-CHG Process Carbon Balance.....	6-12
6-12	Summary of Aqueous Phase Carbon Data	6-13
6-13	Summary of Aqueous Phase Sulfate and Total Sulfur Data	6-14
6-14	Summary of Aqueous Phase Phosphate and Total Phosphorus Data	6-14
6-15	Summary of Aqueous Phase Nitrogen, Ammonia, and pH Data	6-14
6-16	Summary of Aqueous Phase COD Data	6-14
6-17	WRRF Water Discharge Limits	6-17
6-18	Summary of Gas Phase Siloxane Concentrations	6-19
6-19	Summary of Total Si Data	6-19
6-20	Summary of Total Sulfur and Phosphorus Concentrations on CHG Catalyst After Each Test	6-25
7-1	Solids Reduction and Ash Concentration Data from HTL Tests	7-4
7-2	Current Methods of WRRF Sludge Disposal.....	7-7
8-1	Lessons Learned from HTL-CHG Bench-Scale Tests.....	8-1

LIST OF FIGURES

ES-1	Block Flow Diagram of the Genifuel Hydrothermal Process	ES-2
1-1	Process Options for Converting Whole Organic Biomass to Fuel	1-1
1-2	Block Flow Diagram of the Genifuel Hydrothermal Process	1-3
3-1	Digested Solids	3-6
3-2	Raw Primary Sludge (4.5 wt% solids)	3-6
3-3	Batch Filter Press Used for Dewatering Primary Sludge.....	3-7
3-4	Initial Filter Cake Produced from Dewatering of Primary Sludge (12 wt% solids)	3-7
3-5	Dewatered Primary Sludge (~ 26 wt% solids).....	3-7
3-6	Autoclaving Sludge.....	3-8
3-7	Slump Test on Dewatered Primary Sludge Before Autoclaving	3-8
3-8	Slump Test on Dewatered Primary Sludge After Autoclaving	3-9
3-9	Raw Secondary Sludge	3-11
3-10	Polymer Addition to Raw Secondary Sludge	3-11
3-11	Secondary Sludge After Filter Press and Autoclaving	3-12
3-12	Lab Centrifuge Used by Metro Vancouver on Secondary Sludge	3-13
3-13	55L Dewatering Bags.....	3-14
3-14	Dewatered Secondary Sludge from Dewatering Bags	3-14
3-15	Dewatered Secondary Sludge After Autoclaving	3-15
3-16	Slump Test on Dewatered Secondary Sludge Before Autoclaving	3-15
3-17	Slump Test on Dewatered Secondary Sludge After Autoclaving.....	3-15
4-1	BSEL Building at PNNL	4-2
4-2	PNNL Bench-Scale HTL System	4-3
4-3	HTP Lab at PNNL.....	4-4
4-4	HTL System.....	4-4
4-5	HTL PFR.....	4-5
4-6	Liquid Effluent Collector Vessels.....	4-6
4-7	Pressure Let-down and Gas/Liquid Effluent Separation in Rapid Letdown Mode	4-7
4-8	PNNL Bench-Scale CHG System.....	4-10
4-9	CHG Precipitator and Reactor	4-10
4-10	CHG System Components Downstream of Reactor	4-11
4-11	PNNL High-Shear Mixer	4-14
4-12	Diluted Digested Solids at PNNL (16.4 wt% solids) for HTL Feed	4-14
4-13	Primary Sludge As Received at PNNL	4-15
4-14	Diluted Primary Sludge at PNNL (11.9 wt% solids) for HTL Feed	4-15
4-15	As-Received Secondary Sludge	4-16
4-16	Secondary Sludge After High-Shear Mixing	4-17
4-17	20-Mesh Inline Strainer After Filtering Secondary Sludge	4-17
4-18	CHG Syringe Pump Operating on Aqueous Feed (WERF1-CHG)	4-22
4-19	Temperature Data for HTL Test with Digested Solids (WERF-04).....	4-22

4-20	System Pressure Data for HTL Test with Digested Solids (WERF-04)	4-23
4-21	Steady State Liquid Effluent from the HTL Test with Digested Solids Feed (WERF-04) (shown after being refrigerated).....	4-24
4-22	Biocrude (from Figure 4-20) Remaining After Aqueous Phase Separation (WERF-04).	4-4
4-23	The Last Three Steady State Samples of Biocrude from the HTL Test with Digested Solids Feed (WERF-04).....	4-25
4-24	Biocrude from the HTL Test with Digested Solids Feed (WERF-04)	4-25
4-25	Solids in Opened Filter Vessel After the HTL Test with Digested Solids Feed (WERF-04).	4-25
4-26	Filter Element After the HTL Test with Digested Solids Feed (WERF-04)	4-26
4-27	Solids Found in CSTR After the HTL Test with Digested Solids Feed (WERF-04) ...	4-26
4-28	Feed and Effluent Samples from WERF4-CHG.....	4-27
4-29	Temperature Data for CHG Test with HTL Aqueous Phase from Digested Solids (WERF4-CHG)	4-28
4-30	System Pressure Data for CHG Test with HTL Aqueous Phase from Digested Solids (WERF4-CHG)	4-28
4-31	System Pressure Data for HTL Test with Primary Sludge (WERF-02)	4-29
4-32	Temperature Data for HTL Test with Primary Sludge (WERF-02)	4-29
4-33	Steady State Liquid Effluent from the HTL Test with Primary Sludge Feed (WERF-02).	4-30
4-34	Biocrude from the Three Steady State Set-asides (Three Jars on Right) and a Combination of the Three Set-asides Taken Prior to Steady State (Far Left Jar) from the HTL Test with Primary Sludge Feed (WERF-02)	4-30
4-35	Biocrude from the HTL Test with Primary Sludge Feed (WERF-02).....	4-31
4-36	Aqueous Phase Product from Last Steady State Set-aside Taken During the HTL Test with Primary Sludge Feed (WERF-02).	4-31
4-37	Solids in Opened Filter Vessel After the HTL Test with Primary Sludge Feed (WERF-02).	4-32
4-38	Filter Element After the HTL Test with Primary Sludge Feed (WERF-02).....	4-32
4-39	Solids Collected from the Filter Vessel After the HTL Test with Primary Sludge Feed (WERF-02).	4-32
4-40	Temperature Data for CHG Test with HTL Aqueous Phase from Primary Sludge (WERF2-CHG)	4-34
4-41	System Pressure Data for CHG Test with HTL Aqueous Phase from Primary Sludge (WERF2-CHG)	4-35
4-42	Post-IX Feed (far left) and Effluent Samples from WERF2-CHG.....	4-35
4-43	System Pressure Data for HTL Test with Secondary Sludge (WERF-03)	4-36
4-44	Temperature Data for HTL Test with Secondary Sludge (WERF-03)	4-37
4-45	Close-up View of Organic Solids That Formed in the Liquid Product from the HTL Test with Secondary Sludge Feed (WERF-03).....	4-38
4-46	Unsuccessful Attempt to Separate the Organic and Aqueous Product Phases During the HTL Test with Secondary Sludge Feed (WERF-03)	4-38

4-47	Separated Biocrude from the HTL Test with Secondary Sludge Feed (WERF-03) After Centrifuging	4-39
4-48	Liquid Product Collected from Trap 1 at the End of the HTL Test with Secondary Sludge Feed (WERF-03).....	4-40
4-49	Solids Found Inside the CSTR After the HTL Test with Secondary Sludge Feed (WERF-03).....	4-40
4-50	Solid Material Removed from the Entrance to the PFR After the HTL Test with Secondary Sludge Feed (WERF-03).....	4-41
4-51	Temperature Data for CHG Test with HTL Aqueous Phase from Secondary Sludge (WERF3-CHG)	4-42
4-52	System Pressure Data for CHG Test with HTL Aqueous Phase from Secondary Sludge (WERF3-CHG)	4-43
4-53	Post-IX Feed (two on far left) and Effluent Samples from WERF3-CHG.....	4-43
5-1	Block Flow Diagram of Bench-Scale HTL-CHG Process Used at PNNL.....	5-1
6-1	COD Values in CHG Aqueous Product as a Function of Elapsed Steady State Time ..	6-15
6-2	The Dielectric Constant (ϵ) and Dissociation Constant or Ion Product (K_w) of Water at 200 bar (2900 psi)	6-21
6-3	Salt Solubility in High Temperature Water	6-23
6-4	HTL Biocrude Production Rates Over Time	6-26
7-1	Proposed WRRF Process with Incorporated HTP Technology	7-6

LIST OF ACRONYMS

BCIT	British Columbia Institute of Technology
BOD	Biological Oxygen Demand
BOR	Beginning of Run
BPR	Back Pressure Regulator
BSEL	Bioproducts, Sciences, and Engineering Laboratory
CHG	Catalytic Hydrothermal Gasification
CHN	Carbon, Hydrogen, Nitrogen
CHNOS	Carbon, Hydrogen, Nitrogen, Oxygen, Sulfur
COD	Chemical Oxygen Demand
CSTR	Continuous Stirred Tank Reactor
DAFT	Dissolved Air Flotation Thickener
DOE	Department of Energy
DQO	Data Quality Objective
EDTA	Ethylene Diamine Tetraacetic Acid
EIA	Energy Information Agency
EOC	End of Run
EPA	Environmental Protection Agency
FLC	Federal Laboratory Consortium for Technology Transfer
FOG	Fats, Oils, and Grease
GC	Gas Chromatography; Gas Chromatograph
GHG	Green House Gas
HFO	Heavy Fuel Oil
HHV	High Heating Value
HPLC	High Performance Liquid Chromatography
HTL	Hydrothermal Liquefaction
HTP	Hydrothermal Processing
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
IX	Ion Exchange
LIFT	Leaders Innovation Forum for Technology
MS	Matrix Spike
NAABB	National Alliance for Advanced Biofuels and Bioproducts
OES	Optical Emission Spectroscopy
PFR	Plug Flow Reactor
PNNL	Pacific Northwest National Laboratory
PRV	Pressure Relief Valve
QA	Quality Assurance
QAPP	Quality Assurance Project Plan

RAM	Reliability, Availability, and Maintenance
RLD	Rapid Let Down
RNG	Renewable Natural Gas
RPD	Relative Percent Difference
RSD	Relative Standard Deviation
SCWO	Supercritical Water Oxidation
SOP	Safe Operating Procedure
STORS	Sludge to Oil Reactor System
TAN	Total Acid Number
TCD	Thermal Conductivity Detector
TCLP	Toxicity Characteristic Leaching Procedure
TN	Total Nitrogen
TOC	Total Organic Carbon
TP	Total Phosphorus
TSPS	Thickened Screened Primary Sludge
TSS	Total Suspended Solids
TWSS	Thickened Waste Secondary Sludge
VOC	Volatile Organic Compound
WEF	Water Environment Federation
WERF	Water Environment Research Foundation
WTM	Wet Test Meter
WRRF	Water Resource Recovery Facility

EXECUTIVE SUMMARY

The question posed for this study was to determine if Hydrothermal Processing (HTP) technology has potential for treating wastewater solids. After performing several proof-of-concept bench-scale tests, documented in this report, the research team believes that the answer to the question is yes. Accordingly, further evaluation of the Genifuel hydrothermal processing system at a larger scale is recommended. This recommendation is made both to address certain issues that arose in the bench-scale testing and also to obtain further data on economics, energy consumption, and long-term operating behavior in a system more representative of what could be installed at an operating utility.

HTP is a thermochemical process where water is used as the medium for the breakdown and reconstituting of organic matter into relatively simpler chemical compounds at elevated temperatures and pressures. It is particularly suited for aqueous feeds or solid feeds with high water content, as HTP avoids the need (and significant expense) for drying the feed as required in other thermochemical processes such as pyrolysis and gasification. Hydrothermal Liquefaction (HTL) and Catalytic Hydrothermal Gasification (CHG) are two separate and specific forms of HTP that operate at intermediate temperatures and pressures just below the thermodynamic critical point of water (i.e., subcritical), where the water medium is kept in a liquid state. Under these conditions, water exhibits a dramatic change in its solvent nature, resulting in nonpolar organic compounds becoming more soluble and polar inorganic compounds becoming more insoluble by several orders of magnitude. HTL produces a liquid organic phase product referred to as biocrude and CHG produces a methane-rich product gas. Both the biocrude and gas mixture can be utilized as fuels. The Genifuel HTP technology (Figure ES-1) includes versions of both HTL and CHG processes that were developed at the U.S. Department of Energy's (DOE) Pacific Northwest National Laboratory (PNNL) over the past 30 years. Genifuel holds an exclusive license to PNNL's patents for the purpose of commercializing this technology.

Although over the past several decades research has been performed on HTP and several types of high water content biomass feeds such as algae, there has been relatively little work on its application to wastewater treatment sludge. Wastewater treatment sludge is a feed type that should be particularly suited for HTP processing due to its high water content and rich organic matter. Sludge is the main by-product of wastewater treatment processes and can be of considerable expense to treat and/or dispose. HTP has the potential advantages of not only reducing the amount of solids for disposal but also of being able to convert organic matter in the sludge to fuel that can be used or sold. This fuel produced has further potential value with respect to carbon/greenhouse gas (GHG) emission offsets due to its displacement of fossil fuel equivalents. When used for primary or secondary sludge, HTP has an additional advantage of reducing or potentially replacing biological digestion, such as anaerobic digestion. A number of potential unknowns and data gaps for HTP of wastewater solids exist, of most importance being the effect of flow behavior (i.e., pumpability) and composition on product quantity and quality, solids removal, and catalyst performance.

Based on the potential advantages of HTP and sufficient member interest in this technology, the Water Environment Research Foundation (WERF) through its Leaders

Innovation Forum for Technology (LIFT) tasked Leidos with implementing a test program of the Genifuel hydrothermal process as applied to several types of wastewater solids, and assessing and validating the results. Due to limited prior testing with this feed, bench-scale proof-of-concept tests were determined to be the most appropriate to perform. This report describes the results of HTL and CHG bench-scale tests performed at PNNL on three different types of wastewater solids: primary sludge, secondary sludge, and post-digester sludge (also referred to as digested solids). In these bench-scale tests, the specific configuration of the equipment used and certain other aspects (e.g., energy requirements) do not necessarily reflect that which would be installed at a wastewater treatment plant (referred to in this report as water resource recovery facility, or WRRF) at full-scale. However, the chemistry, product yields, and feed behavior characteristics, which are critical to assessing whether the technology can be successfully applied to wastewater solids, is expected to be representative. Based on the bench-scale test results, this report assesses the potential of hydrothermal treatment for processing wastewater sludge of all three types such that one can determine whether further development is warranted for this feed material.

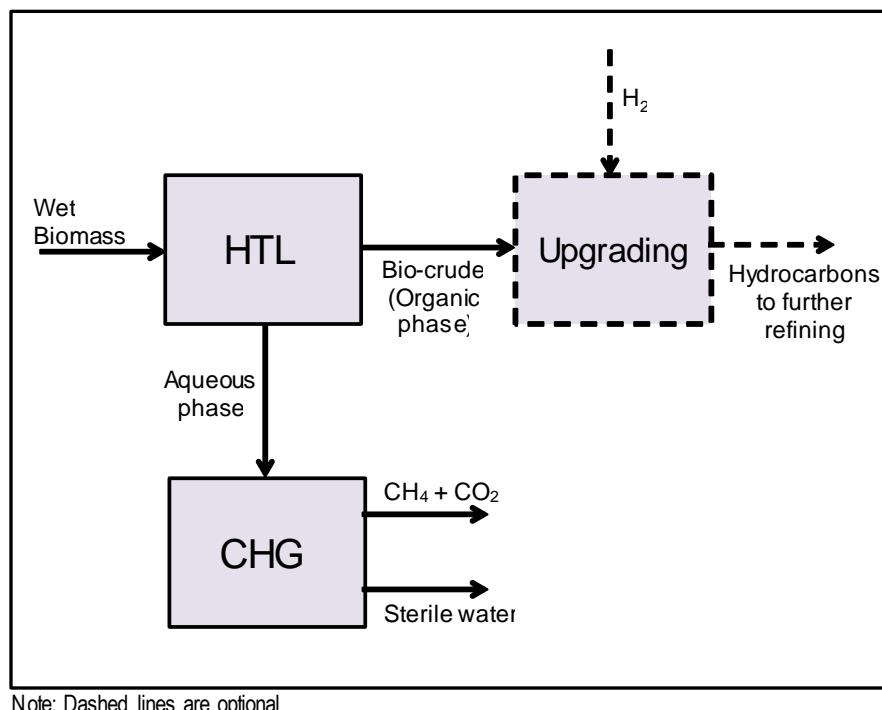


Figure ES-1. Block Flow Diagram of the Genifuel Hydrothermal Process.

Specific objectives for the test program were as follows:

- ◆ Determine a wastewater sludge concentration that can be successfully pumped without interruption during normal operation.
- ◆ Quantify the amount of biocrude oil and methane gas produced from representative sludge feeds.
- ◆ Characterize all feed and product streams with respect to chemical composition.
- ◆ Verify mass balance closure to within 15% for total mass and carbon.
- ◆ Analyze the effect on economic potential of the process based on the quantity and quality of the biocrude oil and methane gas produced and WRRF sludge data.
- ◆ Assess areas of future work based on test observations and results.

All sludge samples for this test program were provided by Metro Vancouver's Annacis Island WRRF in Delta, BC, Canada. Primary and secondary sludge samples (both less than 5 wt% solids) had to be dewatered and autoclaved prior to shipment to PNNL. Autoclaving was a constraint imposed by PNNL Safety (not the HTP technology) for sludge that did not meet Class A biosolids status to protect PNNL staff from the risk of pathogen exposure. Dewatering of primary and secondary sludge was necessary to achieve a high enough feed solids concentration to maximize the HTL biocrude product yields while maintaining steady pumpable flow. The target range of sludge feed solids concentration for the PNNL bench-scale HTL system was 15-20 wt%. Sludge dewatering would be required for a commercial-scale HTL system as well for the same reasons, though the target solids concentration range might be higher because of the larger size equipment and piping diameters. The dewatering procedure for primary sludge consisted of addition of polymer and then use of a batch filter press followed by additional hand pressing of the filter cake with filter paper to concentrate the sludge to about 26 wt%. Secondary sludge, which was more difficult to dewater, was concentrated to 10.9 wt% by use of dewatering bags with added polymer. Attempts to concentrate further to the 15-20 wt% solids target by several methods including both lab-scale and larger size (40 L) centrifugation were unsuccessful within the given time constraints. Digested solids were shipped as normally generated by Metro Vancouver at 28 wt% solids – already above the target feed solids range.

While sludge dewatering was not the major focus of this test program, there were some interesting and important lessons learned through the work performed by Metro Vancouver:

- ◆ Primary and secondary sludge exhibit very different behavior during dewatering.
- ◆ Primary sludge is able to be dewatered without difficulty, at least up to 26 wt% solids on average.
- ◆ Autoclaving of primary sludge appears to have minimal to no effect on physical or chemical structure or appearance.
- ◆ Dewatered primary sludge is not homogeneous, leading to noticeable variation in percent solids concentration each time it is sampled.
- ◆ Secondary sludge is difficult to dewater beyond 11% solids at least with the methods and equipment used in this test program. There are two possible effects at work:
 - Microbe biomass holds water within cell walls which are hard to break.
 - Microbe biomass solids are fine and not easy to separate from water – solids are lost with water if the filter pore size is too large, but the filter blinds if the pore size is too small.
- ◆ Vendor data from several sources suggest that secondary sludge can be dewatered up to 18 wt% solids via centrifuge or other mechanical means, but tests by Metro Vancouver with lab-scale and larger scale (40 L) centrifuges were not able to achieve or validate this claim within the given resource constraints.
- ◆ Autoclaving secondary sludge appears to have a significant effect on its physical structure, causing it to turn to a homogenized, pudding-like material which does not form a filter cake.
- ◆ Secondary sludge and added polymer appear to degrade over time, further hindering the ability to dewater.

It is unlikely that primary and secondary sludge would be treated separately from a practical perspective in a WRRF or in a commercial hydrothermal process. Therefore, in light of the lessons learned in this test program, the best approach for dewatering primary and secondary sludge may be to combine them in a proportion where the beneficial properties of the primary sludge are enough to reach the desired end concentration.

All hydrothermal testing was performed at PNNL's laboratory facility in Richland, WA. The bench-scale HTL and CHG equipment at PNNL consist of separate systems (unlike the intended commercial-scale Genifuel system which would be an integrated one). As a result, bench-scale HTL tests at PNNL were performed separately from the corresponding CHG tests. Feedstock preparation at PNNL consisted of dilution and homogenization of the sludge. The purpose of the preparation work performed at PNNL was to ensure that the sludge was homogeneous and could be pumped to the HTL system via the syringe pump at as high a solids percentage as possible (typically in the range of 15% to 20% solids by weight). Dilution was performed on primary sludge and digested solids only, not secondary sludge.

A total of eight tests were performed in this test program, one HTL and CHG test for each of the three sludge types, with the digested solids tests repeated. In a typical test series, sludge was pressurized and fed via syringe pump to the HTL reactor system. The liquid product consisted of an organic (biocrude) phase and an aqueous phase. The liquid phases were collected in periodic increments and then separated. Solid product was collected continuously in a precipitator/filter vessel at reaction temperature. Gaseous product was analyzed continuously via an on-line gas chromatograph. CHG tests utilized the HTL aqueous phase product as its feed. For these tests, the aqueous phase product was processed through an ion exchange step prior to the CHG test to remove high concentrations of sulfate (which acts as a CHG catalyst poison). The aqueous phase feed was pressurized and fed via syringe pump to the CHG catalytic reactor. Gaseous product was sampled manually at periodic intervals and analyzed off-line via gas chromatograph. The single phase CHG liquid product was sampled at the same periodic intervals as the gas phase product.

The first HTL test performed with digested solids had an unplanned, premature shutdown just as the system was approaching steady state. Because of the limited amount of aqueous product from this first HTL test, the corresponding CHG test was performed with the mostly non-steady state aqueous product as feed. Both HTL and CHG tests with digested solids were repeated, performed successfully to completion under intended conditions, and replaced the first tests with this feed. The HTL test with secondary sludge had a loss of mixing in the stirred tank portion of the reactor system. Though experimental evidence suggests that this occurrence may have affected the product quality and quantity, this test was not repeated due to budgetary constraints. All tests otherwise proceeded as planned, except that in all cases, an additional process step of ion exchange had to be performed on HTL aqueous product to reduce high sulfate concentrations. A summary of HTL and CHG tests performed and key process conditions are provided in Tables ES-1 and ES-2, respectively. Steady state samples of feed and all product phases were collected in each test. A comprehensive set of analyses was performed on each sample either at PNNL or an outside laboratory. This analytical data set was reviewed and validated for precision and accuracy of results.

Table ES-1. HTL Test Matrix and Process Conditions.

Test No.	Sludge Feed	Feed Conc. (wt% solids)	Feed Flow Rate (L/hr)	Reaction Temperature (°C) ^a	Avg. System Pressure (psig)	Liquid Hourly Space Velocity (hr ⁻¹) ^b	Test Duration			No. of Steady State Liquid Samples (Set-asides)
							Total Feed (hrs)	Baseline steady state (hrs) ^c	RLD steady state (hrs) ^c	
2	Primary	11.9	1.5	318-353	2948	2.1	7.4	2.0	1.5	3
3	Secondary	9.7	1.5	276-358	2919	2.1	7.5	2.0	1.0	3
4 ^d	Digested Solids	16.0	1.5	332-358	2906	1.2	7.2	2.7	1.5	4

^a Range indicated spans average temperatures measured over the stirred tank and plug flow reactor sections only (i.e., excludes heated filter temperatures).

^b Based on combined volume of stirred tank and plug flow reactors only (i.e., excludes effects from heated filter vessel).

^c Liquid product samples taken during Baseline steady state period; gas product sample data taken during Rapid Let-down (RLD) steady state period.

^d The first test with digested solids (Test No. 1) ended prematurely due to operator error. Official data for digested solids is from this repeated test.

Table ES-2. CHG Test Matrix and Process Conditions.

Test No.	HTL Aqueous Effluent Feed Source ^a	Feed Flow Rate (mL/hr)	Avg. Reactor Temperature (°C)	Avg. System Pressure (psig)	Reactor Residence Time (min) ^b	Test Duration (hr)		Sulfur Removal (Raney Ni) (g)	Catalyst (Ru on graphite) (g)
						Total Feed	Steady State		
2	Primary	39.7	347	3023	15	49.3	20.6	8.05	10.71
3	Secondary	43.8	346	2883	15	45.4	35.9	8.19	11.82
4 ^c	Digested solids	41.2	348	2959	15	29.4	21.0	8.98	11.65

^a Because of lower than expected quantities of aqueous feed, the aqueous phase portions of all steady state set-asides from the corresponding HTL test were combined into a single feed for each CHG test.

^b Based on catalyst instead of reactor volume; assumes 50% void volume in catalytic reactor.

^c Repeat and replacement of Test No.1.

A summary of key test results is provided in Table ES-3. HTL biocrude and CHG methane product gas were generated in measurable quantities from each of the three sludge feed types tested. In particular, the biocrude yield from digested solids was higher than expected based on the depleted organic content of the feed relative to undigested sludge. Significant reduction in organic content (as measured by total organic carbon and chemical oxygen demand parameters) was also achieved in the final CHG aqueous effluent product in all tests. Specific data provided by personnel from several WRRFs that are members of the WERF Project Steering Committee regarding water discharge requirements and current sludge disposal costs were analyzed and helped provide perspective on the capabilities of the HTL and CHG processes. All objectives of this test program were met as a result of testing and the analysis performed in this report.

Table ES-3. Summary of Test Results.

	Primary Sludge	Secondary Sludge	Digested Solids
HTL Biocrude Yield^a: Total mass basis Carbon basis	37.3% 59.3%	24.8% 38.8%	34.4% 48.7%
CHG Methane Yield^a (carbon basis)	46.7%	60.7%	64.1%
Total Mass Balance^b: HTL CHG	101% 93%	103% 95%	107% 88%
Carbon Balance^c: HTL CHG	94% 67%	97% 99%	111% 88%
Chemical Oxygen Demand (mgO₂/L): Sludge Feed CHG Aqueous Product	187,000 54	153,000 25	203,000 19

^a Yield values normalized per corresponding mass balance value.

^b Calculated as the sum of the mass flow rates of all product output streams divided by the mass flow rate of input sludge feed for the indicated system.

^c Calculated as the sum of the carbon fraction of the mass flow rates for all product output streams divided by the carbon fraction of the mass flow rate of input sludge feed for the indicated system.

Based on the data gathered and observations made during the proof-of-concept, bench-scale HTL and CHG tests with wastewater sludges, the following summary/conclusions can be made:

1. The HTL process is capable of generating separable biocrude from primary sludge and digested solids at yields (34-37%) that are significant with respect to potential revenue to a project, even with feed concentrations that have not been optimized with respect to solids concentration. Based on PNNL tests with other feeds, higher solids concentrations in the feed would be expected to generate higher yields.
2. The HTL process may be capable of generating separable biocrude from secondary sludge, but test results were inconclusive due to equipment failure that occurred during the test. Initial indications of a separable liquid biocrude changed to a solids-like organic phase that was difficult to separate during steady state after mixing stopped in the CSTR. It is not clear to what extent the equipment problems, low feed solids concentration, and autoclaving (constraint of PNNL testing) influenced these observations or by what mechanism. In the absence of these test or program related issues, it is possible that secondary sludge could behave similarly to the other sludge feeds tested. However, if these test observations are inherent to the nature of the secondary sludge, a separation method would need to be developed at commercial scale.
3. Unlike primary sludge, secondary sludge was difficult to dewater beyond 11 wt% solids with the methods tried in this study. While this observation is consistent with the reputation of secondary sludge in the wastewater treatment industry, there is sufficient vendor data to suggest that secondary sludge can be mechanically dewatered up to at least 18 wt% solids with appropriate equipment. Also, unlike primary sludge, autoclaving appears to have a significant degrading effect on the physical structure of secondary sludge (though no autoclaving would be necessary in a commercial-scale HTP system).

4. No significant equipment changes were needed to process sludge feed at the concentrations tested. The feed concentrations (which ranged from 9.7-16.0 wt% solids) were not optimized. It is likely that the HTL system could have processed higher concentrations than that tested but it is not clear how much higher as the solids concentration limits were not determined by these tests. Minor quantities of fouling were observed during testing, but the system is susceptible to solids buildup if there is insufficient turbulence to suspend the solids until reaching the filter vessel.
5. Biocrude quality appears to be comparable to that derived from other biomass feeds (e.g., algae) and needs to undergo upgrading for reduction of oxygen content and total acid number (TAN) values to generate a refinery-compatible feed (unless a refiner is capable and willing to perform the upgrading).
6. Good mass balance closure (to within \pm 15%, as was the objective) was achieved for all total mass and carbon balances across each system except in one case.
7. 94 samples were collected from the HTL and CHG processes to characterize the feedstock samples and product streams. Eighteen measurement methods were used by four laboratories for a total of approximately 2,500 analytical data results. With minor exceptions, these results had adequate precision and accuracy and can be used for an evaluation of the technologies.
8. CHG aqueous feed in all cases had to be processed through an ion exchange column for removal of high sulfate concentrations (catalyst poison) in the HTL aqueous product. As implemented for this test program, the ion exchange process impacted the composition of the CHG feed (e.g., pH increase, significant carbon loss) and is not representative of how sulfate removal would or should be performed in a commercial-scale system. An improved method for sulfate removal needs to be demonstrated.
9. CHG product gas consisted mostly of methane, showed no unusual components, and had a calculated heating value similar to natural gas. The high methane content (75-97 vol%) may have partly been an artifact of testing, as the amount of carbon dioxide in the gas phase was directly affected by the increased pH of the aqueous feed caused by the ion exchange step. On a mass and energy basis, less CHG product gas was generated than HTL biocrude.
10. Siloxane concentrations in the CHG product gas were below detection limits in most cases, and well below the fuel inlet composition limits established by several engine manufacturers. Most silicon appears to partition into the HTL and CHG aqueous phase product.
11. The CHG process is capable of producing aqueous effluent that is sufficiently clean to meet all bacteria-related regulatory limits for water discharge from several WRRFs. The CHG aqueous effluent in these tests also met or came close to meeting BOD and total phosphorus discharge limits, but not total nitrogen. An additional nitrogen removal step would be needed to consider direct discharge of CHG effluent along with treated WRRF effluent. An alternative to avoid this additional step would be to return the CHG aqueous product to the WRRF headworks, or sell it as fertilizer for its nitrogen content. In the former case, the

impact of adding nitrogen to the headworks will need to be carefully assessed for treatment and cost impacts.

12. The CHG Ru/C catalyst and Raney nickel guard bed performed well during testing, but sulfur levels measured on the catalyst and guard solids at the end of each test indicated that poisoning was occurring. The catalyst and guard bed life times beyond the maximum time exposed to feed in these tests (85 hours) and the frequencies of replacement with these sludge-derived aqueous feeds is uncertain. Because of the high catalyst cost (\$114/lb for Ru/C and \$33/lb for Raney Ni), further sulfur content reduction upstream of CHG will be necessary to minimize the frequency of catalyst replacement.
13. The CHG process functions primarily as a polishing stage for the effluent water, as well as a method to obtain more fuel value from additional methane produced and possibly to recover plant nutrients. If aqueous effluent from hydrothermal processing is not intended to be discharged to the environment (e.g., if it is recycled back to the plant headworks), the CHG process may not be necessary or may not justify the added operational expense for the above listed benefits (improved effluent quality, the amount of methane produced, and/or value of nutrients recovered). In this case, it may make sense to consider utilizing only the HTL process.
14. Based on the demonstrated yields and the amount of solids reduction observed relative to typical WRRF sludge quantities, there is potential for cost savings (in terms of fuel displacement and disposal costs) from implementation of hydrothermal processing.
15. The overall results of this proof-of-concept test program are sufficiently promising to justify further investigation of the HTL-CHG technology for application to WRRF sludge.

Based on the results of this proof-of-concept bench-scale test program for HTL-CHG of wastewater sludge, a number of recommendations can be made. In general, it should be noted that while some of the specific recommendations are either related to or a result of issues that occurred during the bench-scale testing, the team does not believe that more bench-scale tests are necessary for this technology and application. The intent would be to resolve or further explore any of the outstanding issues from the current test program during the recommended future pilot-scale testing (see #2 below). The recommendations for future work are as follows:

1. Determine the optimal sludge feed concentration for each sludge type through HTL. This includes verification/demonstration of sufficient dewatering of secondary sludge. The optimization should be based on the expected pump type to be utilized in a commercial-scale system.
2. Perform long-term operation tests on a single, integrated HTL-CHG system at pilot-scale that is representative of the equipment and design that would be installed at a WRRF. If possible, these tests could be performed at a WRRF location. Such tests should be performed with both an optimized, plant representative combination of primary/secondary sludge mixed feed and with digested solids feed. The tests should be of sufficient duration to demonstrate and assess continuous HTL biocrude/aqueous phase product separation, HTL solids removal, and CHG catalyst performance, and to identify at a high level key reliability and availability values and

maintenance (RAM) requirements. Tests should be performed in triplicate to verify reproducibility of results. Upgrading of the biocrude produced should also be performed to assess its quality and value compared to petroleum crude. Performing these tests on a system built and installed directly at a utility would have the advantage of allowing observation of both equipment operation and integration into an actual operating environment.

3. Repeat HTL tests with (non-autoclaved) secondary sludge to confirm biocrude yield and phase separability results under proper functioning experimental conditions. This could be done during pilot-scale tests described in Recommendation #2.
4. Determine the most representative combination of primary and secondary sludge concentrations for WRRFs that do not utilize anaerobic digestion and perform HTL and CHG tests on this combined sludge feed. This could be done during pilot-scale tests described in Recommendation #2.
5. Demonstrate better temperature control and monitoring over the HTL reactor components. Temperature variations of 40°C or more as seen in these bench-scale tests will have a noticeable effect on salt solubility and precipitation. Reactor system temperatures should be kept as uniformly close to the target 350°C value as possible (or slightly higher) to not only maintain more consistent operating conditions but also to maximize product solids (e.g., sulfate) removal prior to CHG.
6. Develop and demonstrate an effective method to remove sulfate species from HTL effluent to a sufficiently low concentration to avoid the need for ion exchange and poisoning of the downstream CHG catalyst. This method may be as simple as maintaining consistent operation at the standard HTL temperature (i.e., 350-360°C) for decreased sulfate solubility and increased precipitation, and should be investigated first. An additional option to explore if temperature alone is insufficient is the use of chemical additives. The additives should be chosen to be compatible with sludge feed and to further reduce sulfate concentration via precipitation under HTL reaction conditions without plugging or interfering with system fluid flow.
7. Determine the CHG ruthenium catalyst replacement frequency with sludge-derived aqueous feeds after adequate means of sulfate removal have been established. Also, assess the amount and impact (if any) of catalyst coking during future long-term operating tests (see Recommendation #2).
8. Perform an energy balance on an integrated, representative pilot-scale system (in conjunction with the recommended long-term operating tests in Recommendation #2). This will allow a relevant and more accurate assessment of the energy input requirements.
9. Produce enough biocrude (without upgrading) to do a burner test and possibly a small internal combustion or diesel engine test (e.g., 10 hp, four-stroke engine) to assess the viability for use of biocrude on-site for power or steam production. A check of engine manufacturers for materials compatibility should be done before any test.

10. Perform a Toxicity Characteristic Leaching Procedure (TCLP) test on HTL solids to determine proper classification for disposal. This could be done during pilot-scale tests described in Recommendation #2 using a sludge feed composition representative of that intended to be processed at a WRRF.
11. In collaboration with WRRF facilities, identify trace organic contaminants (e.g., antimicrobials, flame retardants, hormones, pharmaceuticals, surfactants, pesticides) of highest concern and/or difficulty to eliminate by present means for the wastewater industry. In future HTL-CHG tests (such as the pilot-scale tests in Recommendation #2), analyze both the sludge feeds and CHG effluent for these contaminants in order to determine/verify their fate during hydrothermal processing. If necessary, a test feed could be spiked with a known amount of a particular contaminant for a more controlled test.
12. Characterize the filtrate resulting from dewatering of undigested sludge (prior to HTP) in order to ensure compatibility of this new filtrate stream with WRRF operation when recycled back to the headworks.
13. Identify interested WRRF facilities and perform a detailed site-specific economic analysis to assess the economic viability for a full-scale installation of a HTL-CHG system. This analysis should include estimating the value of biocrude produced via HTL and the costs to upgrade it. In the analysis, consideration of various options (e.g., recycling of CHG aqueous effluent versus collection for sale as a liquid fertilizer) should also be considered to determine the optimal configuration.
14. Perform a full analysis of the greenhouse gas (GHG) reduction potential and associated value of carbon offsets from a representative scale HTL-CHG system (this can be done as part of the recommended long-term operating tests in Recommendation #2).

CHAPTER 1.0

BACKGROUND AND PURPOSE

In recent years, there has been a concerted effort to develop processes that convert organic biomass to usable fuels. The reasons are many and range from decreasing reliance on imported fossil fuels, to providing new markets for domestic farmers, to improving clean up and extracting value from materials previously viewed as wastes. Most of these processes are either biological (e.g., fermentation) or thermochemical in nature (Figure 1-1). Hydrothermal processing (HTP) is a thermochemical process where water is used as the medium for breakdown of organic matter into relatively simpler chemicals at elevated temperatures and pressures (Elliott, 2011). Depending on the particular temperature, products can range from solid char (at about 200°C) (Zhao et al., 2014) to methane and hydrogen gas (at and above 500°C) (He et al., 2014). Table 1-1 compares the various types of HTP and key characteristics. HTP is particularly suited for aqueous feeds or solid feeds with high water content because it avoids the need (and significant expense) for drying the feed as required in other thermochemical processes such as pyrolysis and gasification. Gaseous products can also be formed at lower temperatures through the use of catalysts.

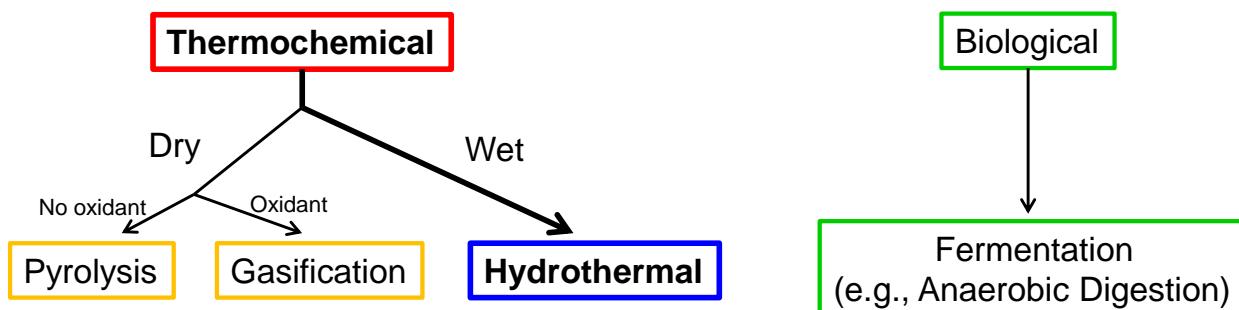


Figure 1-1. Process Options for Converting Whole Organic Biomass to Fuel.

Table 1-1. Types of Hydrothermal Processing.

Process	Oxidant?	Catalyst?	Water State	Product Phase of Interest
Hydrothermal Carbonization (HTC)	No	No	Subcritical	Solid
Hydrothermal Liquefaction (HTL)	No	Possible	Subcritical	Liquid
Catalytic Hydrothermal Gasification (CHG)	No	Yes	Subcritical	Gas
Supercritical Water Gasification (SCWG)	No	Possible	Supercritical	Gas
Wet Air Oxidation (WAO)	Yes	Possible	Subcritical	-
Supercritical Water Oxidation (SCWO)	Yes	Possible	Supercritical	-

Hydrothermal Liquefaction (HTL) is a specific form of hydrothermal processing that operates at intermediate temperatures and pressures just below the thermodynamic critical point of water (i.e., subcritical), where the water medium is kept in a liquid state. Under typical conditions of around 350°C and 200 bar and in the absence of any added air or oxygen, biomass feed is converted to a mixture of slightly oxygenated liquid hydrocarbon products referred to

collectively as biocrude or biocrude oil. This biocrude oil has similarities to fossil crude oil but the oxygen content is higher (typically ranging between 10-30% for biocrude compared to < 1% for fossil crude oil), leading to some unfavorable qualities. Through a subsequent process referred to as Upgrading, the oxygen content of the biocrude oil can be reduced so that the resulting hydrocarbon products can be processed in a standard petrochemical refinery into conventional liquid fuel. Upgrading processes typically achieve oxygen removal via decarboxylation reactions or through addition of hydrogen in hydrodeoxygenation reactions, all in the presence of a catalyst. The ability to process the biocrude via conventional upgrading processes is dependent on the composition of the material. Depending on the relative volumes of biocrude and fossil crude, some refineries can also simply mix the biocrude into the input stream and process the biocrude directly without any intermediate upgrading. Some but not all refineries have the upgrading equipment already installed.

Instead of liquid products produced by HTL, gaseous products can be produced under subcritical hydrothermal conditions through the use of catalysts in a process known as Catalytic Hydrothermal Gasification (CHG). This process produces a mixture of methane and carbon dioxide in a ratio of approximately 60/40 by volume, with a heating value of approximately 23 MJ/m³ (620 BTU/ft³) of mixed gas. As with HTL, the CHG product can also be upgraded by removing the carbon dioxide fraction, resulting in nearly pure methane gas which then can be considered a Renewable Natural Gas (RNG). This gas can be inserted into a natural gas pipeline for distribution. A recent review of HTL, CHG, and Upgrading processes for biomass is provided by Elliott et al. (2015).

It is also possible to directly burn both the biocrude and the gas from CHG without further upgrading. Genifuel states that this could be done, for example with an engine designed for Heavy Fuel Oil (HFO), since the biocrude is similar to Bunker “C” fuel or #6 Fuel Oil (Elliott, 1981), both of which are used in HFO engines such as marine diesels or stationary generators. In this use, both the oil and gas could be used in the same engine to generate electricity. However, care must be taken because the high oxygen content of the biocrude probably will limit its use in internal combustion engines.

The Genifuel hydrothermal process technology includes both HTL and CHG processes but not Upgrading (if required), as shown in Figure 1-2. The HTL portion converts biomass feed into a two phase liquid product. The organic biocrude oil layer is separated from the aqueous layer and is collected for further use. The aqueous layer is sent to the CHG system for conversion of residual organics to gas, primarily methane and carbon dioxide. The result is an aqueous product where more than 99% of the original organic matter has been removed and which contains residual levels of dissolved inorganic components (Elliott et al., 2013; Elliott et al., 2014). The Genifuel hydrothermal technology was developed at the U.S. Department of Energy’s (DOE) Pacific Northwest National Laboratory (PNNL) over the past 30 years. PNNL continues to perform research in the field of hydrothermal processing, most recently with the development of improved HTL processes (Elliott et al., 2014). Genifuel holds an exclusive license to PNNL’s CHG and integrated HTL-CHG process patents for the purpose of commercializing this technology. The success of this collaboration so far and the potential of HTL technology has been recognized by others in several recent awards to note. The PNNL-Genifuel HTL technology was selected as one of the top 100 new technologies by R&D Magazine in November 2015 (R&D Magazine, 2015). This technology was also one of 16

winners (out of 57 nominations) of the Federal Laboratory Consortium's Excellence in Technology Transfer awards in 2015 (FLC, 2015).

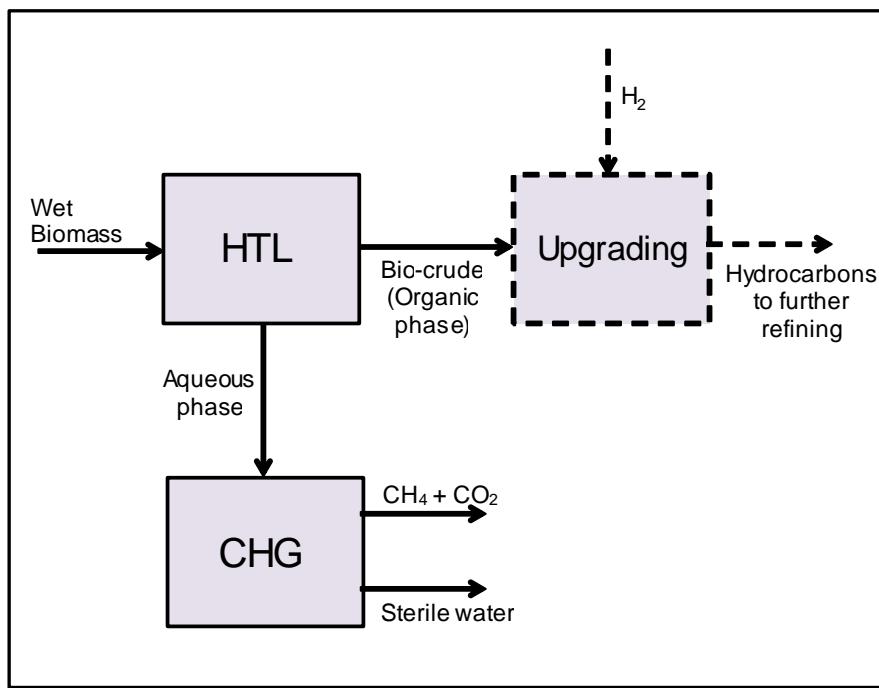


Figure 1-2. Block Flow Diagram of the Genifuel Hydrothermal Process.

Over the past several decades, research groups at universities and national laboratories around the world have been investigating hydrothermal processing of a variety of biomass feed types, such as food and food processing waste, wood, sawdust, agricultural waste, dairy waste, animal manure, and algae. There has been particular interest and considerable work performed with algae (Elliott, 2016). Because of its high water content, algae are an ideal feed for HTL. In addition to avoiding the need to dry the feedstock, hydrothermal processes also avoid the extra cost and effort associated with focusing on cultivating high lipid content algae and subsequent lipid extraction during processing by being able to process all of the biomass. Collectively, these advantages translate into significant potential cost savings (NAABB, 2014), which is critical for effective commercialization of this process. Many organizations have been slow to grasp the significance of these savings, but interest in hydrothermal processes has increased substantially over the past few years as its advantages have been identified and fully realized by more people. As an example, DOE has recently elevated Whole Algae HTL to one of eight current priority research and development pathways for converting biomass to renewable fuels and products (DOE, 2014). HTL has also been one of a few technologies included in recent DOE efforts to identify ways to accelerate the production of fungible hydrocarbon fuels from wet waste biomass (DOE, 2015). The greater interest in hydrothermal processes is also evident by the increasing amount of research and development, signified by the increase in the literature on this topic over the past decade. Based on the hydrothermal processing research performed on algae at PNNL and other institutions, Genifuel recently commissioned a one metric ton per day system for processing algae feed for a large energy company in India (Elliott, 2016).

Similar to algae, wastewater treatment sludge is another feed type that should be ideal for HTL processing due primarily to its high water content but also its potentially high energy content. Sludge is the main by-product of wastewater treatment processes and can be of considerable expense to treat and/or dispose. There are several different types of sludge which vary in composition depending on where in the treatment process they are derived. The most common types of sludge are primary (consisting of heavier materials that sink to the bottom of the primary settling tanks), secondary or waste activated (consisting of the microbial biomass left over from secondary processes and scum), and post-digester (consisting of the residual solids after anaerobic digestion). Post-digester sludge (or digested solids) can also be referred to as biosolids provided that it meets specific U.S. Environmental Protection Agency (EPA) pollutant and pathogen requirements for land application and surface disposal. Any sludge (or biosolids) destined for land application needs to be treated or stabilized before use to reduce the vermin attraction potential and pathogen content.

The current most common sludge treatment options include anaerobic digestion, aerobic digestion, and composting. Anaerobic digestion utilizes microbes that breakdown the organic matter in the absence of oxygen to produce biogas (consisting mainly of methane and carbon dioxide) and residual solids referred to as digestate. Biogas can be used as a fuel to run boilers, engines, or turbines to produce electricity. Aerobic digestion induces microbial breakdown of solids in the presence of added oxygen and normally does not produce methane. Aerobic microbes typically grow faster than anaerobic microbes, but their process has the added cost of oxygen injection without the benefit of methane recovery. Aerobic digestion can also be a less complex process, but typically requires a longer hydraulic retention time than anaerobic digestion. Composting also involves the use of aerobic microbes in either an open or enclosed environment, and is associated with significant materials addition, hauling, and volume of product.

While all three current sludge treatment options result in solids reduction, there are still residual solids that require disposal, either by landfill or land application. In addition to being a water-based process, the combination of HTL and CHG has the added advantage over all of the above options in that it converts the organic matter in the sludge feed to product, effectively reducing the production of biosolids, with only a small quantity of inorganic residuals requiring disposal. Thus, while the HTL-CHG process could be added to an existing facility that already uses one of the above options to improve performance, its greater value would be as a partial or complete replacement for these other options.

Incineration is another potential sludge treatment option that has been used typically in densely populated areas where landfill or land application are not viable options (e.g., large eastern U.S. cities and surrounding regions). However, its negative public perception, permitting considerations, and high energy demand and size requirements associated with heating a high water content feed up to required temperatures make incineration less enticing for most wastewater treatment plants (referred to as water resource recovery facilities in this report).

While a significant amount of research has been performed with HTL on other biomass feeds, such as algae, food processing wastes, and manures, there has been limited previous research in wastewater sludge as a feed for HTL, particularly pre-digester (e.g., primary, secondary) sludge. Some work in the 1980s on an early version of HTL (lower temperature and

pressure) was performed both at PNNL (Molton et al., 1986) and in Japan (Suzuki et al., 1988, Itoh et al, 1994) on conversion of sewage sludge to heavy oil. PNNL performed its study in 1986 under contract to the U.S. EPA, called the Sludge to Oil Reactor System (STORS) project, performed at the Water Engineering Research Laboratory in Cincinnati, OH. This project was successful at producing a heavy oil and char product, even though it used an earlier and less refined technology. However, because of the limits of the technology at the time, it was determined to be only marginally economical and no efforts were made to implement the technology at a water resource recovery facility (WRRF). Nevertheless, these early tests showed that sewage sludge could be successfully processed through a hydrothermal system. More recently, there has been research performed on HTL of digested sludge in a relatively lower temperature (300°C) batch reactor at the University of Illinois at Urbana-Champaign (Vardon et al., 2011). Huang et al. (2013) performed HTL tests with sewage sludge in a batch-scale stirred tank reactor and compared results to tests performed with microalgae and rice straw under identical conditions. Yan-qing et al. (2015) studied the fate and speciation of nitrogen in the aqueous phase product of HTL tests on sewage sludge under different operating conditions. Afif et al. (2011) performed bench-scale CHG tests directly with an activated sludge feed and Raney nickel catalyst.

Relative to HTL, there has been a greater amount of past research on wet air oxidation (Baroutian et al., 2015) and supercritical water oxidation (SCWO) (Shanableh and Gloyne, 1991; Xu et al., 2012) of sewage sludge. In fact, the Zimpro® wet air oxidation process has been used as a pretreatment system to improve dewaterability prior to incineration at some plants. However, wet oxidation and SCWO are very different from HTL, because the focus in the oxidation based technologies is to completely destroy (i.e., mineralize) the organic content under highly oxidative conditions, whereas the goal of HTL is to reform the organic content into usable fuels in the absence of oxygen. Qian et al. (2016) provide a review of research and commercial developments for municipal sewage sludge treatment in supercritical water.

There are some unique aspects of treating wastewater sludge via HTL that make it worth exploring. Unlike algae which has to be grown and therefore adds to the overall cost of fuel production, wastewater sludge is a waste requiring disposal. In contrast, processing sludge via a hydrothermal process will yield biocrude fuel, methane gas, and clean water such that disposal costs (only inorganic residuals) are greatly reduced.

There are several challenges and data gaps associated with hydrothermal processing of wastewater sludge. Wastewater sludge can be of variable composition over time and may contain an increased number of species such as heavy metals compared to other biomass feeds tested such as algae. This could in turn affect such aspects of the Genifuel process as sulfate and phosphate precipitation, catalyst performance, and the ultimate fate of the final water product. Complete characterization of all feed and product streams is therefore important to understanding how the sludge is processed and to interpreting the results. Sludge taken from different parts of a WRRF (i.e., primary sludge, secondary sludge, digested solids) will also vary in organic content compared to each other and thus may affect the quantity and possibly the quality of oil produced, and consequently the process economics. While Genifuel believes that variability of feedstock composition does not significantly affect system performance based on its testing of other biomass feeds, this has not been previously verified for wastewater sludge feeds. It is therefore important to test the different sludge types individually to understand how each type of sludge

behaves and what it produces. Another critical factor in processing feeds successfully is the ability to pump the feed in a continuous, steady manner. While none of the above issues/data gaps associated with wastewater sludge are expected to be insurmountable, they need to be investigated in order to confirm this view or determine appropriate solutions. Due to minimal prior testing with this feed, bench-scale proof-of-concept tests were determined to be the most appropriate direction at this time.

The Leaders Innovation Forum for Technology (LIFT) is a joint initiative by the Water Environment Research Foundation (WERF) and the Water Environment Federation (WEF) to move innovation and new technology more rapidly into practice. WERF leads the Technology Evaluation Program component of LIFT. Under this program, LIFT municipal and industrial water facility owners identify technologies of interest either through LIFT Focus Area activities or LIFT Technology Scans. Based on its potential advantages, the Genifuel HTP technology was initially identified as a technology of interest by the LIFT Biosolids to Energy Focus Area. Several members of the Bay Area Biosolids to Energy Coalition (that includes a number of WERF utility subscribers) also expressed interest in this technology. As a result, a group of facility owners agreed to collaborate in supporting a WERF-led bench scale test of this technology, which is the subject of this report.

This report describes the results of HTL and CHG bench-scale tests performed at PNNL on primary, secondary, and post-digester sludge at PNNL (note that post-digester sludge will be referred to as digested solids in this report). In these bench-scale tests, the specific configuration of the equipment used and certain other aspects (e.g., energy requirements) do not necessarily reflect that which would be installed at a WRRF at full-scale. However, the chemistry, product yields, and feed behavior characteristics (e.g., sludge pumpability), which are critical to assessing whether the technology can be successfully applied to wastewater sludge, should be representative. Based on the bench-scale test results, this report assesses the potential of hydrothermal treatment for handling wastewater sludge. It is concluded that while performance observed in these tests with wastewater sludge is favorable, further testing is required to fully determine viability of the technology.

CHAPTER 2.0

OBJECTIVES

The overall objective of this test program was to assess the performance and viability of the Genifuel combined HTL-CHG process on wastewater sludge. This was accomplished through several, limited proof-of-concept tests conducted with continuous flow, bench-scale equipment located at PNNL. Specific objectives were as follows:

- ◆ Determine a wastewater sludge concentration that can be successfully pumped without interruption during normal operation.
- ◆ Quantify the amount of biocrude oil and methane gas produced from representative sludge feeds.
- ◆ Characterize all feed and product streams with respect to chemical composition.
- ◆ Verify mass balance closure to within 15% for total mass and carbon.
- ◆ Analyze the effect on economic potential of the process based on the quantity and quality of the biocrude oil and methane gas produced and WRRF sludge data.
- ◆ Assess areas of future work based on test observations and results.

CHAPTER 3.0

SLUDGE FEED IDENTIFICATION AND PREPARATION

3.1 Sludge Types

Three different sludge feeds were chosen to be processed during this test program:

- ◆ Primary sludge – solids removed after primary treatment (physical separation by sedimentation) of wastewater; usually on the order of a few percent solids concentration
- ◆ Secondary sludge – also known as waste activated sludge; solids removed after secondary treatment (metabolism of organic pollutants via aerobic microorganisms) of wastewater; also includes scum removed in primary treatment; usually on the order of a few percent solids concentration
- ◆ Post-digester sludge or digested solids – residual solids taken after anaerobic digestion (decomposition via microorganisms in the absence of oxygen) from an initial feed to the digester that includes primary and secondary sludge

With the limited number of tests able to be performed, there was debate as to whether the addition of fats, oils, and grease (FOG) should be included, whether primary and secondary sludge should be combined as one feed, and whether replicate tests should be performed on only one or two feed types. Because many WRRFs combine their primary and secondary sludge streams prior to either anaerobic digestion or disposal, performing HTL tests on a combined primary and secondary sludge feed would have the advantage of being closer to what would be expected as feed at a WRRF. However, because different WRRFs combine the two sludge types in different ratios, it would be difficult to assess the applicability of HTL test results performed with combined feed at one ratio to a WRRF that uses a different ratio. Ultimately, the plan of single HTL tests of extended duration on each of the above individual three feed types was chosen for this test program. This allowed investigation of each of the major sludge feeds independently, with multiple samples taken during each extended run providing data on process stability and reproducibility with each feed. Also, because of the variation in sludge combination ratios and whether or not anaerobic digestion is utilized among different WRRFs, performing tests on each individual sludge type allows the results to be more easily interpreted and applied across a wide variety of operating WRRFs.

3.2 Sludge Feed Requirements

PNNL had three requirements and/or pretreatment steps for sludge feeds to be supplied by a WRRF before they could be received and processed through the HTL bench-scale system:

1. Each sludge type had to be dewatered to a concentration of at least 15-20% solids.
2. A total of approximately 10 gal of each dewatered sludge feed needed to be provided.
3. Each sludge type had to be either certified as Class A biosolids or autoclaved under sufficient conditions (heat to at least 100°C for 5 hours followed by bacteria count analysis) for the resulting product to be considered as or equivalent to Class A biosolids status.

With respect to the dewatering requirement, the goal was to concentrate the solids as much as possible to maximize the HTL product yield yet be sufficiently flowable for the HTL high pressure metering syringe pump to handle (i.e., a shear strength of 170 Pa or less at 20°C). The target range of 15% to 20% solids represented the typical concentration that has been effectively pumped with many wet biomass feeds at PNNL. The actual solids concentration used for each feed in each HTL test was adjusted and set by PNNL after inspection and assessment of the sludge feeds pumpability once it was received.

PNNL internal procedures required that all raw sludge feeds be autoclaved (or certified as Class A biosolids per U.S. EPA standards) before receipt at PNNL to remove pathogens down to a level that would allow for safe handling by its personnel. The autoclave requirement was a constraint for safe use of this feed in the PNNL laboratory environment and is not associated with or necessary for operation of the HTL process from a technical perspective, nor would it be required in a future production installation at a WRRF.

3.3 Selection of Sludge Feed Supplier

The ability to provide all three sludge types while also meeting the above three PNNL requirements for processing were important criteria used to determine the WRRF best able to supply sludge feed samples for this test program. These criteria and additional relevant factors were included in a questionnaire sent to all of the WRRFs represented on the Steering Committee for this test program as well as a few more WRRFs provided by WERF. Follow-up calls to clarify responses and to ask more detailed questions, as well as additional data requests were also made. The answers provided, which are summarized in Table 3-1, were used to choose the WRRF.

Based on the information obtained, Metro Vancouver, of Burnaby, BC, Canada, was recommended by the core test team to provide sludge samples for testing because it appeared to be the most capable of meeting all of the sludge pre-requisites for HTL processing. While most of the WRRFs surveyed could provide samples of pre- and post-digester sludge, Metro Vancouver was the only Steering Committee member that was prepared to de-water both primary and secondary sludge samples. The ability to autoclave sludge samples and the relative closeness of Metro Vancouver to PNNL were also important factors in making this recommendation. This choice of Metro Vancouver was confirmed by WERF and committee members during the project kick-off meeting on April 21, 2015.

All sludge samples for this test program were taken from Metro Vancouver's Annacis Island WRRF in Delta, BC, Canada. The Annacis Island WRRF is one of five WRRFs owned and operated by Metro Vancouver. In 2011, it treated 176.4 billion liters (46.6 billion gallons) of wastewater, which is 40% of the total flow processed by all five Metro Vancouver facilities. The Annacis Island WRRF consists of initial screening and grit removal of incoming raw wastewater, followed by primary and secondary treatment steps. The liquid stream leaving secondary treatment is then disinfected before discharging to the Fraser River. Scum collected from primary and secondary treatment is screened and combined with waste secondary sludge before thickening. Sludge removed from the primary and secondary treatment steps is concentrated in

Table 3-1. WRRF Candidates for Providing Sludge.

	Question	City of Calgary (AL, Canada)	City of Orlando (FL)	City of Santa Rosa (CA)	DC Water (Washington, DC)	Delta Diablo (Antioch, CA)	Metro Vancouver (Burnaby, BC, Canada)	Silicon Valley Clean Water (Redwood City, CA)	Tohopekaliga Water Authority (Kissimee, FL)
1	Can provide samples of pre- and post-digester sludge?	Yes	Yes, but pre-digester sludge is secondary only	Yes	Yes	Yes	Yes	Yes	No
2	Ability to dewater sludge to 15-20% solids (or better)	No	Maybe	Yes, but only for post-digester sludge	Yes	Yes for post-digester sludge; may be able to filter pre-digester sludge in lab	Yes (outside contractor used for dewatering pre-digester sludge)	Yes, but only for post-digester sludge	No (only 14%)
3	Unusual or atypical input waste streams?	Some, as in most cities	Yes (typical domestic wastewater with some industrial high strength waste)	No	No	No (primarily residential suburb input with 5% industrial)	No (60% residential, 20% industrial/commercial, 20% inflow and infiltration)	No (mostly residential, commercial and a few industries, and small amount of landfill leachate)	No
4	Method of handling fats, oils, and grease (FOG)	A FOG treatment facility is currently being constructed	Has extensive program to pretreat at source, not at facility; does not accept FOG from pump trucks	It is skimmed off the surface of the primaries and then pumped to the digesters	Received at the plant headworks	Currently commissioning new receiving system for FOG (previously had not accepted FOG)	FOG is collected in primary and secondary scum only at Annacis Island WRRF. The scums are screened, combined with secondary sludge, thickened, and sent to digesters. Trap FOG delivered by truck is handled by Iona Island WRRF.	FOG from liquid treatment and a special receiving station for community FOG haulers all sent to digesters	Some is retained in upstream Lift Stations, removed and disposed. The remainder is removed at the mechanical bar screens and consumed in the biological process.

	Question	City of Calgary (AL, Canada)	City of Orlando (FL)	City of Santa Rosa (CA)	DC Water (Washington, DC)	Delta Diablo (Antioch, CA)	Metro Vancouver (Burnaby, BC, Canada)	Silicon Valley Clean Water (Redwood City, CA)	Tohopekaliga Water Authority (Kissimee, FL)
5	Plant process description	Conventional activated sludge	Advanced treatment facility utilizing primary and secondary treatment, tertiary filtration, and anaerobic digestion	Facility is an activated sludge tertiary treatment plant utilizing primary and secondary treatment, tertiary filtration, and anaerobic digestion	Utilizes enhanced primary treatment, secondary treatment, tertiary treatment, and thermal hydrolysis and mesophilic anaerobic digestion of sludge	Utilizes primary and secondary treatment, with some of secondary effluent sent to tertiary treatment; anaerobic digestion of sludge	Annacis Island WRRF (proposed facility for HTP) utilizes primary and secondary treatment, and anaerobic digestion of sludge	Utilizes primary and secondary treatment, and digestion and solar drying beds for sludge. Cogeneration plant uses biogas	Utilizes primary and secondary treatment
6	Ability to autoclave sludge samples?	No	Yes, but limited sample size	Yes, but has small autoclave	Yes	Yes, but in small batches	Yes	Yes	No
7	Steering Committee member?	No	Yes	Yes	No	Yes	Yes	Yes	Yes

thickener tanks and then combined before being fed to thermophilic (55°C) anaerobic digesters, where a net 60% volatile solids reduction is typically achieved. The residual digested solids are dewatered to 28 wt% solids via centrifuge and loaded into trucks for use or disposal. Over 100 metric tonnes of digested solids are removed every day from the Annacis treatment facility.

Another WRRF that provided assistance in this test program was Silicon Valley Clean Water. During the planning stage of this test program, the Steering Committee expressed interest in tracking the fate of siloxanes in the sludge feed through the hydrothermal process. Siloxanes are contained in a variety of health and beauty consumer products and ultimately end up in wastewater. The various siloxane species typically partition into the sludge phase during wastewater treatment and then into the biogas produced during anaerobic digestion. Siloxanes in biogas cause significant problems in engines when the biogas is burned as a fuel. The combustion process converts the silicon into silica, which is abrasive, and its insulating properties interfere with proper heat transfer. For this reason, samples of product gas from selected HTL and CHG tests were taken and analyzed for the presence of siloxanes. Silicon Valley Clean Water WRRF, which was first to raise the concern regarding siloxanes during hydrothermal testing, analyzed their biogas in the past for these compounds through an external laboratory. They arranged for siloxane analysis by the same laboratory of the selected HTL and CHG gas phase samples during this test program.

3.4 Sludge Feed Collection and Preparation

Preparation for sample collection and dewatering at Metro Vancouver began in April 2015, with samples taken in May and June 2015. Each sludge type needed to be prepared differently to meet PNNL's requirements due to their inherent differences. Primary sludge, secondary sludge, and digested solids are formally referred to by Metro Vancouver as Thickened Screened Primary Sludge (TSPS), Thickened Waste Secondary Sludge (TWSS), and Biosolids, respectively. A summary of key data on the sludge as collected and as shipped to PNNL is included in Table 3-2.

Table 3-2. Summary of Wastewater Sludge Provided by Metro Vancouver for Testing.

Sludge Type	Quantity Collected (L)	Initial Sludge Concentration (wt% solids)	Final Sludge Concentration (as shipped)	Quantity Shipped (L)	Date Shipped
Primary (TSPS)	280	4.5%	26.0% solids	40	June 2, 2015
Secondary (TWSS)	120	3.9%	10.9% solids	40	June 22, 2015
Digested Solids (Biosolids)	40	~28% ^a	~28% solids ^a	40	May 27, 2015

^a Average value; minimum value of 26.1% and maximum value of 29.9% observed over past year prior to collection.

3.4.1 Digested Solids

At Annacis Island WRRF, digested solids are normally concentrated well above PNNL's sludge feed requirements as part of normal plant operations. Over the past year (2014-15), the solids concentration in the digested solids from Annacis Island varied between 26.1-29.9 wt% solids, for an average value of 28 wt% solids. Thus, no dewatering of digested solids was necessary. Also, because the solids resulting from anaerobic digestion are already Class A, no autoclaving of the digested solids was needed prior to shipment to PNNL.

As a result, samples of digested solids could be collected and shipped directly to PNNL without any adjustments by Metro Vancouver. Because of this, early samples were sent to PNNL in April and early May 2015 so that PNNL could get a head start on evaluating the pumpability of this sludge type. The official shipment of digested solids for HTL testing was collected and shipped to PNNL on May 27, 2015 (Figure 3-1).



Figure 3-1. Digested Solids.

3.4.2 Primary Sludge

The primary sludge sampled at Annacis Island when collected on May 20, 2015 had a concentration of 4.5 wt% solids (Figure 3-2). The dewatering procedure involved addition of a cationic polyelectrolyte polymer and then use of a batch filter press (Figure 3-3). At the ratios used, the polymer constituted about 2% of the sludge solids mass. The filter press was operated at 40 psi with 300 μm filter paper for 20 minutes. This dewatering approach was able to reach a solids concentration of about 12 wt% (Figure 3-4). Metro Vancouver personnel found that additional hand pressing of the filter cake with a sheet of the same size filter paper was able to further concentrate the sludge to about 26 wt% on average (Figure 3-5).



Figure 3-2. Raw Primary Sludge (4.5 wt% solids).



Figure 3-3. Batch Filter Press Used for Dewatering Primary Sludge.



Figure 3-4. Initial Filter Cake Produced from Dewatering of Primary Sludge (12 wt% solids).



Figure 3-5. Dewatered Primary Sludge (~ 26 wt% solids).

The dewatered sludge was then autoclaved for five hours at 121°C (Figure 3-6). A sample of the autoclaved sludge was sent out for fecal coliform analysis to verify that the concentration was below the limit for certifying as Class A biosolids, which was confirmed by the results. Samples of both pre- and post-autoclave sludge were taken for proximate (molecular composition) and ultimate (chemical element) analyses to assess whether the autoclave process had any effect on the sludge. Results, shown in Table 3-3, indicated little change between the pre- and post-autoclave samples. A slump test was also performed on both pre- and post-autoclave sludge samples. The slump test revealed no slump at all in both pre- and post-autoclave sludge samples (Figures 3-7 and 3-8). The overall results indicated that autoclaving appeared to have very little effect on the physical and chemical structure of the primary sludge.



Figure 3-6. Autoclaving Sludge.



Figure 3-7. Slump Test on Dewatered Primary Sludge Before Autoclaving.

After receiving clearance through the fecal coliform lab analysis results, Metro Vancouver shipped the dewatered and autoclaved primary sludge to PNNL on June 2, 2015. Detailed data from the dewatering and autoclaving preparation work performed by Metro Vancouver on both primary and secondary sludge is included in Table 3-4.

Table 3-3. Comparison of Pre- and Post-Autoclave Samples of Dewatered Primary Sludge.

Proximate Analysis					
Measurement	Method	Pre-autoclave		Post-autoclave	
		As sampled	Dry	As sampled	Dry
Moisture, total (%)	ASTM E949	73.73	–	70.27	–
Ash (%)	ASTM E830	2.05	7.79	2.40	8.08
Volatile matter (%)	ASTM E897	21.59	82.17	24.23	81.47
Fixed carbon* (%)	ASTM D3172	2.63	10.04	3.10	10.45
Sulfur (%)	ASTM D4239 A	0.14	0.54	0.16	0.54
Ultimate Analysis					
Measurement	Method	Pre-autoclave		Post-autoclave	
		As sampled	Dry	As sampled	Dry
Moisture, total (%)	ASTM E949	73.73	–	70.27	–
Ash (%)	ASTM E830	2.05	7.79	2.40	8.08
Sulfur (%)	ASTM D4239 A	0.14	0.54	0.16	0.54
Carbon (%)	ASTM D5373	12.93	49.23	14.81	49.79
Hydrogen (%)	ASTM D5373	1.74	6.61	1.93	6.50
Nitrogen (%)	ASTM D5373	1.02	3.90	1.24	4.17
Oxygen* (%)	ASTM D5373	8.39	31.93	9.19	30.92
Energy Analysis					
Measurement	Method	Pre-autoclave		Post-autoclave	
		As sampled	Dry	As sampled	Dry
Gross Calorific Value (Btu/lb)	ASTM D5865	2450	9323	2771	9319
Slump Test					
Amount of slump (mm)		–	0	0	0

*By difference



Figure 3-8. Slump Test on Dewatered Primary Sludge After Autoclaving.

Table 3-4. Sludge Preparation Data.

Data	Primary Sludge (TSPS)	Secondary Sludge (TWSS)	
Date sample pulled	May 20, 2015	June 16, 2015	
Initial (raw) solids concentration	4.5 wt%	3.9 wt%	
Initial sludge volume collected	~280 L (14 buckets)	~120 L (10 buckets)	
Dewatering method/equipment used	Filter press followed by hand press	Tencate Geotube dewatering bags for 48 hours	
Type of polymer added	Zetag 7563	Zetag 7563	
Quantity of polymer added	0.3 wt% polymer added at a ratio of 1.5L polymer per 5L of sludge (mass ratio of polymer to sludge solids is ~ 2%)	0.3 wt% polymer added at a ratio of 1.5L polymer per 5L of sludge; note: already contains polymer (Zetag 8147) added upstream in the treatment process in the Dissolved Air Flotation Thickener (DAFT)	
Sit time for sludge after polymer addition	10 minutes	10 minutes	
Dewatering batch sizes	5 L	55 L per dewatering bag, with 2 bags used	
Date of dewatering	May 20-23, 2015	Jun 16-18, 2015	
Dewatering process description	Add polymer, add 5L of sludge to filter press, remove sample from filter press and hand press any remaining liquid from cake on same filter paper	Add polymer and then add 55 L of sludge to each filter bag	
Time in dewatering bag	—	48 hours	
Filter press pressure	40 psi	—	
Filter press time	20 minutes	—	
Filter type and pore size	300 micron Nitex	—	
Final solids concentration	26.0% (avg.)	10.9% (avg.)	
Visual appearance of removed water	Colorless and cloudy	Colorless and cloudy	
Final sludge volume	40 L (+ 5 L sent for analysis)	40 L (+ 5 L sent for analysis)	
Autoclave batch size	10 L	10 L	
Autoclave temperature	121°C	121°C	
Autoclave time	5 hours	5 hours	
Date of autoclaving	May 21-23, 2015	June 18-21, 2015	
Date of shipment to PNNL	June 2, 2015	Jun 22, 2015	
Filtrate COD	1950 mg/L 1960 mg/L*	After 3 hours	605 mg/L 605 mg/L*
		After 24 hours	2505 mg/L 2520 mg/L*
		After 48 hours	2500 mg/L 2480 mg/L*
Fecal coliform analysis after autoclaving	<18 MPN/100 mL (non-detect)	<18 MPN/100 mL (non-detect)	

* Duplicate

3.4.3 Secondary Sludge

The behavior of secondary sludge during the dewatering and autoclaving process was found to be very different from that of primary sludge. Contrary to the relative ease of dewatering primary sludge, secondary sludge proved to be difficult to concentrate beyond 10.9 wt% solids. This is not unusual, as it has been noted by others that secondary sludge is far more difficult to dewater than primary sludge (Xu and Lancaster, 2009). Several different but ultimately unsuccessful approaches were tried by Metro Vancouver staff to reach the 15-20 wt% solids target over the course of several weeks in May and June 2015.

The first sample of secondary sludge was collected at the same time the primary sludge sample was collected on May 20, 2015 (Figure 3-9). This first sample had a concentration of 5.6 wt% solids. The filter press used with a 400 μm filter was able to concentrate the sludge with added cationic polyelectrolyte polymer (Figure 3-10) to only 9.6 wt% solids. A larger filter paper pore size allowed too much solids to pass into the filtrate, while a smaller filter paper pore size caused blinding. A dewatering bag was then tried followed by manual sheet filtering. This approach yielded slightly better results of 9-11 wt% solids.



Figure 3-9. Raw Secondary Sludge.



Figure 3-10. Polymer Addition to Raw Secondary Sludge.

Since the secondary sludge contains a large amount of microbes from the secondary treatment process, it is unclear if the difficulties experienced in dewatering beyond 11 wt% were due to the size of the solid particles being too close to that of water, or if the remaining water was trapped within the cell walls of the microbes. In the latter case, the thought was that trying a process that could disrupt or rupture the cell walls might allow for more water separation. As a result, Metro Vancouver attempted to autoclave some of the secondary sludge first and then dewater through the filter press in hopes that the thermal conditions inherent to the autoclaving process would achieve cellular wall rupture. However, the secondary sludge after autoclaving proved to be unfilterable, having a consistency of pudding (Figure 3-11; compare to well-formed filter cake achieved with primary sludge in Figure 3-4).



Figure 3-11. Secondary Sludge After Filter Press and Autoclaving.

Tests were performed with secondary sludge in a lab-scale (non-decanting) centrifuge by Metro Vancouver (Figure 3-12) in the hope that centrifugation might also provide a means of cellular wall rupture. Several tests were performed for different durations and intermediate decanting of water. Data from these lab centrifuge tests are included in Table 3-5. A slight improvement in solids concentration (maximum of 12.6 wt%) was observed. In early June, Metro Vancouver was also able to gain access to a larger size (40 L capacity) centrifuge located at the British Columbia Institute of Technology (BCIT). The hope was that a larger-scale centrifuge would be more successful in concentrating the sludge than the lab-scale unit. This concept was supported by vendor data which stated that a larger scale decanter centrifuge can achieve concentrations of up to 18 wt% solids with secondary sludge (Havrin, no date). The tests on the BCIT centrifuge were unsuccessful, however, possibly due to the fact that the sludge which had been collected now several weeks earlier showed signs of degradation, and also possibly because the centrifuge could not achieve high enough g-forces.



Figure 3-12. Lab Centrifuge Used by Metro Vancouver on Secondary Sludge.

Table 3-5. Lab-scale Centrifuge Results with Secondary Sludge.

Description	Date	Speed (rpm)	Time (min.)	wt% Solids
Straight (raw) TWSS	5/22/15	4000	10	6.5
TWSS + polymer	5/22/15	4000	10	7.6
TWSS + polymer after filtering	5/22/15	4000	10	9.1
Description	Date	Speed (rpm)	Time (min.)	wt% Solids after 18 hrs.
wt% Solids after 64 hrs.				
Dewatered TWSS (no centrifuge)	5/26/15	-	-	10.0
TWSS	5/26/15	4000	10	11.0
TWSS, decanted after 10 min	5/26/15	4000	20	12.4
TWSS	5/26/15	4000	20	11.6
TWSS, decanted every 10 min	5/26/15	4000	30	12.1
TWSS	5/26/15	4000	30	11.8
				11.5

It was finally decided that the best approach would be to collect a fresh sample of secondary sludge and use a slightly optimized approach with dewatering bags. The second sludge sample was collected on June 16, 2015 and had a lower concentration than the first sample of 3.9 wt% solids. The dewatering bags were filled to a higher volume (55 L) and held for a longer duration (48 hours) than previously (Figure 3-13). Ultimately, an average concentration of 10.9 wt% solids was achieved with this approach (Figure 3-14). Thus, the desired target solids concentration (15-20 wt% solids) could not be achieved with secondary sludge in the time available for this test program.



Figure 3-13. 55L Dewatering Bags.



Figure 3-14. Dewatered Secondary Sludge from Dewatering Bags.

The dewatered secondary sludge was then autoclaved under the same conditions as that used for the primary sludge (Figure 3-15). Pre- and post-autoclave samples were taken for proximate and ultimate analyses and for performing slump tests, as was performed with the primary sludge (Figures 3-16 and 3-17). As noted earlier, autoclaving appeared to have a noticeable effect on the physical structure of the autoclaved secondary sludge, unlike that seen with the primary sludge. While pre- and post-autoclaving sludge samples experienced measurable slumping, the post-autoclave sample slump was greater, being reduced almost to a puddle. This increased fluidity may have been a benefit to subsequent HTL processing by

making the sludge easier to pump. There do not appear to be significant differences in the ultimate and proximate analysis results between pre- and post-autoclave samples (Table 3-6).



Figure 3-15. Dewatered Secondary Sludge After Autoclaving.



Figure 3-16. Slump Test on Dewatered Secondary Sludge Before Autoclaving.



Figure 3-17. Slump Test on Dewatered Secondary Sludge After Autoclaving.

As with the primary sludge, a sample of the autoclaved, dewatered secondary sludge was sent out for fecal coliform analysis to verify that the concentration was below the limit for certifying as Class A biosolids. Once confirmed by the lab results, Metro Vancouver shipped the dewatered and autoclaved secondary sludge to PNNL on June 22, 2015. Detailed data from the dewatering and autoclaving preparation work performed by Metro Vancouver on the secondary sludge that was shipped to PNNL (i.e., the second sample collected at Metro Vancouver) is included in Table 3-4.

Table 3-6. Comparison of Pre- and Post-Autoclave Samples of Dewatered Secondary Sludge.

Proximate Analysis		Method	Pre-autoclave		Post-autoclave	
Measurement			As sampled	Dry	As sampled	Dry
Moisture, total (%)	ASTM E949		90.90	–	85.52	–
Ash (%)	ASTM E830		1.51	16.63	2.37	16.39
Volatile matter (%)	ASTM E897		6.94	76.25	11.01	76.01
Fixed carbon* (%)	ASTM D3172		0.65	7.12	1.10	7.60
Sulfur (%)	ASTM D4239 A		0.06	0.71	0.10	0.70
Ultimate Analysis						
Measurement		Method	Pre-autoclave		Post-autoclave	
Measurement			As sampled	Dry	As sampled	Dry
Moisture, total (%)	ASTM E949		90.90	–	85.52	–
Ash (%)	ASTM E830		1.51	16.63	2.37	16.39
Sulfur (%)	ASTM D4239 A		0.06	0.71	0.10	0.70
Carbon (%)	ASTM D5373		4.39	48.20	6.87	47.46
Hydrogen (%)	ASTM D5373		0.59	6.50	0.94	6.47
Nitrogen (%)	ASTM D5373		0.81	8.85	1.27	8.79
Oxygen* (%)	ASTM D5373		1.74	19.11	2.93	20.19
Energy Analysis						
Measurement		Method	Pre-autoclave		Post-autoclave	
Measurement			As sampled	Dry	As sampled	Dry
Gross Calorific Value (Btu/lb)	ASTM D5865		860	9451	1340	9251
Slump Test						
		Pre-autoclave		Post-autoclave		
Amount of slump (mm)	–	180		> 220		

* By difference

3.5 Lessons Learned from Sludge Feed Preparation Efforts

While sludge dewatering was not the major focus of this test program, there were some interesting and important lessons learned through the work performed by Metro Vancouver:

- ◆ Primary and secondary sludge exhibit very different behavior during dewatering.
- ◆ Primary sludge is able to be dewatered without difficulty, at least up to 26 wt% solids on average.
- ◆ Autoclaving of primary sludge appears to have minimal to no effect on physical or chemical structure or appearance.

- ◆ Dewatered primary sludge is not homogeneous, leading to a noticeable variation in percent solids concentration each time it is sampled.
- ◆ Secondary sludge is difficult to dewater beyond 11% solids, at least with the methods and equipment used here. There are two possible effects at work:
 - Microbe biomass holds water within cell walls which are hard to break.
 - Microbe biomass solids are fine and not easy to separate from water – solids are lost with water if the filter pore size is too large, but the filter blinds if the pore size is too small.
- ◆ Vendor data from several sources suggest that secondary sludge can be dewatered up to 18 wt% solids via centrifuge or other mechanical means, but tests by Metro Vancouver with a lab-scale and larger scale centrifuge were not able to achieve or validate this claim within the given resource constraints.
- ◆ Autoclaving secondary sludge appears to have a significant effect on its physical structure, causing it to turn to a homogenized, pudding-like material which does not form a filter cake.
- ◆ Secondary sludge and added polymer appear to degrade over time, further hindering the ability to dewater.

It is unlikely that primary and secondary sludge would be treated separately from a practical perspective in a WRRF or in a commercial hydrothermal process. Therefore, in light of the lessons learned in this test program, the best approach for dewatering primary and secondary sludge may be to combine them in a proportion where the beneficial properties of the primary sludge are enough to reach the desired end concentration.

CHAPTER 4.0

HYDROTHERMAL PROCESSING TESTS

This chapter presents a description of the HTL and CHG test equipment at PNNL, additional sludge feed preparation work performed at PNNL, a summary of each test performance and observations made, and a summary of process monitoring data for each test. Leidos personnel were on-site at PNNL for one week during the test period where performance of one HTL and one CHG test was observed, as well as the associated feed preparation work and some post-test on-site lab analyses. Leidos maintained frequent contact with PNNL personnel during the remainder of the test period to monitor test progress and results. PNNL staff performed all testing and associated equipment maintenance and preparation, and coordinated all sample collection and shipment to laboratories (onsite or external) for analysis. All raw process monitoring data (both manual and automated collection) and analytical data were compiled into data packages for each test by PNNL and provided to Leidos for review. The data packages also included integrated mass and elemental balances and biocrude yield calculations in an extensive spreadsheet format. Leidos reviewed and verified all of the raw data, calculations, and associated assumptions (e.g., start of steady state periods) provided by PNNL. In addition, all analytical data were compiled, reviewed and verified by Leidos and analyzed for precision and accuracy (see Chapter 5.0). Any inconsistencies or errors found were corrected as necessary after discussion with PNNL staff. In general, the final verified values reported here did not differ significantly from the values developed by PNNL. Additional calculations not performed by PNNL but necessary to meet specific objectives of this study (e.g., CHG CH₄ yield values) were performed by Leidos from the PNNL-provided data packages. All summary tables and graphs in this report were prepared by Leidos using the verified PNNL data and calculations.

4.1 Test Location

All testing was performed at PNNL's laboratory facility in Richland, WA using a bench-scale version of the Genifuel process. The Hydrothermal Processing (HTP) laboratory at PNNL is housed in the Bioproducts, Sciences, and Engineering Laboratory (BSEL) (Figure 4-1), which PNNL shares with Washington State University/Tri-Cities in Richland, WA. The HTP laboratory contains two high-pressure, 5 ft by 20 ft floor-length reactor enclosures. Each reactor enclosure contains one independent HTL system. One of these enclosures also contains the CHG system. All WERF tests were performed exclusively on the HTL system in the enclosure located with the CHG system. The feeding portion of the HTL and CHG systems and the control and data logging systems are outside the enclosures. The HTP lab also contains wet chemical bench-space for feedstock and sample handling and supporting equipment, such as gas chromatographs (GCs), balance scales, chemical oxygen demand (COD) equipment, and fume hoods. Other supporting analytical equipment used for these tests was located in the facility Analytical Laboratory also in the BSEL. For WERF tests, chemical analyses were either performed directly in the HTP lab, sent to the facility Analytical Laboratory for analysis, or shipped to an outside commercial laboratory for analysis (see Section 5.4 for details). Feedstock preparation at PNNL, which consisted of dilution and homogenization of the sludge, was performed with either a high-shear mixer or immersion mill located across the hall from the HTP lab in the high-bay Biorefinery Laboratory.



Figure 4-1. BSEL Building at PNNL.

The PNNL bench-scale, continuous flow HTL and CHG systems have been used previously to process a variety of biomass feeds as part of other DOE-directed work as well as direct customer-funded research. The WERF tests with wastewater sludge described in this report were one part of a larger series of tests being conducted with wet waste feeds by PNNL with this equipment. Tests with some of these other feeds were conducted during the same time period in between the WERF sludge feed tests.

The bench-scale HTL and CHG equipment at PNNL consist of separate systems. This differs from the most probable Genifuel process full-scale design, where the HTL and CHG system components would be part of one operating system running at the same time. As a result, bench-scale HTL tests at PNNL were performed separately from the corresponding CHG tests. The HTL aqueous phase effluent from each test was saved and stored under refrigeration until it could be processed through the CHG system at a later time (in some cases, up to several weeks later).

4.2 Equipment and Process Descriptions

The following subsections describe the equipment, normal process flow, and typical operating procedures for the PNNL bench-scale HTL and CHG systems.

4.2.1 Hydrothermal Liquefaction (HTL)

A process flow diagram of the HTL system used for testing is shown in Figure 4-2. The two feed tanks are metal, cylindrical vessels configured in parallel and pressurized with air to 20-50 psig (nominal value of 40 psig) (Figure 4-3). One cylinder has a capacity of 24 L and the other has a capacity of 20 L. The main feed pump is a Teledyne Isco syringe pump, which has dual 500 ml chambers. As one chamber is discharging, the other is filling, allowing for continuous feed delivery at a fixed flow rate to the HTL system at a system operating pressure of about 2900 psi. After leaving the syringe pump, feed is passed through an oil-jacketed, tube-in-tube preheater of 0.5 in. outer diameter. PNNL has found that the oil provides a smoother and steady heatup in the preheater than electric heaters. The preheater heats the feed only part way

(~ 130°C) up to its final temperature. The feed then enters a 1 L heated, continuous stirred tank reactor (CSTR), typically through the bottom, where it reaches its target reaction temperature of 350°C (Figure 4-4). The CSTR, which is an Autoclave Engineers MagneDrive model, is electrically heated and has a magnetically driven stirring rod. For most (but not all) tests, the working volume of the CSTR is reduced to 415 mL by using a spacer. While the material of construction for most of the HTL system is 316 stainless steel, the CSTR is made of the high nickel alloy, inconel. The presence of the CSTR allows the preheated sludge feed to transition to its final temperature without the risk of overheating (and formation of undesired char) as could occur in a heated tube. After leaving the CSTR through a top port, flow is passed through an oil jacketed, tube-in-tube, tubular reactor of 0.5 in. outer diameter and maintained at 350°C that operates as a plug flow reactor (PFR) (Figure 4-5). The heated portion of the tubing that functions as the reactor has a volume of 300 ml. Note that all heated sections are insulated and heating tape is used on connecting tubing to avoid external heat loss and maintain temperature.

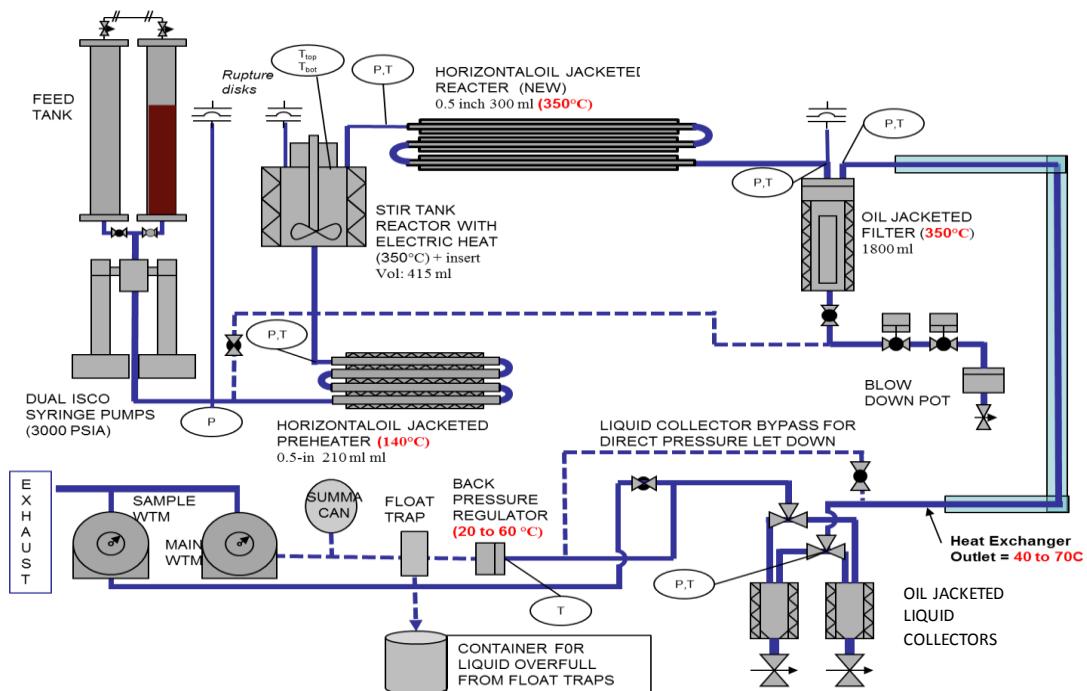


Figure 4-2. PNNL Bench-Scale HTL System.



Figure 4-3. HTP Lab at PNNL.

The HTL feed cylinders are at far right, with the HTL feed syringe pump to the left of the cylinders. The similar syringe pumps in the center foreground are for the CHG system. The heated and pressurized sections of both the HTL and CHG systems are located on the opposite side of the panels behind the pumps.



Figure 4-4. HTL System.

CSTR (without stirring rod) is at lower left of photo. Open filter vessel (surrounded by insulation) is in front of CSTR. The PFR (not shown) sits on frame work above the CSTR. CHG system is at far right of photo.



Figure 4-5. HTL PFR.

Left PFR disconnected from system. Right PFR installed surrounded by insulation.
Downstream gas effluent components are shown in back of right photo.

After leaving the PFR, the flow enters an oil-jacketed filter vessel for solids removal. This 1800 ml vessel is maintained at the 350°C reactor temperature or slightly below in order to ensure precipitation of certain inorganic salts, especially phosphates and sulfates, which have low solubility at this temperature (see Section 6.4.3 for details on this behavior). These inorganic solids are referred to as ash. The specific type of solids collected and removed in the filter varies depending on the feed being processed and its composition. Solids either fall by gravity to the bottom of the vessel or are caught in a filter element as flow leaves the top of the vessel. The filter can be backflushed when necessary by briefly opening the valve at the bottom of the vessel. Because the stirred tank reactor and plug flow reactor are both kept at the target reaction temperature, the volumes of both reactors are used to determine the residence time at temperature. The filter vessel is also kept at reaction temperature and its volume can also be included in the residence time calculation, but in this case including the filter volume would be a conservative choice because some of the fluid flow passes straight through the filter vessel and does not see its full volume. Thus the actual residence time needed to achieve the measured conversion would be less than that calculated. After leaving the filter vessel, the flow enters a water jacketed, tube-in-tube cool down heat exchanger. The flow exiting the heat exchanger is still at pressure but reduced in temperature to 40-70°C. The cooling water is a closed loop system that is cooled via a chiller.

After leaving the heat exchanger, the cooled but still pressurized process flow can be directed in one of two ways depending on how the system is being operated. During Baseline mode, where the focus is on liquid sample collection, the process flow enters a system of two parallel, pressurized (with N₂) collector vessels (Figure 4-6). While one vessel is collecting effluent, the other is emptied by first slowly venting the N₂ and then draining the liquid contents into a bucket. The vented gas travels through a separate exit line and wet test meter (WTM) (to measure gas flow) than the main process gas effluent. The oil and aqueous liquid phases are then transferred to a separatory funnel or glass jar to begin phase separation and subsequent analyses. Once emptied, the collector vessel is pressurized with N₂ again to await process flow transfer.

when the other vessel is filled. The main process gas effluent flows on past the liquid collection vessel downstream through two condensers and then through the main back pressure regulator (BPR), where pressure is reduced to ambient. The process gas then proceeds downstream through the equipment described in the paragraph below.



Figure 4-6. Liquid Effluent Collector Vessels.

During Rapid Letdown (RLD) mode, where the focus for this testing was on gas sample collection, the combined liquid and gas effluent bypasses the collector vessels (path shown as the lower dotted line in Figure 4-2) and is depressurized after passing through the BPR. The liquid and gas phases are then separated at ambient pressure, with the liquid collecting in one of two float traps while the gas passes through a condenser, coalescer (filled with glass Raschig rings), and a knockout trap. A more detailed view of this part of the system is shown schematically in Figure 4-7. One float trap is located beneath the condenser for collection of mostly the aqueous phase while the second float trap is located beneath the coalescer for collection of mostly the oil phase. The liquid phases were not quantified for this testing during the RLD mode. A side sample line allows access to the online micro-gas chromatograph for analysis, and for attachment of a SUMMA® canister for collection of gas for offsite siloxane analysis. There is also a port for manual collection of gas samples via syringe for injection into a separate GC with a thermal conductivity detector (TCD) for analysis of permanent gases. The gas flow then proceeds downstream through a WTM for totalizing the gas flow and exits into the facility ventilation system.

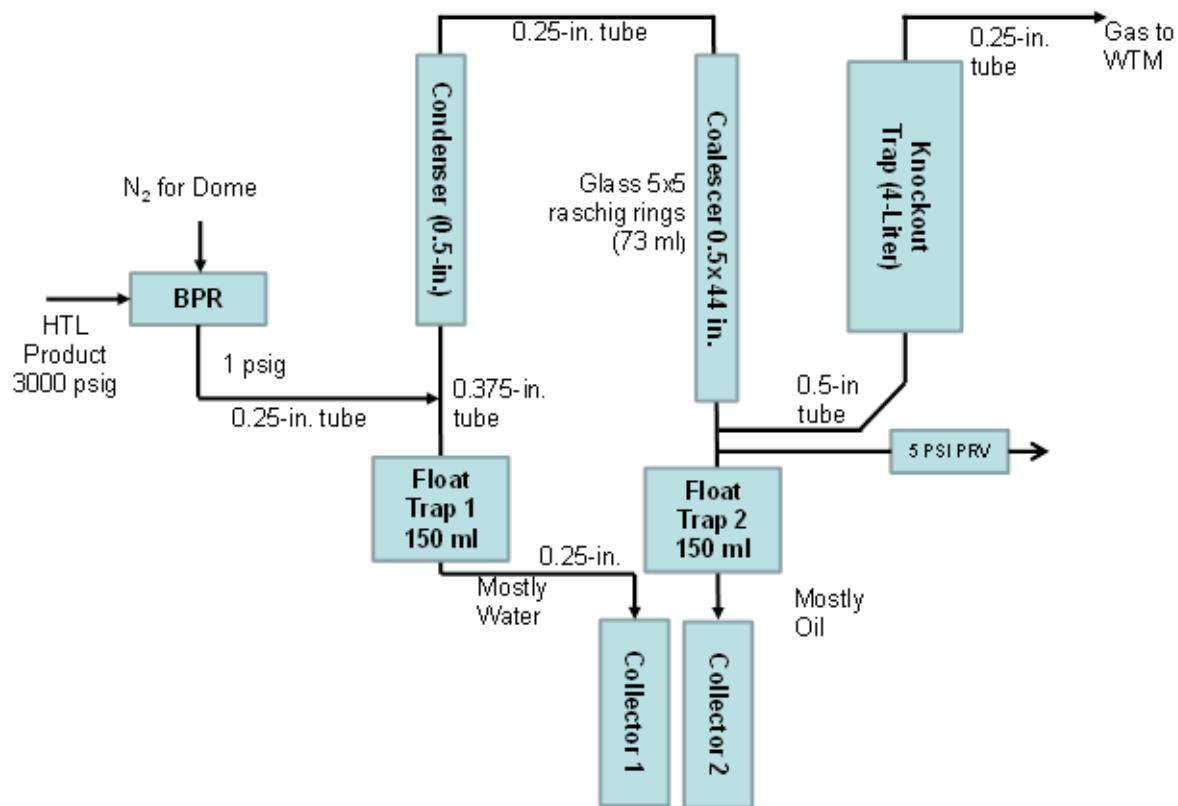


Figure 4-7. Pressure Let-Down and Gas/Liquid Effluent Separation in Rapid Let-Down Mode.

RLD mode is believed to generate more representative gas samples because it allows for better separation of gaseous and liquid products after pressure letdown and avoids the dilution from the relatively large quantities of N₂ needed for liquid collection under pressure in Baseline mode. Note that because of the two operating modes, formal liquid and gas samples are not taken at the same time during HTL tests.

Prior to performing each HTL test, PNNL staff generated a run plan which provided specific details for the lab operators on how to conduct the particular test to be performed. Prior to performing each test, the sludge feed had to be checked, and in some cases diluted and/or size reduced, to be sure that it could be pumped by the HTL system syringe pump (see Section 4.3).

During operation, the HTL system was first pressurized and then heated with water flow. In some cases, the system was pressurized and partially heated the day before the test and allowed to sit at temperature and pressure overnight (with water flow stopped). On the day of the test, the system was allowed to reach its thermal set point on water flow while sludge feed was loaded into the feed cylinders. A feed sample was taken at this time. Once at set point, the syringe pump was set to begin loading its next empty internal chamber with sludge feed (instead of reloading with water). At the pump feed rate, it typically took about 20 minutes to empty a chamber. The test was formally begun when the syringe pump began pumping sludge to the system. The system was then allowed several hours to reach steady state on sludge feed.

The HTL system was always started in Baseline mode for these tests. Each liquid effluent collector vessel could hold about 40 minutes worth of effluent before having to be emptied. After first switching to sludge feed, the liquid effluent was mostly water and the gas effluent flow was usually low. As operation continued, the oil phase liquid product and gas flow quantities began to increase in quantity. Steady state was defined by PNNL as being reached when the liquid product showed visibly consistent output of aqueous and oil liquid phases. This definition is subjective but was based on the significant previous experience of PNNL staff running the HTL system with other biomass feeds. Once it appeared that the system was approaching steady state, the liquid effluent in the collector vessels was saved (each collection is referred to as a set-aside). Since steady state is typically reached about three hours after starting feed, the first set-aside was usually taken about two hours after starting feed. The intent was to take six consecutive set-asides with steady state hopefully being confirmed (via subsequent chemical analysis) for the last four (or at least the last three) set-asides. This would provide the intended three liquid samples for each test. Gas effluent was sampled and analyzed automatically by the on-line GC every four minutes throughout testing. However, because of the relatively large amounts of N₂ gas used during Baseline mode to pressurize the collector vessels, the gas data was not representative until after the switch to RLD mode. Process Monitoring data on temperatures, pressures, and flow rates were recorded manually every 40 minutes (coinciding with each collector vessel draining). More extensive and automated collection of Process Monitoring data was performed by the computer control system throughout the entire test for archiving and for trend observation using LabView software. Automated Process Monitoring data was collected at a frequency of every 15 minutes during the initial overnight system heatup, but was increased to every one minute during the actual test.

After at least three consecutive set-asides were assessed qualitatively by PNNL staff to represent steady state (constituting at least two hours at steady state), the HTL system was switched to RLD mode (see above for the difference between Baseline and RLD modes of operation). After switching modes, a certain amount of time was allowed for N₂ gas (left from its use in pressurizing the collector vessels) to clear the system and reestablish steady state. The return to steady state was determined by PNNL staff as when gas effluent composition and flow was stable and consistent. Occasional manual gas samples were taken and analyzed in an off-line GC to more quickly assess when gas composition had stabilized. Official gas effluent data was

measured by the on-line GC, which continued to sample automatically every four minutes and analyze for H₂S, light hydrocarbons, and permanent gases (CO₂, CO, H₂, O₂, N₂, CH₄, C₂H₆, and C₂H₄). Once steady state was re-established, manual process monitoring data was recorded every 30 minutes. Automated process monitoring data continued to be collected at one minute intervals. When gas samples for offsite siloxane analysis were taken, the required SUMMA® canister was filled near the end of the steady state period in order to best ensure a representative sample. As it typically took about one hour for steady state to be established after the switch to RLD mode, operation was allowed to run for about one hour more at steady state for adequate gas sample collection.

After a sufficient number of gas samples were collected, the syringe pump was set to begin loading its next empty internal chamber with water. Water was pumped for about two hours to fully flush the system. At this point, the heat to the system and water flow were turned off. The following day, system pressure was reduced back to ambient, water flow was stopped, and all components were shut down. The system was then opened and certain components such as the filter vessel and CSTR were disassembled to allow for inspection, collection of solids, and cleaning. A second sludge feed sample was taken at the end of the test as the residual feed in the feed cylinders was removed.

With respect to test instrumentation and calibration for both HTL and CHG systems, balances are calibrated annually and check weights are used to verify balance performance daily. Auto pipettes are checked daily (deionized water and balance). Thermocouples are inherently robust ($\pm 2^{\circ}\text{C}$). If they give a suspect number, they are checked and/or replaced. Transducers are rated as $\pm 0.5\%$, but they drift. Using the LabView, data software, PNNL sets all transducers to the syringe pump pressure at the beginning of each test. The syringe pumps are zeroed at the start of each test. The syringe pump transducer is checked annually. Syringe pump flowrates are checked during each test via mass balance. Flowrate reading is checked whenever maintenance is performed (typically twice per year) or annually (bucket and stop watch check). Using water (in bucket and stop watch check), PNNL typically comes within 1 gram for one liter of volume pumped (assuming water at 1 g/cm³).

4.2.2 Catalytic Hydrothermal Gasification (CHG)

A process flow diagram of the CHG system used for testing is shown in Figure 4-8. The CHG system utilizes a Teledyne Isco 500 ml dual chamber syringe pump similar to that used in the HTL system (Figure 4-3). Because feed rates are more than an order of magnitude slower than that used in the HTL system due to the smaller scale of the CHG system, there is no formal feed tank for the CHG system. Instead, the aqueous phase feed is placed in a large flask or storage bottle and the syringe pump chambers fill when necessary directly from the flask via a flexible tubing line. The syringe pump provides continuous feed delivery at a fixed flow rate to the CHG system at system operating pressure (about 2900 psig). After leaving the syringe pump, the pressurized feed enters a heated precipitator (Figure 4-9). The precipitator is a dead-ended section of large diameter tubing that allows inorganic salts not removed previously in the HTL system to drop out of the main process flow, which reverses direction and exits through the top. The precipitator is encased in an aluminum block which is heated by externally attached electric heaters up to the full reactor temperature of about 350°C. Note that at this temperature, most salts of concern with respect to the downstream catalyst (e.g., sulfates) have very low solubility and will precipitate out of the feed solution (see Section 6.4.3). Most of these salts should have been

removed during the HTL test, but the precipitator was left in place for these CHG tests as additional insurance. Note that the CHG catalyst is deactivated (or poisoned) by sulfur compounds (both oxidized and reduced), and these must be removed from the feed prior to reaching the reactor.

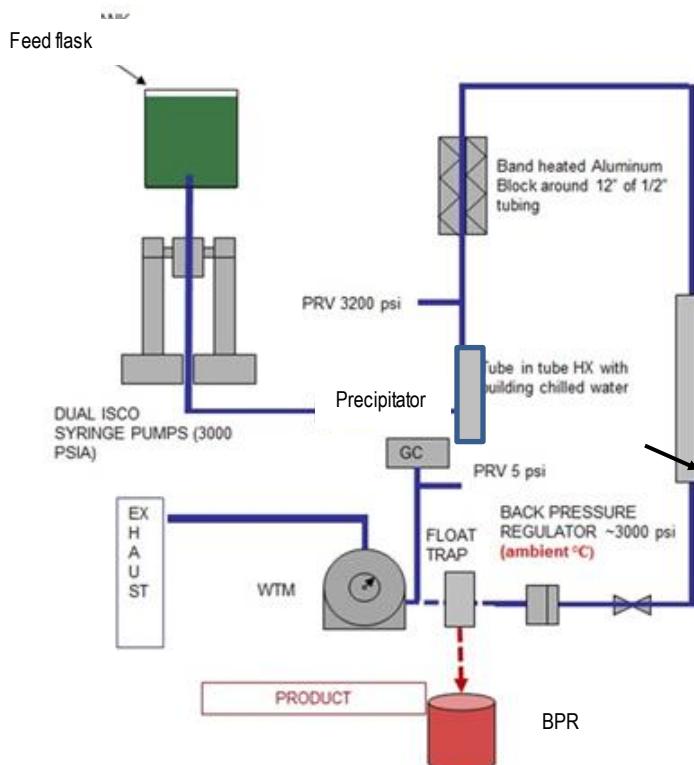


Figure 4-8. PNNL Bench-Scale CHG System.



Figure 4-9. CHG Precipitator and Reactor.

The precipitator is the cylindrical, insulated component in the center left of photo, and the reactor is the similar shaped component to the upper right of the precipitator.

After the precipitator, the main flow enters the reactor. The reactor consists of a 12-inch length of 0.5 inch outer diameter tubing surrounded by an aluminum block, to which electric band heaters are attached (as with the upstream precipitator) to maintain the fluid flow at about 350°C. The first one-third of the reactor contains Raney nickel solids and the remaining two-thirds of this section contains the catalyst, which consists of ruthenium on a graphite backing. The Raney nickel is used to strip reduced sulfur compounds from the feed. Oxidized sulfur compounds (i.e., sulfates) must be removed via precipitation or other means upstream of the reactor. The two sections of the reactor are separated by a screen. After leaving the reactor, the flow enters a water jacketed, tube-in-tube cool down heat exchanger and then passes through the system BPR (Figure 4-10). Now at ambient conditions, the flow then passes through a liquid/gas separator. Liquid effluent is collected in a pot situated on top of a scale to measure the mass of liquid product over time. Liquid samples are taken directly from the end of the tubing that empties into the collection pot. The gaseous product proceeds downstream to the WTM and facility ventilation system, with a side sample port for manual sample collection via syringe for off-line GC analysis. A side line prior to the sample port was also added for location of the SUMMA® canister to be filled for collection of effluent gas for off-site siloxane analysis.



Figure 4-10. CHG System Components Downstream of Reactor.

As noted earlier, the operation of the CHG system is independent of the HTL system. They are not integrated in operation and in theory can be run in parallel with separate feeds. Because the CHG system is co-located with the HTL system in the same lab, uses similar support equipment and space in the lab, and typically has a longer operating duration, two separate tests being performed at the same time would be difficult to manage, though it can be done. The HTL and CHG systems were not operated simultaneously during this test program.

The aqueous phase portion of the liquid effluent collected during HTL tests (i.e., set-asides) was used as the feed for the corresponding CHG test. Each set-aside for every HTL test

was transferred to a storage bottle and stored under refrigeration until the corresponding CHG test was performed. Because of the limited volume of HTL aqueous effluent collected and the long time needed for the CHG system to reach steady state due to the low flow rates utilized, a separate CHG test could not be performed on each individual steady state set-aside as originally specified in the Quality Assurance Project Plan (QAPP) for this test program. Instead, the three steady state set-asides per HTL test were combined into one CHG feed. Thus, only one CHG test was performed per HTL test (instead of three). However, at least three liquid and gas effluent samples were taken during each CHG test instead of one as originally specified. As a result, the minimum total number of CHG samples per HTL feed was maintained. The three non-steady state (i.e., initial) set-asides per HTL test were also combined and used to start the CHG test.

Each CHG test took several days to complete because of the low flow rates (~ 40 ml/hr) involved and residence times required. Consequently, the CHG system is designed to run by itself unattended. For each CHG test, the reactor was first loaded with fresh catalyst in order to ensure that each test started on the same basis. After reassembling the system, it was leak checked under pressure with N₂ gas. H₂ gas was then added to the system to ensure that the catalyst was not oxidized. The system was then repurged with N₂. Water flow was then introduced into the system via the syringe pump to displace the N₂. Once this was done, the heaters were turned on. Typically, the system was allowed to stay at pressure and temperature overnight with water flow. The next morning, the syringe pump was stopped, both pump chambers were emptied of water, and the combined mixture of the first three HTL aqueous phase set-asides was loaded into the syringe pump chambers. The pump was then restarted. Because of the low feed rates, it would typically take about 1.5-2 hours before the first volume of feed made its way through the system. A sample of feed was also taken at the start to confirm the COD level. Process monitoring data on temperatures, pressures, and flow rates were first recorded manually at the start of feed flow and subsequently was recorded whenever liquid and gas effluent samples were taken. More extensive and frequent (every 10 minutes) collection of process monitoring data was performed by the computer control system throughout the entire test for archiving and for trend observation.

Remaining feed was loaded into the syringe pump once a chamber had emptied. Once the feed consisting of the first three set-asides was loaded, the combined mixture of the last three aqueous phase HTL set-asides (most closely representing HTL steady state) was loaded into the next syringe pump chamber to empty and would continue to be added to each empty chamber until all of it had been loaded. Steady state operation on feed typically lasted the entire day and overnight into the next day. Samples of liquid and gas effluent were taken periodically but at unspecified frequencies during the day. Liquid samples were taken in a small vial directly from the end of the system. Gas samples were always taken manually via syringe from the sample port upstream of the WTM and injected into an offline GC with TCD for analysis. When possible, arrangements were made for one or more evening samples to be taken. Typically, more than the required three samples were taken throughout the test, with the last three (most representative of steady state) being used as the official samples. Once a sufficient number of samples were taken, a gas sample for siloxane analysis was taken, if required for the given run. Because of the low flow rates, the SUMMA® canister used for sample collection (which was under vacuum) could not be filled at one time without drawing air back into the system. As a result, the valve to the canister was opened in short intervals until the WTM indicated about 20-30 ml of backflow. The canister valve was then shut until the WTM indicated a positive volume of 20-30 ml before

opening the valve again. This procedure was repeated over several hours until sufficient volume had been captured in the SUMMA® canister. Because of the time required, the sample for siloxane analysis was usually taken during the morning of the next day, with the exact start time dependent on the amount of feed remaining. Usually there was enough feed to last into the morning of the next day.

Once the last volume of feed was loaded into the syringe pump, a flask of water was set up with flexible tubing such that subsequent chamber refills would be with water. Once the last chamber with feed emptied, flow continued with water and the formal test ended. It still took several hours for the system to be fully flushed with water. This would be determined when effluent gas flow (as indicated by the WTM) stopped. At this point the heaters were turned off. Once the system temperature had dropped to about 150°C, the pressure was dropped back to ambient and the syringe pump stopped. N₂ gas was then used to purge the system, which also helped dry the catalyst. The reactor was removed and opened and the catalyst was inspected once the system was fully cooled, which was typically on the next or some later day.

4.3 Sludge Feed Preparation at PNNL

In addition to the sludge preparation work performed at Metro Vancouver (and described in Chapter 3.0), further preparation of the sludge feeds for testing was carried out at PNNL. The particular preparation work varied among the three different sludge feeds as described below. The overall goal of all preparation work performed at PNNL was to ensure that the sludge was homogeneous and could be pumped to the HTL system via the syringe pump at as high a solids percentage as possible. A summary of sludge feed preparation work performed at PNNL is included in Table 4-1.

Table 4-1. Sludge Preparation Work at PNNL.

Sludge Type	As-Received Concentration (wt % solids)*	Dilution	Screen	Mixer	Final Concentration (wt % solids)
Primary	26.0	Yes	No	High shear + Immersion mill	11.9
Secondary	10.9	No	20 mesh	High shear	10.0
Digested Solids	28	Yes	No	High shear	16.4

* Measured at Metro Vancouver

4.3.1 Digested Solids

Two five-gallon buckets of digested solids (28 wt% solids) were received at PNNL from Metro Vancouver on May 28, 2015. The total weight of sludge received was measured to be 30.2 kg. About half of this material was placed into a high-shear mixing vessel (Figure 4-11) for homogenization and dilution. The other half was archived and stored under refrigeration. Because the sludge as received was too thick to pump, about 6 kg of water was added to the mixer vessel. The mixer vessel had a recirculation loop with a diaphragm pump. After mixing the initial dilution water, the mixture was considered by PNNL staff to still be too thick to pump. After an additional 1 kg of water was added, marginal flow was achieved through the diaphragm pump. With another 1 kg of water added, the resulting sludge was able to be pumped through the diaphragm pump. While still very thick, the sludge was now judged by PNNL staff to be pumpable by the HTL syringe (feed) pump. Because of the apparent high sludge viscosity, the sludge was not processed through an inline strainer on the mixer as would normally have been

done. A small amount of sludge was manually forced through a 20-mesh screen without difficulty. Visual inspection revealed some fine, hard solids in the sludge, but no large solids. A sample of the diluted feed was taken and analyzed to be 16.4 wt% solids (Figure 4-12). Samples of the diluted sludge taken before and after the repeat HTL test performed with this feed about one month later had a slightly lower concentration 16.0 wt% solids.



Figure 4-11. PNNL High-Shear Mixer.



Figure 4-12. Diluted Digested Solids at PNNL (16.4 wt% solids) for HTL Feed.

4.3.2 Primary Sludge

Two five-gallon buckets of autoclaved, dewatered primary sludge (26 wt% solids) were received at PNNL from Metro Vancouver on June 5, 2015. The total weight of sludge received was measured to be 27.3 kg. It was noted by PNNL staff that the as-received sludge had the texture and appearance of “browned hamburger” (Figure 4-13). The sludge could be compressed and there was no free water evident. It was noted that a number of $\frac{1}{4}$ in. diameter fibrous paper clumps were observed in the sludge, which could be broken up with moderate force.



Figure 4-13. Primary Sludge As Received at PNNL.

An initial dilution test was performed in a beaker on 500 g of sludge to determine the amount of water necessary to transform the material into a pumpable slurry. After a dilution to about 16.7 wt% solids, the diluted sludge exhibited some flow and could be rolled into a ball. This was initially judged by PNNL to be of sufficient dilution to be pumped. However, when the sludge was run through the high-shear mixer, the paper clumps caused the diaphragm pump to plug multiple times. As a result, the sludge was further diluted and the immersion mill was utilized to breakup the clumps. While the resulting feed was suspected of now being a little more diluted than necessary to pump through the HTL system, PNNL staff wanted to err on ensuring an uninterrupted HTL test rather than striving to obtain the highest sludge concentration possible for these proof-of-concept tests. Samples of the diluted feed taken during the HTL test were analyzed to be 11.9 wt% solids (Figure 4-14).



Figure 4-14. Diluted Primary Sludge at PNNL (11.9 wt% solids) for HTL Feed.

4.3.3 Secondary Sludge

Two five-gallon buckets of autoclaved, dewatered secondary sludge were received at PNNL from Metro Vancouver on June 23, 2015. The total weight of sludge received was measured to be 29.0 kg. PNNL staff described the as-received sludge to be a thick slurry with small globs of thicker gel. It was noted that a small lab spatula could stand up straight in the sludge (Figure 4-15), that the sludge did not settle over time, and that the sludge could be taken up and ejected easily with a small, plastic hand syringe. As a result, the sludge was assessed to be pumpable as is with no dilution needed. This was expected based on the fact that the secondary sludge (at 10.9 wt% solids) was below the target concentration range of 15-20 wt% solids, which could not be achieved due to the difficulties experienced with dewatering this material at Metro Vancouver (see Section 3.4.3).



Figure 4-15. As-Received Secondary Sludge.

While no dilution water was added, the secondary sludge was placed in the high-shear mixer for 45 minutes to homogenize the material. The shear mixing resulted in a smoother, more consistent material (Figure 4-16). After this, the sludge was pumped through the mixer's 20-mesh inline strainer using the diaphragm pump. A significant amount of small particles covered the strainer exterior after its use (Figure 4-17). These particles were mostly soft, though a number of larger particles appeared to be grit. The homogenized and screened sludge was then put back in the five gal buckets and stored under refrigeration until needed for its HTL test. Samples of the prepared sludge were taken and analyzed to be 10.0 wt% solids, which is slightly less than the 10.9 wt% solids measured by Metro Vancouver before shipping to PNNL. Samples of the sludge taken before and after the repeat HTL test performed with this feed the next day had a slightly lower concentration of 9.7 wt% solids.



Figure 4-16. Secondary Sludge After High-Shear Mixing.

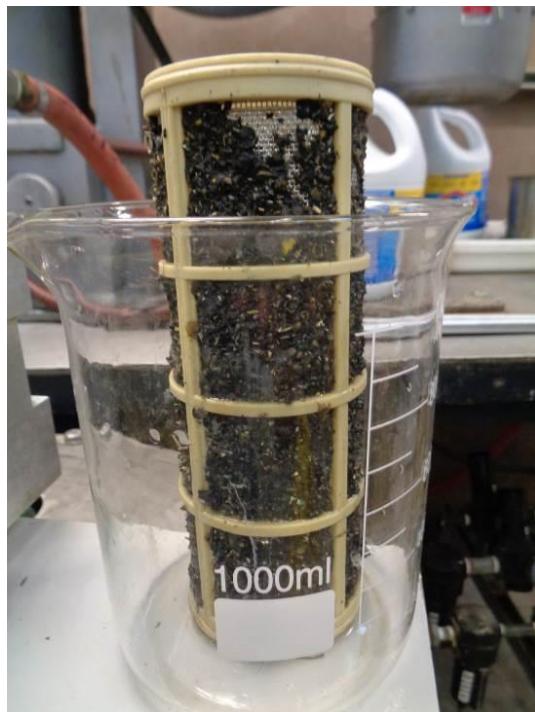


Figure 4-17. 20-Mesh Inline Strainer After Filtering Secondary Sludge.

4.4 Tests Performed

Table 4-2 summarizes the HTL and CHG tests performed at PNNL as part of this test program. The first HTL test performed with digested solids (WERF-01) had an unplanned, premature shutdown just as the system was approaching steady state under Baseline operation. This shutdown occurred before any reliable gas phase samples could be taken. While a corresponding CHG test was run with the limited aqueous phase HTL product available, it was ultimately decided to repeat the HTL and CHG tests with digested solids. The repeated tests (designated as WERF-04 and WERF4-CHG) were performed for the full planned durations with all samples successfully collected. Thus, a total of eight tests were performed. The limited data from the first digested solids tests have been reviewed but only data from the repeated tests with digested solids are presented and discussed in this report.

Table 4-2. Tests Performed.

Sludge Feed Type	HTL Test	HTL Test Date	CHG Test	CHG Test Date
Digested Solids	WERF-01*	June 4-5, 2015	WERF1-CHG	June 22-24, 2015
Primary	WERF-02	June 16-17, 2015	WERF2-CHG	Aug. 10-14, 2015
Secondary	WERF-03	June 24-25, 2015	WERF3-CHG	Aug. 17-21, 2015
Digested Solids	WERF-04	July 9-10, 2015	WERF4-CHG	Sept. 13-17, 2015

* Shortened test due to unplanned shutdown

The time needed to complete all of the planned experiments was longer than originally planned due to several additional concurrent projects being performed with the same equipment by PNNL staff. Each test took several days to complete, from initial heat-up through final shutdown. Liquid products from HTL tests were stored under refrigeration while waiting for the corresponding CHG test to be performed with the HTL aqueous phase product.

Tables 4-3 and 4-4 provide key operating data associated with HTL and CHG tests, respectively. Note that HTL feed concentrations indicated are the average of samples taken of the sludge from the feed cylinder at the beginning and end of the test. Thus, there may be slight differences from the concentrations measured immediately after sludge homogenization at PNNL following the original receipt of the sludge (Table 4-1). In CHG tests, both liquid and gas effluent samples were collected at the same time (unlike in HTL tests). However, not all CHG liquid samples were analyzed, and of those that were, not everyone had the same analyses performed. All CHG gas samples were analyzed via GC but not all results were used in data reduction. The choice of samples to analyze and use in data reduction was made at the discretion of PNNL staff. Table 4-5 summarizes the samples taken in CHG tests. A more complete presentation of all Process Monitoring data for each test is provided in Section 4.5.

Table 4-3. HTL Test Matrix.

Test No.	Sludge Feed	Feed Conc. (wt% solids)	Feed Flow Rate (L/hr)	Reaction Temperature (°C) ^a	Avg. System Pressure (psig)	Liquid Hourly Space Velocity (hr ⁻¹) ^{b,c}	Mean Residence Time (min) ^d	Test Duration			No. of Steady State Liquid Samples (Set-asides)
								Total Feed (hrs)	Baseline steady state (hrs)	RLD steady state (hrs)	
1	Digested Solids	16.4	1.5	325-353	2914	2.1	17	3.4	0.7	–	1
2	Primary	11.9	1.5	318-353	2948	2.1	18	7.4	2.0	1.5	3
3	Secondary	9.7	1.5	276-358	2919	2.1	19	7.5	2.0	1.0	3
4	Digested Solids	16.0	1.5	332-358	2906	1.2	30	7.2	2.7	1.5	4

^a Range indicated spans average temperatures measured over the CSTR and PFR sections only (i.e., excludes heated filter temperatures).

^b Based on combined volume of stirred tank and plug flow reactors only (i.e., excludes effects from heated filter vessel).

^c Based on feed volumetric flow at ambient conditions.

^d Estimated assuming fluid at reactor conditions has the density of pure water at the average reaction temperature and pressure.

Table 4-4. CHG Test Matrix.

Test No.	HTL Aqueous Effluent Feed Source	Feed Flow Rate (mL/hr)	Avg. Reactor Temperature (°C)	Avg. System Pressure (psig)	Reactor Residence Time (min) ^a	Test Duration (hr)		Sulfur Removal (Raney Ni) (g)	Catalyst (Ru on graphite) (g)
						Total Feed	Steady State		
1	WERF-01 ^b	41.4	346	2914	15	25.2	17.3	8.96	11.19
2	WERF-02 ^c	39.7	347	3023	15	49.3	20.6	8.05	10.71
3	WERF-03 ^c	43.8	346	2883	15	45.4	35.9	8.19	11.82
4	WERF-04 ^c	41.2	348	2959	15	31.4	25.4	8.98	11.65

^a Based on catalyst instead of reactor volume; assumes 50% void volume in catalytic reactor.

^b Feed consisted of aqueous phase portions of all set-asides generated (steady and non-steady state) in HTL WERF-01.

^c Because of lower than expected quantities of aqueous feed, the aqueous phase portions of all steady state set-asides from the corresponding HTL test were combined into a single feed for each CHG test.

Table 4-5. CHG Effluent Samples.

Test	Liquid Samples		Gas Samples	
	Taken	Analyzed	Taken/Analyzed	Used
WERF1-CHG	4	1	4	2
WERF2-CHG	7	2-4	4	4
WERF3-CHG	9	3	9	4
WERF4-CHG	5	3	6	5

4.4.1 Digested Solids

The first HTL test (WERF-01) was performed with digested solids that were diluted and homogenized after receipt at PNNL to a consistency that could be pumped. System heat-up with water began on June 4, 2015 with the switch to sludge feed occurring early the next day. The first evidence of oil was observed in the liquid collector vessels about two hours after switching to feed. The amount of oil visible in each vessel (collected in 40-minute increments) increased over time as expected. Just as the system was transitioning to steady state, an operator closed an incorrect valve while switching from one collector vessel to the other. This caused a high pressure alarm which stopped the feed pump. After correcting the collector vessel valve configuration, the pump was restarted. However, an unexpected pressure pulse upon restart blew a rupture disk and the system was shutdown.

After shutdown, PNNL staff determined that the last full set-aside could be considered at steady state based on the behavior observed to that point and experience with previous feeds. With only one liquid sample (set-aside), it is difficult to verify that steady state was achieved over the full time that the sample was taken. Nevertheless, since it was not clear whether PNNL would be able to repeat this test, PNNL decided to proceed with oil separation and performing a CHG test with the available aqueous phase. Because the aqueous phase from a single set-aside was not enough material to conduct a CHG test, the aqueous phase from the preceding set-aside that was approaching steady state was also used. The aqueous phases from the two set-asides were combined into a single feed for performing the CHG test.

Prior to performing the CHG test, analysis of the HTL aqueous phase indicated a sulfate concentration of 193 ppm. This concentration is too high in sulfur for the CHG catalyst and would deactivate it in a relatively short period of time. The Raney nickel guard bed prior to the CHG catalyst is effective mainly at removing reduced sulfur compounds, and is not as good at removal of oxidized sulfur compounds such as sulfate. As a result, the aqueous phase had to be processed through an ion exchange column to remove the sulfate. Subsequent analysis after ion exchange confirmed an acceptable sulfate concentration (< 10 ppm).

The CHG test (WERF1-CHG) was performed a few weeks after the HTL test. At the time, PNNL staff did not anticipate repeating the HTL test with digested solids. Heat-up began with water on June 22, 2015, with the transition to aqueous feed taking place the next morning (Figure 4-18). Because of the slow feed rate, it requires about three hours for material to pass completely through the system. Steady state was declared about 5.6 hours after the start of feed on June 23. The system was allowed to run overnight at steady state until early the next morning. Several gas and liquid effluent samples were taken during the steady state period. After the last sample set was taken on the morning of June 24, a gas sample for siloxane analysis was started. Because of the slow feed rate and corresponding low gaseous effluent rate, the SUMMA® canister could only be opened for short periods at a time to avoid too much back flow. It took about 3.5 hours before sufficient gas effluent had been captured, at which point the system was switched back to water feed and shutdown.



Figure 4-18. CHG Syringe Pump Operating on Aqueous Feed (WERF1-CHG).

DI water (flask on right) is used to start and end each CHG test. In this photo, HTL aqueous phase feed (jar on left) has been loaded into the syringe pump cylinder. The remainder will load when the pump cylinder is empty.

Because of the lack of HTL gas effluent data, limited HTL liquid effluent, and the need to demonstrate reliable system operation with the digested solids feed, it was ultimately decided to repeat the HTL and CHG tests with digested solids in order to generate a more complete and consistent data set. The repeat HTL test (WERF-04) was started on July 9, 2015, with the switch to sludge feed early the next day. Because of a problem with solids buildup in the CSTR during the preceding run performed with secondary sludge (see Section 4.4.3), the insert in the CSTR was removed to allow access to the full 1 L volume. Thus the space time in the system for this run was increased (i.e., slower space velocity) compared to previous runs. This run was successfully performed for its full duration without incident. Plots of key temperatures and pressures during the test are shown in Figures 4-19 and 4-20, respectively.

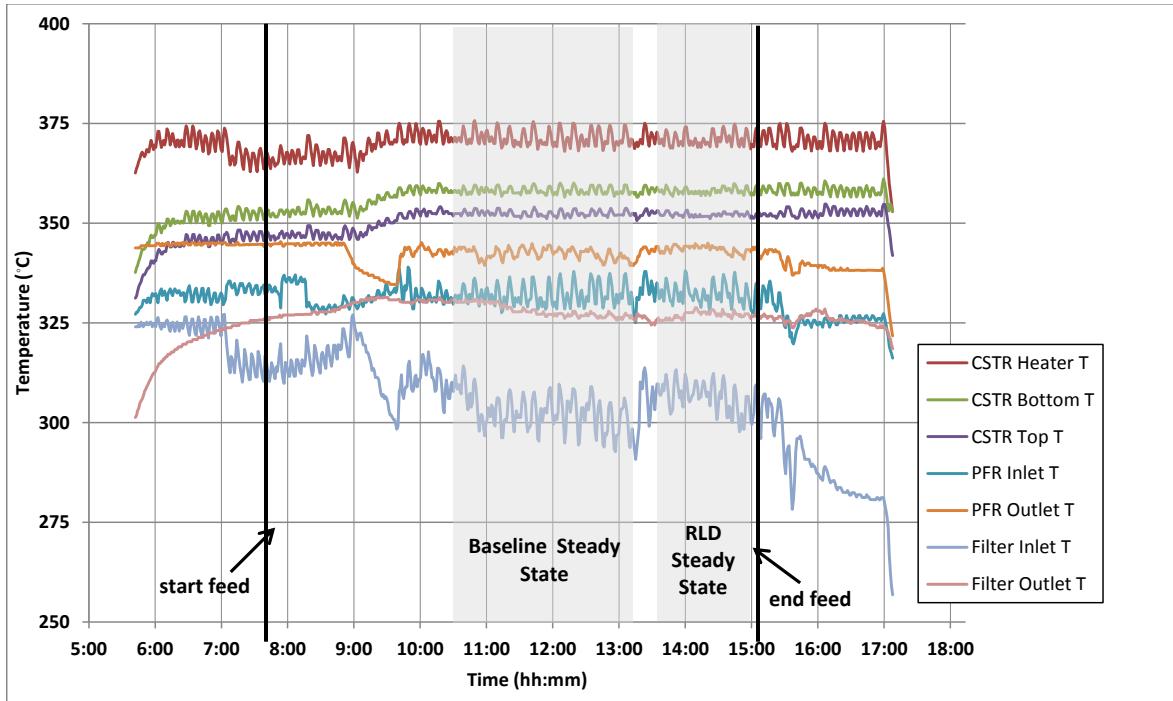


Figure 4-19. Temperature Data for HTL Test with Digested Solids (WERF-04).
Shaded regions indicate steady state.

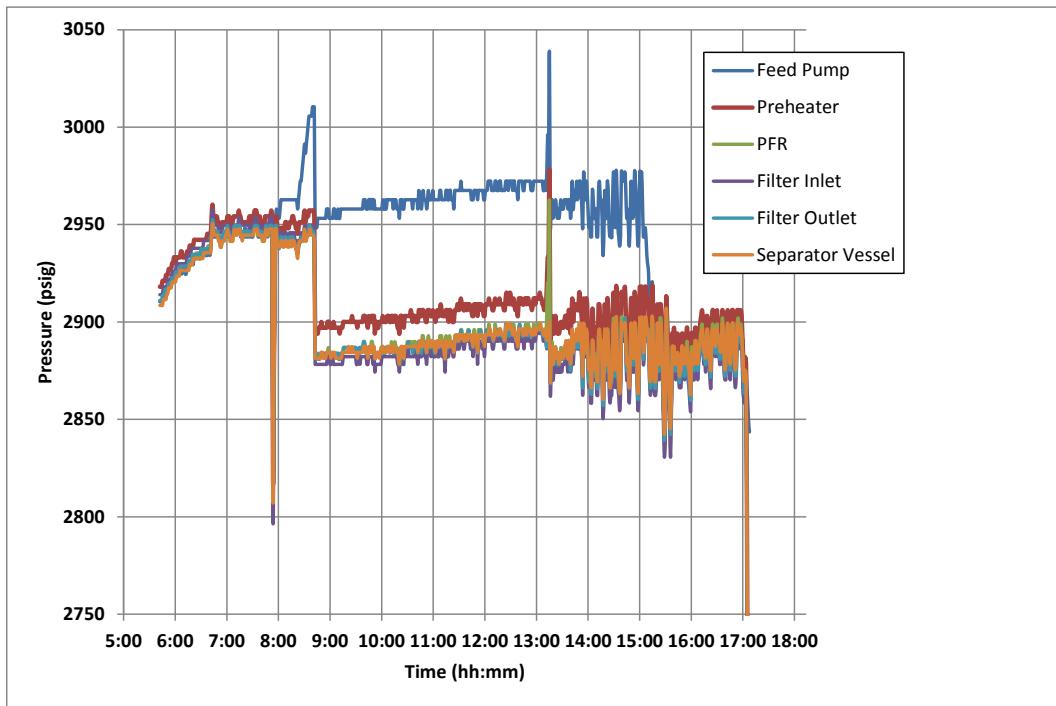


Figure 4-20. System Pressure Data for HTL Test with Digested Solids (WERF-04).

A total of four set-asides of liquid effluent at steady state were collected in WERF-04. Biocrude was first observed in the liquid set-aside taken about two hours after the start of feed. The first set-aside under steady state conditions was taken 3.3 hours after the start of feed. Some of the oil phase floated at the top of the sample and some sank to the bottom. Based on past experience with this type of oil formation, the liquid effluent from each steady state set-aside was placed in glass jars and refrigerated after collection (Figure 4-21). After several hours under refrigeration, the oil was more viscous, resulting in more coalescing and sticking to the glass jar walls, which in turn made it easier to separate from the aqueous phase by decanting the aqueous phase (Figures 4-22, 4-23, and 4-24). Subsequent operation in RLD mode for 1.5 hours after returning to steady state (which took about 20 minutes after changing modes) was allowed for sufficient on-line gas sample collection and analysis before switching back to water feed to end the test. A gas sample for siloxane analysis was also taken during a 1 hr period in RLD steady state. A significant quantity of solids was collected in the filter vessel after the test (Figures 4-25 and 4-26). Inspection of the CSTR after the test showed a small amount of spherical, hard 1/8 in. diameter nodules at the bottom of the reactor (Figure 4-27), which was otherwise clear.

The corresponding CHG test (WERF4-CHG) for the aqueous phase from the repeat HTL test with digested solids was not performed until September 15, 2015. Ion exchange of the aqueous phase for removal of high sulfate concentrations (200 ppm) again needed to be performed. Subsequent analysis confirmed an acceptable sulfate concentration (< 10 ppm).



Figure 4-21. Steady State Liquid Effluent from the HTL Test with Digested Solids Feed (WERF-04).
Shown after being refrigerated.



Figure 4-22. Biocrude (from Figure 4-20) Remaining After Aqueous Phase Separation (WERF-04).



Figure 4-23. The Last Three Steady State Samples of Biocrude from the HTL Test with Digested Solids Feed (WERF-04).



Figure 4-24. Biocrude from the HTL Test with Digested Solids Feed (WERF-04).



Figure 4-25. Solids in Opened Filter Vessel After the HTL Test with Digested Solids Feed (WERF-04).

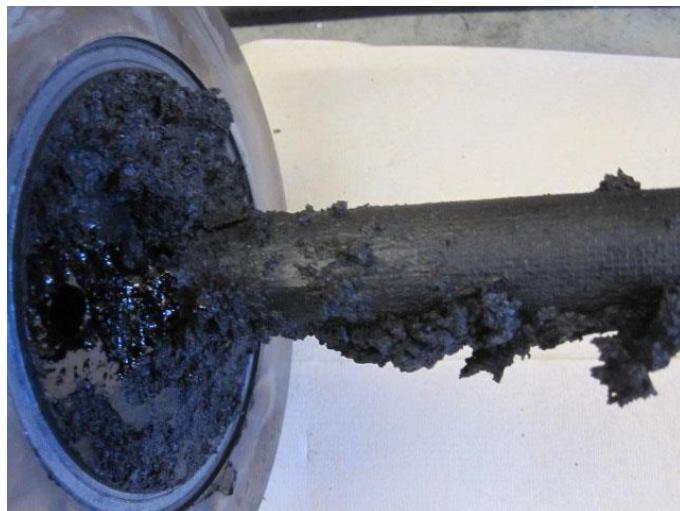


Figure 4-26. Filter Element After the HTL Test with Digested Solids Feed (WERF-04).



Figure 4-27. Solids Found in CSTR After the HTL Test with Digested Solids Feed (WERF-04).

Heat-up of the CHG system began with water on September 13, 2015 and continued overnight. As was the case with the preceding CHG tests, all non-steady state aqueous phase samples from the HTL test (WERF-04) were combined to make one CHG feed (Feed 1) used to bring the system to steady state. The aqueous phases from the four steady state HTL set-asides were combined to create a second feed (Feed 2), which would be used as the official CHG test feed once steady state was reached. The switch from water to Feed 1 took place early the next morning (September 14). Operation on Feed 1 continued all day. The switch to Feed 2 occurred early on the following morning (September 15). Steady state on Feed 2 was declared two hours after the switch to Feed 2, when the first gas and liquid effluent samples were taken (Figure 4-28).

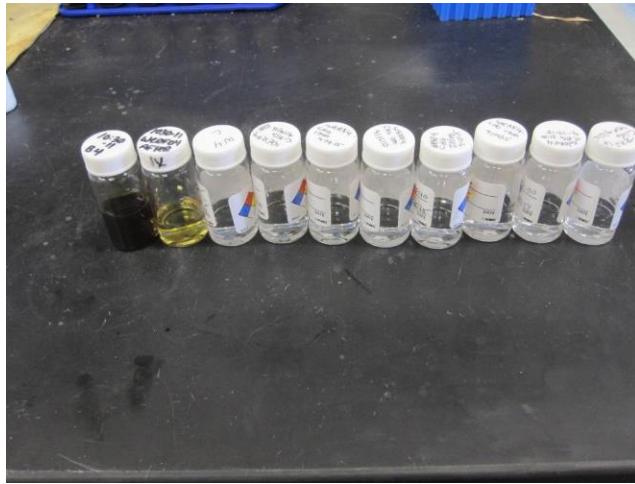


Figure 4-28. Feed and Effluent Samples from WERF4-CHG.
From left to right aqueous phase HTL product (pre-ion exchange), aqueous phase CHG feed (post-ion exchange), and eight samples of CHG aqueous effluent

System temperatures were stable throughout the steady state period, which lasted 25.4 hours (Figures 4-29). Approximately a 10°C difference consistently occurred across the reactor length during the test. System pressure readings showed some variance in absolute value during the test, but all individual readings tracked each other consistently (Figure 4-30). A total of five gas and liquid effluent samples were taken during the steady state period. After the last samples were taken the morning of September 16, the system was allowed to run for another 24 hours to use up the remaining amount of Feed 2 before the system was switched back to water feed and shutdown.

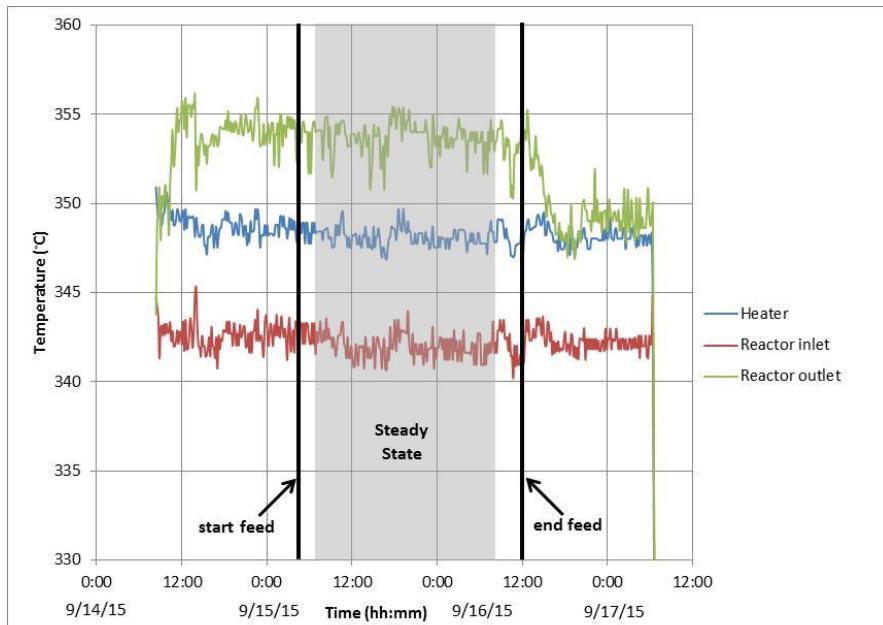


Figure 4-29. Temperature Data for CHG Test with HTL Aqueous Phase from Digested Solids (WERF4-CHG).
Shaded regions indicate steady state.

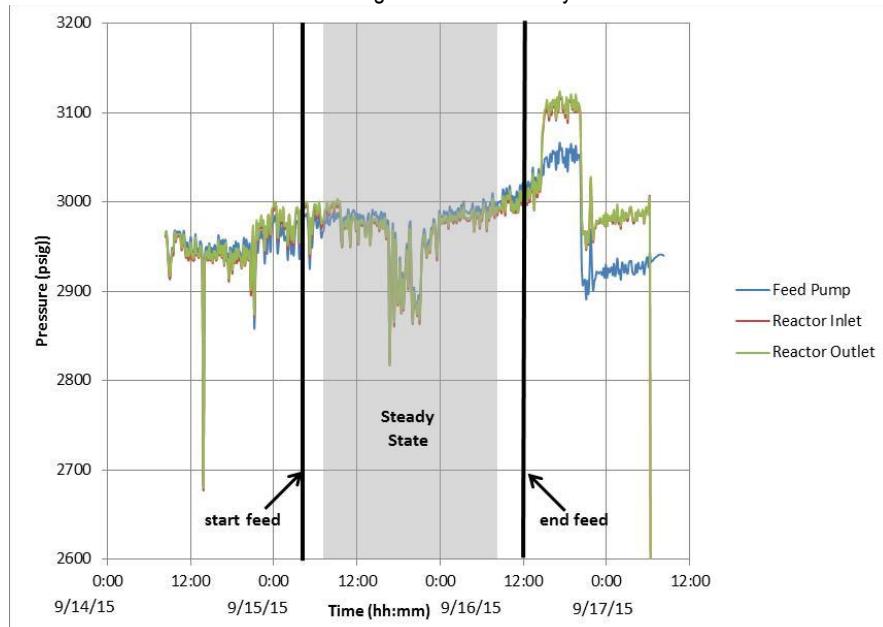


Figure 4-30. System Pressure Data for CHG Test with HTL Aqueous Phase from Digested Solids (WERF4-CHG).
Shaded regions indicate steady state.

4.4.2 Primary Sludge

The HTL test with primary sludge (WERF-02) was performed with the diluted and homogenized feed that was prepared at PNNL after receipt of the sludge from Metro Vancouver. System heat-up with water began on June 16, 2015 with the switch to sludge feed occurring early the next day. This run was successfully performed for its full duration as planned. About 20 minutes after the switch to feed, there was an unexplained pressure spike that occurred in the preheater. While this spike did not reoccur, there was a relatively small but steady rise in all pressures measured throughout the test (Figure 4-31). The slow pressure rise was seen in all tests and it is not clear if this is due to a gradual buildup of solids near the pressure transducers over time and if it is unique to sludge feeds or not. Reaction temperatures across the heated sections of the system (CSTR, PFR, and filter vessel) showed a notable variation as seen in the tests with digested solids, though the range was not as large (Figure 4-32).

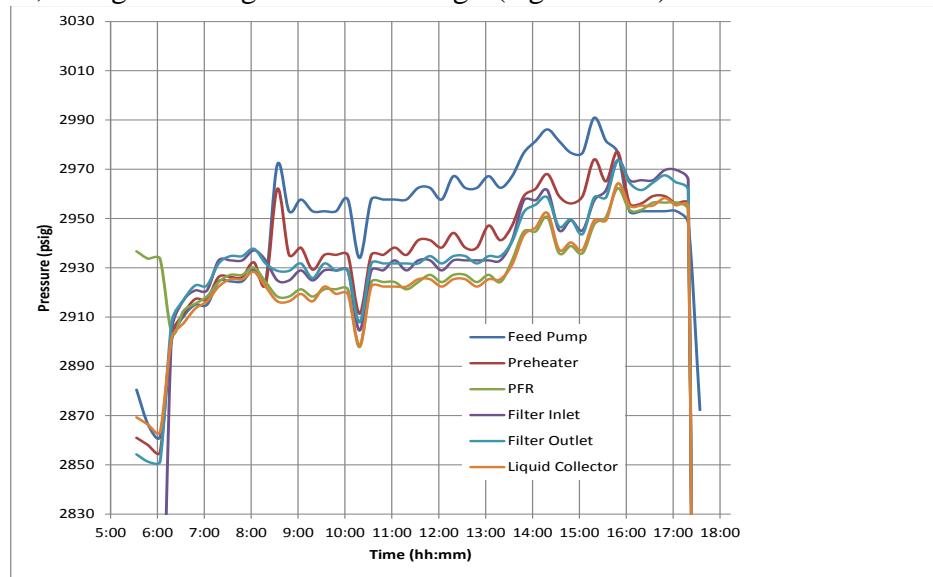


Figure 4-31. System Pressure Data for HTL Test with Primary Sludge (WERF-02).

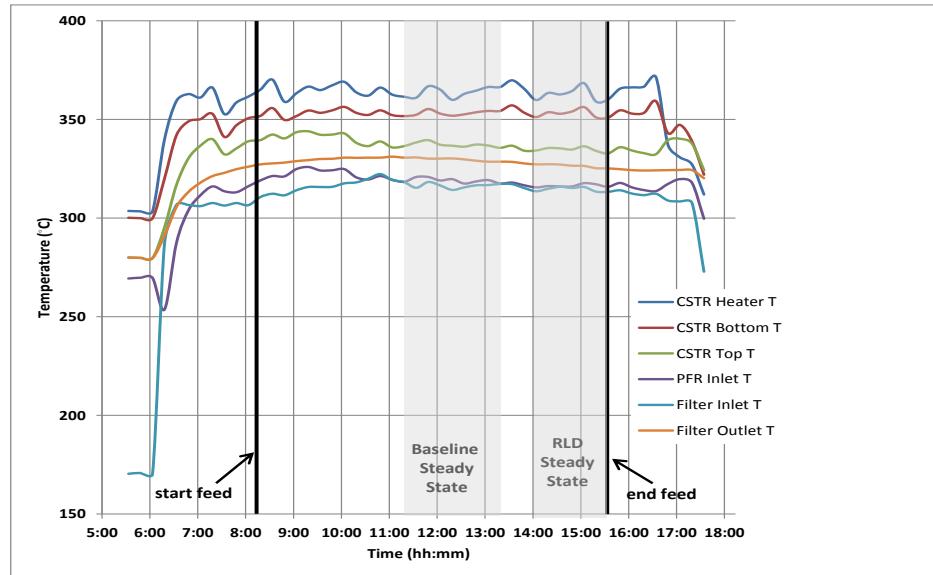


Figure 4-32. Temperature Data for HTL Test with Primary Sludge (WERF-02).

Shaded regions indicate steady state.

A total of three set-asides of liquid effluent at steady state were collected in WERF-02. A separable amount of biocrude was first observed in the liquid set-aside taken about two hours after the start of feed. The first set-aside taken under steady state conditions was taken 3.9 hours after the start of feed. As with the digested solids sludge feed, some of the oil phase floated at the top of the sample and some sank to the bottom (Figure 4-33). This made it difficult to cleanly separate all of the oil from the aqueous phase using the standard separatory funnel. The last set-aside was transferred to a jar and allowed to cool overnight in a refrigerator before phase separation was performed, which was more efficient (Figures 4-34, 4-35, and 4-36). Subsequent operation in RLD mode for 1.5 hours after returning to steady state (which took about 40 minutes after changing modes) was allowed for sufficient online gas sample collection and analysis before switching back to water feed to end the test. A gas sample for siloxane analysis was also taken during a one hour period in RLD steady state.



Figure 4-33. Steady State Liquid Effluent from the HTL Test with Primary Sludge Feed (WERF-02).



Figure 4-34. Biocrude from the Three Steady State Set-asides (3 Jars on Right) and a Combination of the Three Set-asides Taken Prior to Steady State (Far-Left Jar) from the HTL Test with Primary Sludge Feed (WERF-02).



Figure 4-35. Biocrude from the HTL Test with Primary Sludge Feed (WERF-02).

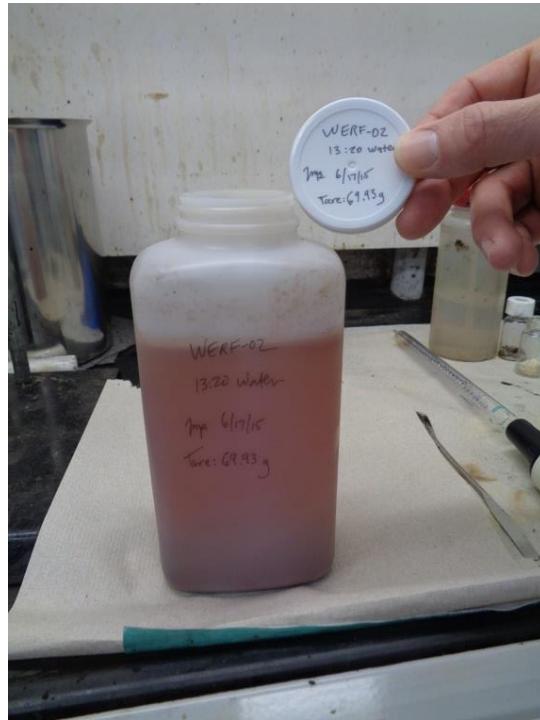


Figure 4-36. Aqueous Phase Product from Last Steady State Set-Aside Taken During the HTL Test with Primary Sludge Feed (WERF-02).

During system inspection after the test, the filter vessel was about half full with wet solids (Figures 4-37, 4-38, and 4-39). The rest of the system was noted as being relatively clean with no flow restrictions. It was also noted that there were not a lot of inorganic solids (or ash) generated in this test. It is not clear whether any odors were detected during the inspection.



Figure 4-37. Solids in Opened Filter Vessel After the HTL Test with Primary Sludge Feed (WERF-02).



Figure 4-38. Filter Element After the HTL Test with Primary Sludge Feed (WERF-02).



Figure 4-39. Solids Collected from the Filter Vessel After the HTL Test with Primary Sludge Feed (WERF-02).

The corresponding CHG test (WERF2-CHG) was not performed until almost two months after the HTL test due to PNNL staff and equipment constraints. As with the aqueous product from digested solids HTL tests, high sulfate concentrations (60 ppm) determined by IC analysis required processing this material through an ion exchange column. Subsequent re-analysis of the resulting solution indicated acceptable sulfate levels for running through CHG. Heat-up of the CHG system began with water on August 9, 2015 and continued overnight. All non-steady state aqueous phase samples from the HTL test (WERF-02) were combined to make one CHG feed (Feed 1) used to bring the system to steady state. The aqueous phases from the three steady state HTL set-asides were combined to create a second feed (Feed 2), which would be used as the official CHG test feed once steady state was reached.

The switch from water to Feed 1 took place early the next morning. Operation on Feed 1 continued all day. Early the next day, a leak was noticed at the feed pump and flow was stopped to rebuild the pump heads. The system remained hot and at pressure under static conditions until flow was resumed about 1.2 hours later. The system ran throughout the day, but shut down unexpectedly overnight. The BPR was cleaned early the next morning (August 12) and the system was restarted. About 3.5 hours later, the system had reached its thermal setpoint again and the switch to Feed 2 was made. Not long after, the BPR plugged and shut the system down. PNNL staff cleaned out the BPR again and installed a new diaphragm. Shortly after restarting, the same occurrence happened again. At this point, the BPR was replaced and the system restarted, but the main heater had inadvertently been tripped during the previous shutdown. As a result, the system temperature dropped to about 220°C (the preheater was still functioning) and remained at this temperature overnight. The problem was noticed and the main heater restarted the next morning (August 13). It is not clear why the BPR experienced plugging problems, but no further problems occurred with the BPR once it was replaced.

With the system back at its proper thermal setpoint after a few hours, steady state was declared and sample collection began. The system operated normally with no further upsets during the steady state period and for the rest of the test. System temperatures and pressures were stable and consistent throughout the steady state period (Figures 4-40 and 4-41). A total of seven liquid samples were taken during the remainder of the day and into the next morning (Figure 4-42). Only four of the corresponding gas samples were valid due to a computer software problem with the GC analyzer when the first two samples were taken and low GC carrier gas flow during the last sample. After the last samples were taken the following morning (August 14), a gas sample for siloxane analysis was taken over a four hour period. Once the SUMMA® canister was filled, the system was allowed to run for a few more hours to use up the remaining amount of Feed 2 before the system was switched back to water feed and shutdown.

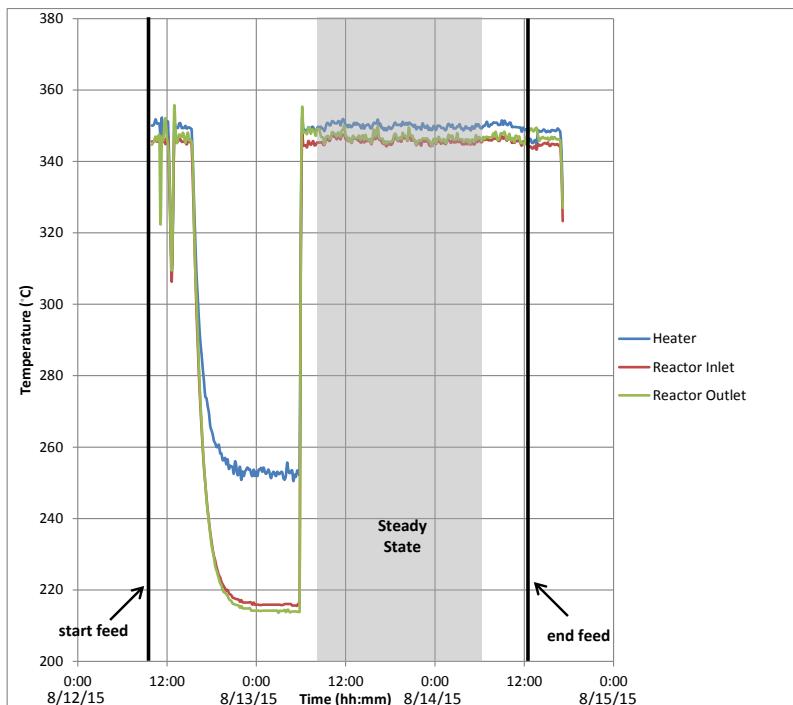


Figure 4-40. Temperature Data for CHG Test with HTL Aqueous Phase from Primary Sludge (WERF2-CHG).
Shaded regions indicate steady state.

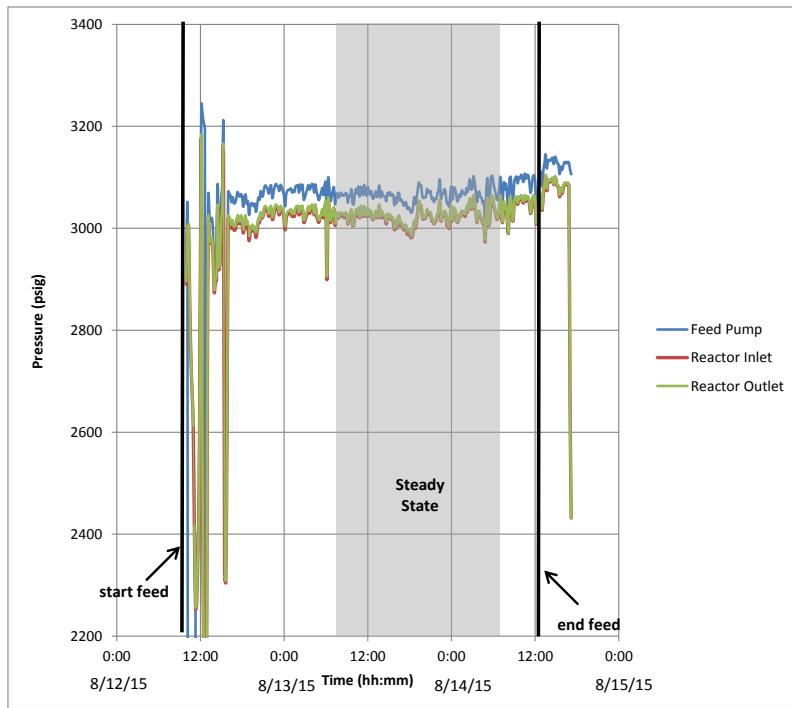


Figure 4-41. System Pressure Data for CHG Test with HTL Aqueous Phase from Primary Sludge (WERF2-CHG).
Shaded regions indicate steady state.



Figure 4-42. Post-IX Feed (far left) and Effluent Samples from WERF2-CHG.

4.4.3 Secondary Sludge

The HTL test with secondary sludge (WERF-03) was performed with the homogenized feed that was prepared at PNNL on the previous day. As with the other HTL tests, system heat-up with water began on June 24, 2015 with the switch to sludge feed occurring early the next day. While the test lasted its full intended duration and all planned samples were collected, it did not proceed as smoothly as those with primary sludge and digested solids, as described below.

Shortly after switching from water flow to sludge feed, the first of several sudden drops in pressure occurred in the liquid collector vessels (Figure 4-43). The pressure drops ranged from as low as 40 psig to as high as about 250 psig, and typically occurred around the time when flow was switched from one collection vessel to the other. PNNL staff speculated that one of the valves to the collection vessels might be leaking but did not believe this was serious enough to stop the run. All but one of the pressure drops occurred prior to reaching the first steady state (in Baseline mode). At this point, a new pressure-related trend was noticed. About four hours after switching to sludge feed, the system pressure began to rise. The pressure increase was significantly greater upstream of the CSTR and PFR. The pressure increase continued steadily throughout the rest of the test, reaching a maximum of about 3040 psig (140 psig above the nominal 2900 psig set point) shortly after the switch from sludge feed back to water. After this, the pressure began to decrease back toward its normal setpoint until shutdown.

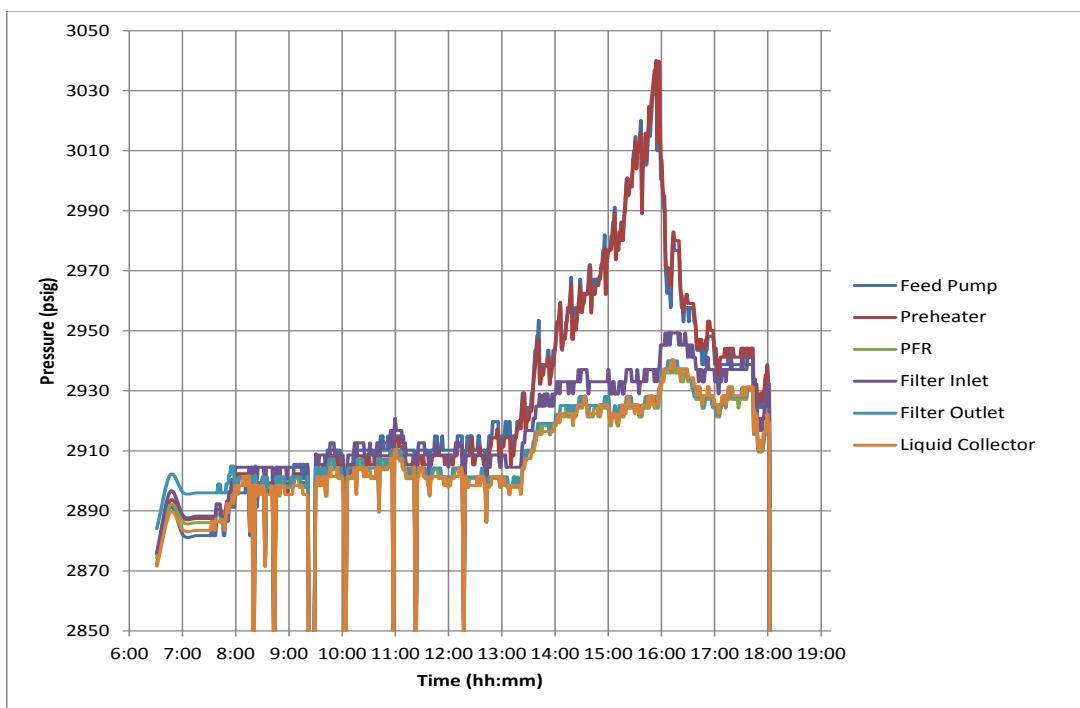


Figure 4-43. System Pressure Data for HTL Test with Secondary Sludge (WERF-03).

About 30 minutes after the switch to sludge feed, it was noticed that both the CSTR top and PFR inlet temperature readings started to decrease (Figure 4-44). By the time the first steady state was reached, the two temperatures had steadied at values of about 290°C and 280°C, respectively. These temperatures were well below normal behavior based on previous tests. The temperature at the bottom of the CSTR (where feed enters the reactor) was roughly steady at its typical value of about 358°C, but during this test was unusually higher than the temperature of

the external heater element (measured between the CSTR wall and heater element). Thus there was a difference of about 70-80°C between the measured temperatures at the bottom and top of the CSTR and inlet to the adjacent PFR.

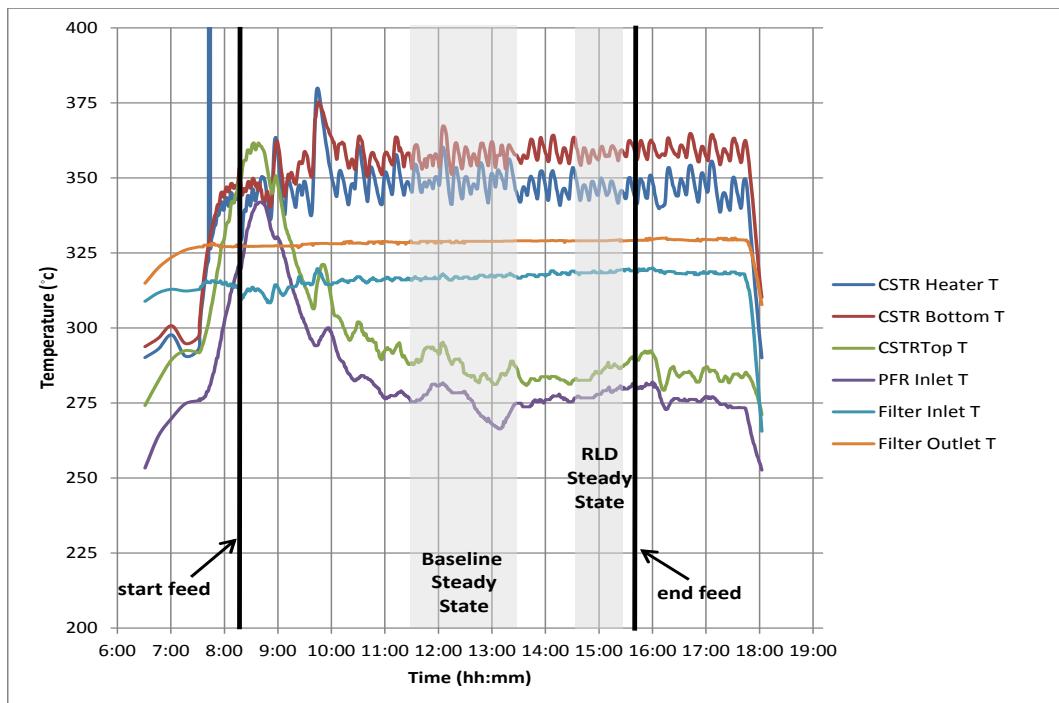


Figure 4-44. Temperature Data for HTL Test with Secondary Sludge (WERF-03). Shaded regions indicate steady state.

A total of three set-asides of liquid effluent at steady state were collected in WERF-03. Evidence of an organic phase was first observed in the liquid set-aside taken about 1.8 hours after the start of feed. The organic phase observed in the first few set-asides prior to steady state, was small in quantity, but appeared to be a distinct and separable oil as seen with the primary sludge and digested solids feeds. By the time steady state was achieved, however, the appearance of the organic phase had changed dramatically. The first set-aside under steady state conditions was taken 3.8 hours after the start of feed. No easily separable organic phase was observed in the liquid effluent. Instead, a significant amount of what appeared to be fluffy solid-like material was seen mostly floating at the top but also extending well below the liquid surface when collected liquid effluent was placed in a separatory funnel (Figure 4-45). The distribution of these solids was such that there was no way to cleanly separate them from the background aqueous phase in the separatory funnel in initial attempts made during the ongoing test (Figure 4-46). PNNL staff speculated that the solids could be an organic phase consisting of a high concentration of polymerizing fatty acids to explain the observed appearance and behavior. Cases of inseparable oil have been seen by PNNL staff in the past with other biomass feeds, but only rarely.



Figure 4-45. Close-Up View of Organic Solids That Formed in the Liquid Product from the HTL Test with Secondary Sludge Feed (WERF-03).



Figure 4-46. Unsuccessful Attempt to Separate the Organic and Aqueous Product Phases During the HTL Test with Secondary Sludge Feed (WERF-03).

The steady state set-asides were placed in jars and stored in the refrigerator. Based on initial observations, PNNL staff thought that a separable oil phase could not be produced and only sent one combined phase liquid sample out for analysis just to see if any information could be salvaged/learned. When inspected the next day, the solid material in the jars had clumped together and sunk to the bottom, allowing some hope of separation. During later analysis, the solids from one steady state set-aside were collected and processed by centrifugation three times with aqueous rinses in between (Figure 4-47). Though the aqueous portion was sacrificed in the process, PNNL staff were able to ultimately concentrate the solids into a liquid oil product. This oil product appeared to be more viscous and physically different from the oils derived from the other sludge feeds. The weight percent of this organic phase out of the total liquid product was assumed to be representative of oil quantities in the other two steady state set-asides and was

used to calculate the oil in these other two set-asides. Because it was unclear how much water was contained in the oil phase, PNNL staff decided to dry the oil by heating it to 103°C. After drying, the oil became more tar-like (probably due to polymerization and the evaporation of some volatiles that had occurred at the drying temperature), which prevented some analyses from being performed.



Figure 4-47. Separated Biocrude from the HTL Test with Secondary Sludge Feed (WERF-03) After Centrifuging.

Another unusual observation during this test was a relatively low gas rate and slow decrease in residual nitrogen in the gas effluent once all liquid samples were taken and the switch was made to RLD mode. While the return to steady state conditions (as indicated by the drop in N₂ concentration to zero in the gas effluent) can be as quick as 20 minutes after the switch to RLD mode, a low but notable concentration of N₂ was still observed after 1.2 hours after the switch. Despite this fact, PNNL staff declared steady state at this point and ran for one hour until enough effluent gas data had been gathered and feed was switched back to water. It is unclear why the decrease in N₂ concentration was slower than usual in this test.

The day after the test, the system was opened and partially disassembled for inspection. Significant amounts of separable oil were discovered in the two float traps that normally collect liquid effluent during RLD mode (Figure 4-48). It is unclear whether some of this oil may have accumulated from overflow of the liquid collector vessels due to a possible emulsion formation during Baseline mode. Because of this uncertainty, the mass of trap oil was not included as part of the official oil yields calculated for this test. With respect to chemical composition, however, the trap oil should be the same as that collected in the set-asides during Baseline mode. Because the drying of the centrifuged oil from the steady state set-aside had altered this sample, some chemical analyses for the oil or biocrude phase in this test were performed on the trap oil instead. The source material (i.e., centrifuged set-aside or trap oil) for each organic phase analysis in this test is specified with the analytical results in Chapter 5.0.

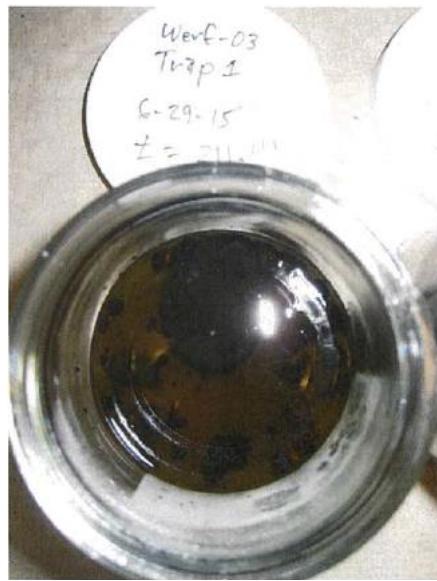


Figure 4-48. Liquid Product Collected from Trap 1 at the End of the HTL Test with Secondary Sludge Feed (WERF -03).

During the post-test inspection, the filter element and vessel were found to be relatively clean of solids. However, the CSTR was found to be packed with solid material when opened (Figure 4-49). A small amount of oil was also observed in the vessel. It was discovered that the impeller was detached from the stirring rod, indicating that there was no mixing in the CSTR during some or all of the test. It is suspected that the problem was caused primarily by use of a reactor configuration that was not effective for the level of inorganic solids (typically salts) or ash contained in the secondary sludge feed. Any inorganic salts present in the feed will precipitate upon reaching reaction conditions in the CSTR (see Section 6.4.3). The higher ash content of the secondary sludge feed relative to the previously tested primary sludge feed indicates a higher inorganic solids content. It is thought that the higher solids accumulation led to increased torque, which in turn led to pressure on the set screw/sheer pin (that holds the impeller to the stirring rod shaft) until it gave way, allowing the impeller to spin free.



Figure 4-49. Solids Found Inside the CSTR After the HTL Test with Secondary Sludge Feed (WERF -03).

Based on the amount of solid material seen in the CSTR, it was thought that mixing probably stopped early in the test. This is consistent with the temperature data, which shows the CSTR top and PFR inlet temperatures starting to uncharacteristically drop shortly after the start of feed (Figure 4-44). The temperature drop might be explained by an accumulation of solid particles around the thermocouple or thermowell due to the lack of mixing. The solids can act as an insulator, thus indicating a false decrease in temperature. Nevertheless, a perceived drop in temperature would call for more heat to the reactor, which might also explain why the CSTR bottom temperature (where feed enters) was higher than expected.

The CSTR solids were collected for analysis. The presence of these solids and the possible interference with HTL feed conversion and temperature measurement is the reason that the spacer insert in the CSTR was removed for the subsequent WERF-04 test to provide more reactor volume availability to accommodate this higher ash content feed. In addition, a solid strand or “snake” of material several inches long was removed from the entrance to the PFR (Figure 4-50). Though the material had a rubber-like or gasket material appearance, it was determined to be feed-derived. This material was also taken for analysis.



Figure 4-50. Solid Material Removed from the Entrance to the PFR After the HTL Test with Secondary Sludge Feed (WERF-03).

The corresponding CHG test (WERF3-CHG) was performed one week after WERF2-CHG. As with all HTL aqueous phase feeds in this test program, ion exchange was again required for removal of high sulfate concentrations (161 ppm). Subsequent analysis confirmed an acceptable sulfate concentration.

Heat-up of the CHG system began with water on August 17, 2015 and continued overnight. As was the case in WERF2-CHG, all non-steady state aqueous phase samples from the HTL test (WERF-03) were combined to make one CHG feed (Feed 1) used to bring the system to steady state. The aqueous phases from the three steady state HTL set-asides were combined to create a second feed (Feed 2), which was used as the official CHG test feed once steady state was reached. The switch from water to Feed 1 took place early the next morning

(August 18). Operation on Feed 1 continued all day. Early the next morning (August 19), problems with the BPR were experienced similar to that which occurred in the previous test (WERF2-CHG). The BPR was replaced with a different model at this time and the test was resumed. No further problems with the new BPR were experienced during the remainder of the test. The switch to Feed 2 occurred early that afternoon and steady state on Feed 2 was declared 1.25 hours later.

Steady state operation was maintained for almost 36 hours, from the afternoon of August 19 through the early morning of August 21, which was notably longer than the other CHG tests. System temperatures and pressures were stable throughout the steady state period. A roughly 10°C difference consistently occurred across the reactor length, with a slight overall temperature rise over the test period (Figure 4-51). All system pressure readings were very close to each other and steady, but with occasional brief decreases (Figure 4-52). A total of nine gas and liquid effluent samples were taken during the steady state period (Figure 4-53). After the last samples were taken, a gas sample for siloxane analysis was taken over a period of 3.75 hours. Once the SUMMA® canister was filled, the system was allowed to run for about an hour more to use up the remaining amount of Feed 2 before the system was switched back to water feed and shutdown.

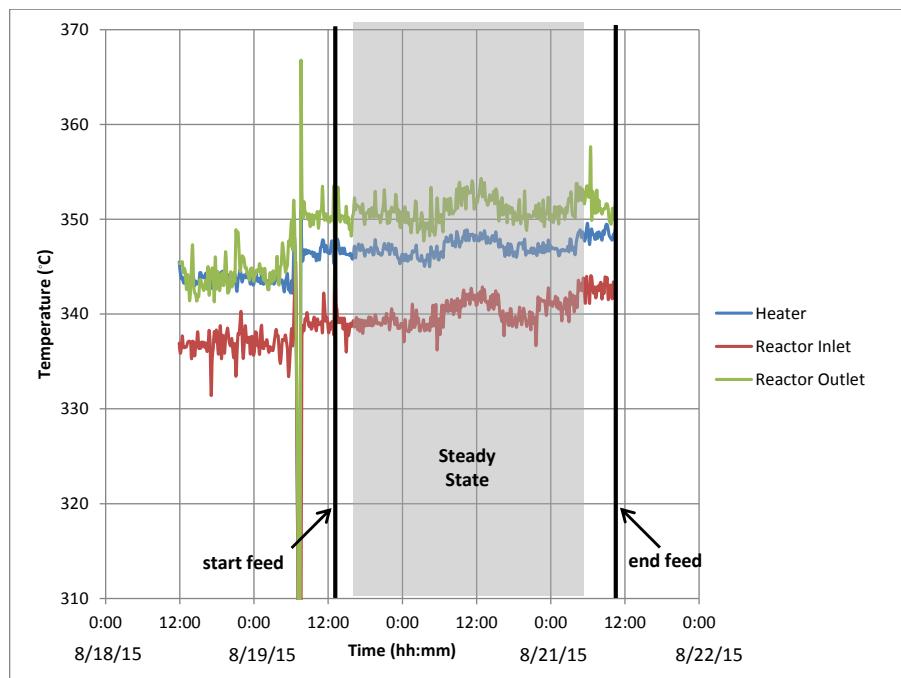


Figure 4-51. Temperature Data for CHG Test with HTL Aqueous Phase from Secondary Sludge (WERF3-CHG).
Shaded regions indicate steady state.

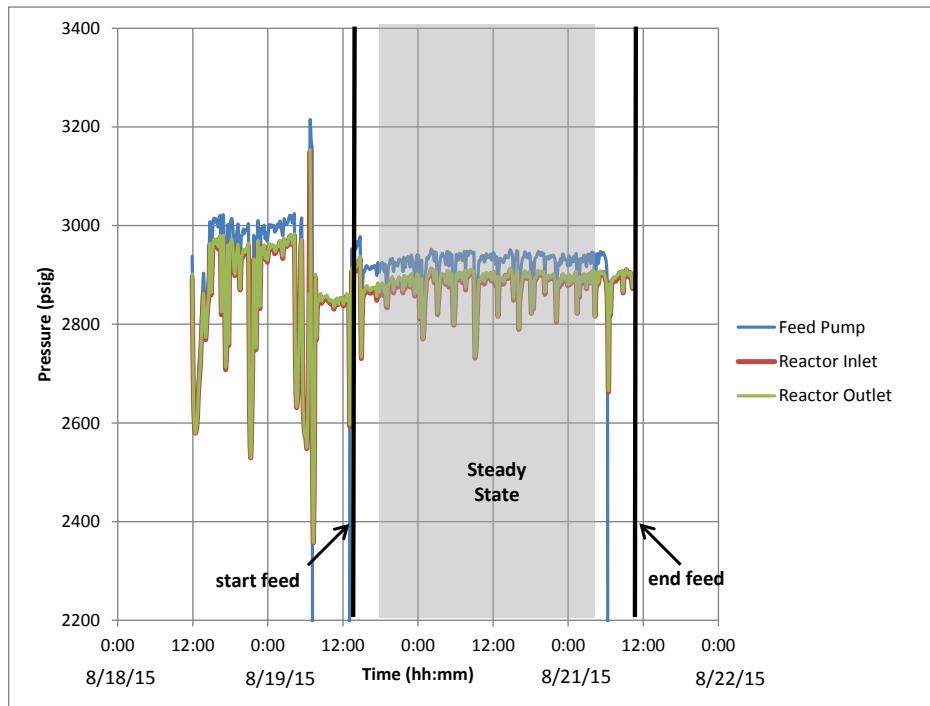


Figure 4-52. System Pressure Data for CHG Test with HTL Aqueous Phase from Secondary Sludge (WERF3-CHG).
Shaded regions indicate steady state.



Figure 4-53. Post-IX Feed (two on far left) and Effluent Samples from WERF3-CHG.

4.5 Process Monitoring Data

Tables 4-6 and 4-7 contain a compilation of Process Monitoring data collected during all HTL and CHG tests, respectively. For each variable, the average or most representative steady state value is shown. In some cases (e.g., duration, feed volume pumped, and generation rate of solids), the value provided is the total for the full time operating on feed.

Table 4-6. HTL Process Monitoring Data^a.

Data	Period ^b	Test (Feed)		
		WERF-02 (Primary sludge)	WERF-03 (Secondary sludge)	WERF-04 (Digested solids)
Test duration (hr)	Total feed SS - B SS - BR	7.42 2.00 3.50	7.53 2.00 3.00	7.17 2.67 4.18
Total feed volume pumped (L)	Total feed SS - B SS- BR	11.10 2.98 5.21	11.22 3.00 4.50	10.72 4.00 6.21
Sludge feed rate (L/hr)	SS - BR	1.49	1.50	1.50
Sludge feed tank temperature (°C)	SS - BR	Ambient ^c	Ambient ^c	Ambient ^c
Sludge feed pressure (psig)	SS - BR	2971	2933	2965
Preheater inlet temperature (°C)	SS - BR	Ambient ^c	Ambient ^c	Ambient ^c
Preheater outlet temperature (°C)	SS - BR	129	138	129
Preheater oil temperature (°C)	SS - BR	130-140	140	130-140
Preheater outlet pressure (psig)	SS - BR	2951	2931	2905
CSTR heater temperature (°C)	SS - BR	363	348	371
CSTR temperature – top of reactor (°C)	SS - BR	336	287	352
CSTR temperature – bottom of reactor (°C)	SS - BR	353	358	358
PFR inlet temperature (°C)	SS - BR	318	276	332
PFR outlet temperature (°C)	SS - BR	341 ^d	344 ^d	343
PFR oil temperature (°C)	SS - BR	298	298	295
PFR inlet pressure (psig)	SS - BR	2933	2907	2890
Solids filter inlet temperature (°C)	SS - BR	316	317	304
Solids filter inlet pressure (psig)	SS - BR	2942	2915	2885
Solids filter outlet temperature (°C)	SS - BR	328	329	328
Solids filter outlet pressure (psig)	SS - BR	2942	2908	2888
Mass of solids collected (g)	Total feed	129.3	224.6	637.4
Heat exchanger outlet temperature (°C)	SS - BR	34.8	32.1	33.3
Liquid effluent temperature (°C)	SS - B	48.9	44.2	48.8
Liquid effluent collection pressure (psig)	SS - B	2924	2899	2892
Liquid phase organic product (biocrude) total mass (g)	SS - B	147	67	206
Liquid phase organic product (biocrude) mass flow rate (g/hr)	SS - B	73.4	33.5	77.3
Liquid phase aqueous product total mass (g)	SS - B	2854	2946	3955
Liquid phase aqueous product mass flow rate (g/hr)	SS - B	1424	1471	1478
Liquid effluent organic phase (biocrude) description	SS - B	Black color that floats and sinks; no emulsion	Dark, clumpy, floating solids; difficult to separate from aqueous phase	Black color that floats and sinks; no emulsion
Liquid effluent aqueous phase description	SS - B	Orange-brown color	Orange-brown color	Orange-brown color
Gas effluent temperature (°C)	SS - BR	26.0	27.4	31.2
Total effluent gas volume (L)	SS - R	31.2	7.5	16.2

^a Average or representative values during the period indicated.^b Total feed: corresponds to all operation while processing sludge feed; SS-B: corresponds to Steady State operation in Baseline mode (liquid sample collection) only; SS-R: corresponds to Steady State operation in RLD mode (gas sample collection) only; SS-BR: corresponds to Steady State operation in Baseline and RLD modes.^c Not measured.^d Approximated as external wall temperature measured at the last U-bend in the tubing near the end of the PFR.

Table 4-7. CHG Process Monitoring Data.

Data	Test (Feed)		
	WERF2-CHG (WERF-02 Aqueous Phase)	WERF3-CHG (WERF-03 Aqueous Phase)	WERF4-CHG (WERF-04 Aqueous Phase)
Test duration (hr): Total Feed	49.3	45.4	31.4
Total Steady State	20.6	35.9	25.4
Total feed volume pumped (L): Total Feed	1.95	1.98	1.29
Total Steady State	0.81	1.53	1.04
Feed rate (ml/hr)	39.7	43.8	41.2
Feed temperature (°C)	22.6	22.4	24.4
Feed pressure (psi)	3065	2923	2969
Reactor band heater temperature (°C)	350	347	348
Reactor bottom (inlet) temperature (°C)	346	340	342
Reactor top (outlet) temperature (°C)	347	351	354
Reactor inlet pressure (psig)	3021	2881	2963
Reactor outlet pressure (psig)	3024	2885	2965
Reactor IP (psig)	3	4	2
Initial catalyst (Ru/C) weight (g)	10.71	11.82	11.65
Initial Raney Ni (reduced sulfur removal) (g) ^a	8.05	8.19	8.98
Effluent temperature after heat exchanger (°C)	21.0	21.0	23.2
Liquid effluent mass (over steady state period) (g)	755	1487	915
Liquid effluent temperature (°C)	20.8	20.6	22.5
Liquid effluent pressure (psig)	N/A	N/A	0.3
Liquid effluent description	Clear, colorless	Clear, colorless	Clear, colorless
Total gas effluent volume (L)	4.2	13.9	11.5
Gas effluent temperature (°C)	20.7	20.5	22.4
Final catalyst weight (g)	10.07	Not measured	Not measured
Final Raney Ni weight (g)	6.29	Not measured	Not measured
Mass of solids collected in precipitator (g)	0 (no solids observed)	0 (no solids observed)	0 (no solids observed)

^a Pyrophoric material stored in water; mass determined by difference in mass of storage container before and after loading reactor.

CHAPTER 5.0

SAMPLING AND ANALYTICAL RESULTS

5.1 HTL Sampling Strategy and Procedures

A block flow diagram of the bench-scale process as utilized for these tests is shown in Figure 5-1 with numbered sampling locations. The analyses that were planned to be performed and the sampling frequency for each sample location are shown in Table 5-1. Deviations to Table 5-1 are discussed in Sections 5.3.1 to 5.3.5. Detailed information regarding each measurement method is provided in Section 5.4. Note that no analytical data from the first HTL and CHG tests with digested solids (WERF-01 and WERF1-CHG) are included in this section (see Section 4.4.1). These tests were repeated as WERF-04 and WERF4-CHG. The one exception is for siloxane analysis of the CHG product gas phase, where the allocated sample for digested solids was taken during WERF1-CHG.

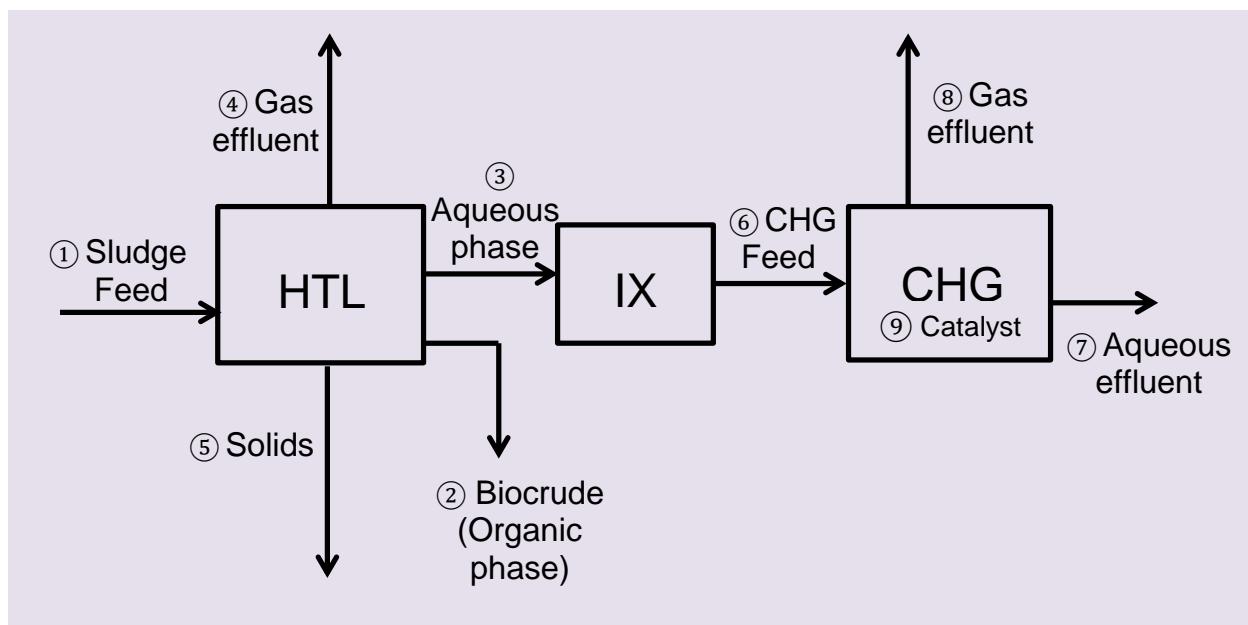


Figure 5-1. Block Flow Diagram of Bench-Scale HTL-CHG Process Used at PNNL.

Table 5-1. HTL Sampling Strategy.

Measurement	Planned Number of Samples Taken Per Test ^a				
	HTL Sludge Feed (#1)	HTL Biocrude (#2)	HTL Aqueous Phase Product (#3)	HTL Solid Phase Product (#4)	HTL Gas Product (#5)
Ammonia	–	–	3	–	1
Anions	–	–	3	–	–
Ash	2	3	–	1	–
COD	2	–	3	–	–
Density	2	3	–	–	–
Dissolved Organics	–	–	3	–	–
Dry Solid Content	2	–	–	–	–
Elemental (CHNOS) Analysis	1	3	–	1	–
Elemental (CHN) Analysis	–	–	3	–	–
Filtered Oil Solids	–	3	–	–	–
Hydrogen Sulfide	–	–	–	–	1
Light hydrocarbons and permanent gases	–	–	–	–	1
Metals	1	3	3	1	–
Moisture	–	3	–	–	–
pH	2	–	3	–	–
Product Weight	–	–	–	1	–
Siloxanes	–	–	–	–	1
TAN	–	3	–	–	–
TOC	1	–	3	1	–
Kinematic Viscosity	–	3	–	–	–

^a Numbers in individual headings below represent locations indicated in Figure 5-1

5.2 CHG Sampling Strategy

Representative samples were planned to be collected from the CHG sample locations as listed in Table 5-2. The analyses that were performed and the sampling frequency for each sample location are also listed. The number of ammonia, COD, pH, and gas samples collected was dependent on the length of the CHG run. Therefore, the minimum number of samples collected is provided in the table. Deviations to Table 5-2 are discussed in Sections 5.3.6 to 5.3.9. Detailed information regarding each measurement method is provided in Section 5.4.

Table 5-2. CHG Sampling Strategy.

Measurement	Planned Number of Samples Taken Per Test ^a					
	CHG Feed		CHG Aqueous Phase Product (#7)	CHG Gas Product (#8)	CHG Sulfur Removal (#9)	CHG Catalyst (#9)
	Pre IX ^b (#3)	Post IX ^b (#6)				
Ammonia	–	–	5	1	–	–
Anions	–	1	3	–	–	–
COD	1	1	5	–	–	–
Dissolved Organics	1	1	3	–	–	–
Elemental (CHN) Analysis	1	1	3	–	–	–
Light hydrocarbons and permanent gases	–	–	–	4	–	–
Metals	–	1	1	–	1	1
pH	–	–	1	–	–	–
Siloxanes	–	–	–	1	–	–
TOC	1	1	1	–	–	–

^a Numbers in individual headings below represent locations indicated in Figure 5-1^b IX = ion exchange

5.3 Analytical Data

This section presents a summary of the data for the samples that were collected during the HTL and CHG tests. Complete data sets are shown in Appendix A for the Primary Sludge tests (WERF-02 and WERF2-CHG), Appendix B for the Secondary Sludge tests (WERF-03 and WERF3-CHG), and Appendix C for the Digested Solids tests (WERF-04 and WERF4-CHG). Note that only data with positive results (concentrations above the detection limit) are shown in this section. Results which did not yield a positive concentration are provided in the complete data sets in the Appendices with specific detection limits.

5.3.1 HTL Feedstock Characterization

Sludge feedstock samples were analyzed for ash, chemical oxygen demand (COD), density, dry solid content, the elements carbon, hydrogen, nitrogen, oxygen and sulfur (CHNOS), metals, pH and total organic carbon (TOC). Separate beginning of run (BOR) and end of run (EOR) samples were analyzed for ash, COD, density, dry solid content, and pH. The exception to this was the density measurement for WERF-02 (primary sludge feed) that was performed on the EOR sample due to an excess of gas bubbles in the BOR sample. The average result for the BOR and EOR samples is presented in Table 5-3. The remaining analyses were performed on a composite of the BOR and EOR feedstock matrices.

Table 5-3. HTL Sludge Feedstock Characterization.

Measurement	Units	Primary Sludge (WERF-02)	Secondary Sludge (WERF-03)	Digested Solids (WERF-04)
Ash	wt% dry	7.5	16.2	28.1
COD	mg O ₂ /L	187,000	153,000	203,000
Density	g/mL @ 20°C	1.04	0.998	1.05
Dry Solid Content	wt%	11.9	9.71	16.0
Elemental Analysis				
Carbon	wt% dry	47.8	43.6	38.7
Hydrogen	wt% dry	6.50	6.55	5.68
Nitrogen	wt% dry	3.64	7.90	4.48
Oxygen	wt% dry	33.6	29.0	27.9
Sulfur	wt% dry	0.48	0.72	1.63
Metals (reported on a dry weight basis)				
Aluminum	ppm (wt/wt)	2,220	3,330	7,850
Barium	ppm (wt/wt)	43.8	170	329
Calcium	ppm (wt/wt)	4,890	9,030	23,400
Chromium	ppm (wt/wt)	82.3	50.0	37.8
Copper	ppm (wt/wt)	246	590	840
Iron	ppm (wt/wt)	6,020	26,200	38,800
Potassium	ppm (wt/wt)	785	4,280	1,770
Magnesium	ppm (wt/wt)	984	2,920	6,600
Manganese	ppm (wt/wt)	53.4	250	373
Sodium	ppm (wt/wt)	424	890	527
Phosphorus	ppm (wt/wt)	6,880	33,300	29,900
Sulfur	ppm (wt/wt)	4,130	6,420	17,600
Silicon	ppm (wt/wt)	190	280	270
Strontium	ppm (wt/wt)	53.7	110	137
Titanium	ppm (wt/wt)	36	94.0	162
Zinc	ppm (wt/wt)	303	530	1,070
Zirconium	ppm (wt/wt)	< 40	51	70
pH		5.09	6.03	7.73
TOC	wt% dry	44.6	40.9	35.3

5.3.2 Biocrude Characterization

Three samples of biocrude oil were collected during the Baseline mode steady state of the HTL process. Biocrude oil samples were analyzed for ash, density, elements CHNOS, filtered oil solids, metals, moisture, total acid number (TAN), and kinematic viscosity. The results shown in Table 5-4 are the average from the results of the 3 samples. There were two types of biocrude oil recovered from the WERF-03 (secondary sludge feed stream) run. Biocrude oil from the 12:40 aqueous set-aside was recovered after centrifugation. Reasonable quantities of phase separable oil were also recovered from Float Trap #2 at the end of the test. While quantities of trap oil could not be used in calculation of yields and mass balances because of uncertainty as to when it accumulated, the trap oil was analyzed because its composition was believed to be representative of the biocrude oil from the aqueous set-asides. Results for both types of biocrude oil are reported in Table 5-4, each from a single analysis. While the elemental analyses of the two biocrude types from WERF-03 are comparable, the metal analyses are not. Based on this data, it is not clear which biocrude type is more representative of what can truly be formed from secondary sludge.

Table 5-4. Biocrude Oil Characterization.

Measurement	Units	Primary Sludge (WERF-02)	Secondary Sludge (WERF-03)		Digested Solids (WERF-04)
			Trap Oil	12:40 Biocrude	
Ash	wt%	0.3	0.46	6.15 ^a	0.19
Density	g/mL @ 20°C	1.000	0.9846	NA ^b	1.013
Elemental Analysis					
Carbon	wt%	66.6	56.6	71.4	67.9
Hydrogen	wt%	10.3	10.7	8.68	9.74
Nitrogen	wt%	3.7	3.55	5.02	3.86
Oxygen	wt%	12.4	11.0	7.32	11.85
Sulfur	wt%	0.55	0.76	0.89	1.00
Filtered Oil Solids	%	0.18	0.25	NA ^b	0.23
Metals					
Aluminum	ppm (wt/wt)	64.9	77.8	107	83.8
Calcium	ppm (wt/wt)	< 30	< 50	57.1	< 25
Iron	ppm (wt/wt)	58.9	79.0	111	225
Phosphorus	ppm (wt/wt)	< 30	73	< 45	< 25
Potassium	ppm (wt/wt)	77.1	134	136	63
Magnesium	ppm (wt/wt)	< 30	29	72.0	< 25
Manganese	ppm (wt/wt)	< 30	29	< 45	< 25
Nickel	ppm (wt/wt)	< 30	23	< 45	< 25
Sodium	ppm (wt/wt)	56.9	62	251	< 25
Sulfur	ppm (wt/wt)	1,900	2,600	8,240	9,770
Silicon	ppm (wt/wt)	55	210	20,900	390
Titanium	ppm (wt/wt)	< 30	< 50	46.7	< 25
Moisture	wt%	13.0	28.6	1.0 ^c	13.5
TAN	mg KOH/g	65.0	38.3	44.8	36.0
Kinematic viscosity	cSt @ 40°C	571	624	NA ^b	1,160

^a The high ash content may be a result of the consolidation of the solids during the centrifugation process to recover the biocrude oil.

^b NA – not analyzed, as specified in the QAPP

^c The biocrude oil recovered from the centrifuged 12:40 set-aside was dried at 103°C prior to analysis, resulting in low moisture content.

5.3.3 HTL Aqueous Product Characterization

Three samples of the aqueous product were collected during the Baseline mode steady state of the HTL process. HTL aqueous product samples were analyzed for ammonia, anions, COD, dissolved organics, elements CHN, metals, pH, and TOC. The results shown in Table 5-5 are the average from the results of the three samples.

Table 5-5. HTL Aqueous Product Characterization.

Measurement	Units	Primary Sludge (WERF-02)	Secondary Sludge (WERF-03)	Digested Solids (WERF-04)
Ammonia as Nitrogen	mg/L	1,330	4,520	4,960
Anions				
Chloride	mg/L	59.7	102	94
Phosphate	mg/L	24.6	714	72
Sulfate	mg/L	60.2	161	200
COD	mg O ₂ /L	41,000	73,000	48,200
Dissolved Organics				
Acetic Acid	wt%	0.35	0.32	0.38
Acetone	wt%	0.13	0.06	0.18
Butanoic Acid	wt%	< 0.03	0.06	< 0.03
2-Butanol	wt%	0.061	< 0.03	< 0.03
Ethanol	wt%	< 0.03	0.03	0.04
Glycerol	wt%	0.050	0.05	0.06
Glycolic Acid	wt%	0.086	< 0.03	< 0.03
p-Cresol	wt%	0.034	0.04	0.08
2-Pentanone	wt%	< 0.03	< 0.03	0.05
Propanoic Acid	wt%	0.12	0.12	0.09
Elemental Analysis				
Carbon	wt%	1.26	2.62	1.88
Hydrogen	wt%	11.0	12.1	11.5
Nitrogen	wt%	0.26	0.72	0.57
Metals				
Aluminum	ppm (wt/vol)	2.65	1.71	< 1.0
Calcium	ppm (wt/vol)	2.81	1.57	< 1.0
Iron	ppm (wt/vol)	1.05	< 1.0	< 1.0
Potassium	ppm (wt/vol)	71.3	275	117
Magnesium	ppm (wt/vol)	3.10	1.29	1.30
Sodium	ppm (wt/vol)	67.1	101	74.7
Phosphorus	ppm (wt/vol)	11.9	290	33.1
Sulfur	ppm (wt/vol)	102	157	280
Silicon	ppm (wt/vol)	260	190	301
Strontium	ppm (wt/vol)	2.50	< 1.0	< 1.0
pH		6.42	8.04	8.01
TOC	mg/L	11,700	23,500	17,000

Due to the organic/aqueous phase separation challenges with the samples collected during the HTL test with secondary sludge (WERF-03) (see Section 4.4.3), the sampling/analysis strategy deviated from the QAPP and from that performed in the other two HTL tests. Of the three steady state set-asides, the first (12:00) was analyzed for ammonia, COD, and pH of the liquid phase only. The second set-aside (12:40) was processed to remove the biocrude phase by centrifugation. Analyses for anions, ammonia, metals, dissolved organics, COD, and pH were performed on the 12:40 aqueous portion, including the aqueous supernatant from the centrifugation of the biocrude oil solids reclamation process. The third set-aside (13:20)

underwent liquid phase analysis only for the full set of planned analyses (ammonia, anions, COD, pH, TOC, elements CHN, metals and dissolved organics). For metals and dissolved organics, data shown in the table is the average of the results from the 12:40 and 13:20 set-aside analyses. It should be noted that two samples were analyzed for ammonia during the WERF-02 run as compared with three samples outlined in the QAPP.

Note that high performance liquid chromatography (HPLC) analysis showed the presence of several organic acid species in the HTL aqueous effluent at low concentrations, despite pH measurements that indicated close to neutral or basic conditions in tests with all three sludge feeds. It is likely that these organic acids formed during analysis when exposed to the acidic HPLC eluent and that they were actually present in the aqueous effluent in their conjugate base forms, since the acidic forms as stated would likely not exist at the pH values indicated in the aqueous effluent.

5.3.4 HTL Solid Product Characterization

The total amount of solid material from the filter and filter housing was measured at the end of the WERF-02 and WERF-04 HTL runs. That mass is reported as product weight in Table 5-6. Aliquots of the solid product were characterized for ash, elements CHNOS, metals, and TOC. As described in Section 4.4.3, the filter and filter housing were relatively clean following the WERF-03 HTL run, but the CSTR contained solid material. This material was analyzed and the results are reported below. An additional solid sample was found at the entrance to the PFR and collected following the WERF-03 run. Results for this “snake” sample are also given in the table below. The dash (–) in the table indicates that the measurement was not done, nor was it planned in the QAPP.

Table 5-6. HTL Solid Product Characterization.

Measurement	Units	Primary Sludge (WERF-02)	Secondary Sludge (WERF-03)		Digested Solids (WERF-04)
			CSTR Solids	“Snake”	
Ash	wt%	64.4	64.5	1.67	73.3
Elemental Analysis					
Carbon	wt%	28.4	26.9	–	20.3
Hydrogen	wt%	2.98	3.22	–	2.54
Nitrogen	wt%	1.77	1.49	–	1.14
Oxygen	wt%	16.2	20.5	–	15.4
Sulfur	wt%	0.46	0.69	–	1.70
Metals					
Aluminum	ppm (wt/wt)	17,500	13,600	540	20,000
Barium	ppm (wt/wt)	579	667	< 50	844
Calcium	ppm (wt/wt)	48,100	46,000	702	66,000
Chromium	ppm (wt/wt)	847	1,070	78	309
Copper	ppm (wt/wt)	2,130	2,510	131	2,340
Iron	ppm (wt/wt)	34,200	34,700	2,680	58,400
Potassium	ppm (wt/wt)	1,700	1,700	158	3,030
Magnesium	ppm (wt/wt)	10,200	12,400	424	18,100
Manganese	ppm (wt/wt)	624	1,060	54	979
Sodium	ppm (wt/wt)	714	528	79.1	793
Nickel	ppm (wt/wt)	749	8,570	183	968
Phosphorus	ppm (wt/wt)	55,400	60,600	2,820	59,200
Sulfur	ppm (wt/wt)	3,870	4,840	2,800	15,900
Silicon	ppm (wt/wt)	80.5	206	246	82.9
Strontium	ppm (wt/wt)	263	380	73.4	375
Titanium	ppm (wt/wt)	< 40	78	74.3	< 25
Zinc	ppm (wt/wt)	3,070	2,950	81	3,500
Zirconium	ppm (wt/wt)	30.0	< 50	< 50	< 25
Product Weight	g	129	225	3.02	637
TOC	wt%	26.6	26.0	–	19.2

5.3.5 HTL Gas Product Characterization

Gas samples were analyzed every four minutes by gas chromatograph with a thermal conductivity detector (GC-TCD). Only gas data during operation in RLD mode after steady state was re-established (i.e., after the levels of nitrogen diminished) were analyzed, corresponding to a period of approximately 1 or 1.5 hours. The concentrations for these data points were averaged and a single value is shown for each analyte in Table 5-7. The data tables in the appendices list the minimum and maximum concentrations, in addition to the average value. Data for ammonia are not reported due to difficulties with the analytical method. Two gas samples were collected in SUMMA® canisters for siloxane analysis, one for the WERF-02 run and the second for the WERF-04 run. Nine siloxane compounds were analyzed, none were detected. The specific analytes are listed in Section 5.4.12 and detection limits are provided in Appendices A, B, and C.

Table 5-7. HTL Gas Product Characterization.

Measurement	Units	Primary Sludge (WERF-02)	Secondary Sludge (WERF-03)	Digested Solids (WERF-04)
Permanent Gases and Light Hydrocarbons				
Isobutane	vol%	< 0.01	0.02	0.06
n-Butane	vol%	0.18	0.31	0.77
1-Butene	vol%	0.11	0.37	0.43
cis-2-Butene	vol%	0.15	0.65	0.28
trans-2-Butene	vol%	< 0.01	< 0.01	0.26
Carbon Dioxide	vol%	95.1	77.9	85.0
Carbon Monoxide	vol%	< 0.01	0.08	< 0.01
Ethane	vol%	0.54	0.52	0.99
Ethylene	vol%	0.12	0.78	0.40
Hydrogen	vol%	0.95	1.49	1.22
Hydrogen Sulfide	vol%	0.33	0.40	1.53
Isopentane	vol%	< 0.01	0.15	0.30
Methane	vol%	1.20	2.50	6.17
Nitrogen	vol%	0.54	8.9	0.82
Oxygen	vol%	< 0.01	0.01	< 0.01
Isopentane	vol%	< 0.01	0.15	0.30
n-Pentane	vol%	0.050	0.06	0.05
2-Methyl-2-butene	vol%	0.052	0.21	0.36
1-Pentene	vol%	0.11	0.33	0.05
cis-2-Pentene	vol%	0.036	0.12	0.08
Propane	vol%	0.42	0.47	1.23

5.3.6 CHG Feed – Pre and Post Ion Exchange

The HTL aqueous phase products from each feed stream were passed through an ion exchange column to reduce the sulfate concentration prior to performing CHG tests. In addition to sulfate analysis, multiple components were measured as shown in Table 5-8. None of these analyses apart from COD were originally planned in the QAPP. The dash (–) in Table 5-6 indicates that the measurement was not done, nor was it planned in the QAPP.

Table 5-8. CHG Feed – Pre and Post Ion Exchange.

Measurement	Units	Primary Sludge HTL Aqueous Product (WERF-02)		Secondary Sludge HTL Aqueous Product (WERF-03)		Digested Solids HTL Aqueous Product (WERF-04)	
		Pre Ion-Exchange	Post Ion-Exchange	Pre Ion-Exchange	Post Ion-Exchange	Pre Ion-Exchange	Post Ion-Exchange
Anions							
Chloride	mg/L	–	< 4.0	–	< 4.0	5.09	< 4.0
Phosphate	mg/L	–	< 4.0	–	4.38	47.1	< 4.0
Sulfate	mg/L	–	< 4.0	–	< 4.0	283	< 4.0
Elemental Analysis							
Carbon	wt%	1.88	0.64	1.92	0.705	1.82	0.94
Hydrogen	wt%	11.1	11.7	11.2	11.6	10.7	11.6
Nitrogen	wt%	<0.05	0.08	< 0.05	0.3	0.58	0.36
COD	mg O ₂ /L	40,800	20,300	72,300	21,700	49,900	23,700
Dissolved Organics							
Acetic Acid	wt%	<0.03	0.35	0.32	0.03	0.37	0.04
Acetone	wt%	0.04	0.13	0.06	0.04	0.16	0.14
Butanoic Acid	wt%	<0.03	<0.03	0.06	<0.03	<0.03	<0.03
2-Butanol	wt%	<0.03	0.06	<0.03	<0.03	<0.03	<0.03
p-Cresol	wt%	0.03	0.03	0.04	<0.03	0.08	0.07
Ethanol	wt%	<0.03	<0.03	<0.03	0.04	0.10	0.10
Glycerol	wt%	0.05	0.05	0.05	0.04	0.05	0.05
Glycolic acid	wt%	<0.03	0.09	<0.03	<0.03	<0.03	<0.03
Methanol	wt%	0.05	<0.03	<0.03	0.21	0.28	0.18
Propanoic Acid	wt%	<0.03	0.12	0.12	<0.03	0.09	<0.03
Metals							
Aluminum	ppm (wt/vol)	–	2.58	–	< 1.0	< 1.0	< 1.0
Phosphorus	ppm (wt/vol)	–	< 1.0	–	2.21	33.8	< 1.0
Potassium	ppm (wt/vol)	–	91.7	–	328	136	141
Magnesium	ppm (wt/vol)	–	2.46	–	< 1.0	< 1.0	< 1.0
Silicon	ppm (wt/vol)	–	7.9	–	40	270	139
Sodium	ppm (wt/vol)	–	80.2	–	84.3	79.4	104
Sulfur	ppm (wt/vol)	–	21.7	–	46.0	187	36.6
pH		6.44	9.25	8.05	9.35	8.01	9.15
TOC	mg/L	17,100	5,470	–	6,320	15,100	8,680

5.3.7 CHG Aqueous Product Characterization

Multiple samples of the aqueous product were collected during the steady state of the CHG process for analysis of ammonia, pH, and COD. Specifically, seven aqueous product samples were collected during the WERF2-CHG run (six for ammonia), nine during the WERF3-CHG run, and five during the WERF4-CHG run. Three CHG aqueous product samples were analyzed for anions, dissolved organics, elements CHN, metals, and TOC. The exception was the CHG run using the WERF-02 aqueous product feed in which only two samples were analyzed for elements CHN and TOC. The results shown in Table 5-9 are the average from the results of all samples analyzed. There were no results above the detection limit of 0.03 wt% for the dissolved organics method, and therefore they are excluded from the Table 5-6. The dissolved organics method compounds of interest are provided in Section 5.4.5.

Table 5-9. CHG Aqueous Product Characterization.

Measurement	Units	Primary Sludge (WERF2- CHG)	Secondary Sludge (WERF3- CHG)	Digested Solids (WERF4- CHG)
Ammonia as Nitrogen	mg/L	2,080	5,520	5,430
Anions				
Chloride	mg/L	< 4.0	< 4.0	< 4.0
Phosphate	mg/L	< 4.0	< 4.0	< 4.0
Sulfate	mg/L	5.80	< 4.0	< 4.0
COD	mg O ₂ /L	54	25	19
Elemental Analysis				
Carbon	wt%	0.16	0.28	0.32
Hydrogen	wt%	11.2	11.3	11.6
Nitrogen	wt%	0.11	0.36	0.35
Metals				
Aluminum	ppm (wt/vol)	< 1.0	2.8	< 1.0
Magnesium	ppm (wt/vol)	< 1.0	< 1.0	< 1.0
Phosphorus	ppm (wt/vol)	< 1.0	< 1.0	< 1.0
Potassium	ppm (wt/vol)	72	325	133
Silicon	ppm (wt/vol)	24	17	53
Sodium	ppm (wt/vol)	82	84.9	86.2
Sulfur	ppm (wt/vol)	2.67	< 1.0	< 1.0
pH		9.30	9.35	9.13
TOC	mg/L	530	971	1,130

5.3.8 CHG Gas Product Characterization

The CHG gas samples were analyzed manually during steady state, removing the effluent gas with a gas-tight syringe and injecting it into a GC-TCD within minutes of the collection of the corresponding aqueous set-asides. Four gas samples were analyzed during the WERF2-CHG run, nine during the WERF3-CHG run, and five during the WERF4-CHG run. All data resulting from the injections from the CHG process are averaged and presented in Table 5-10. One gas sample was collected in a SUMMA® canister for siloxane analysis during each CHG run. The siloxane data reported for the WERF4-CHG process was collected during the WERF1-CHG run (refer to Section 6.4.2). Nine compounds were analyzed and only trimethylsilanol was detected in one CHG test (WERF1-CHG). The additional analytes in the siloxane method are listed in Section 5.4.12, with detection limits given in Appendices A, B, and C.

Table 5-10. CHG Gas Product Characterization.

Measurement	Units	Primary Sludge (WERF2-CHG)	Secondary Sludge (WERF3-CHG)	Digested Solids (WERF4-CHG)
Permanent Gases and Light Hydrocarbons				
Carbon Dioxide	vol%	21.6	0.2	0.63
Ethane	vol%	1.19	< 0.01	0.09
Hydrogen	vol%	1.5	2.96	1.80
Methane	vol%	73.5	81.0	93.7
Nitrogen	vol%	1.61	15	3.53
Oxygen	vol%	0.4	0.36	0.21
Trimethylsilanol	mg Si/m ³	< 0.049	< 0.046	0.050

5.3.9 CHG Sulfur Removal and Catalyst

Following each CHG run, the Raney Nickel (R-Ni) used for sulfur removal and the ruthenium on graphite backing catalyst (Ru/C) were analyzed by ICP for metals. PNNL also had a sample of fresh catalyst and Raney Nickel analyzed as well for a base case comparison. All catalyst data is presented in Table 5-11. The complete set of metals data for the fresh catalyst and Raney Nickel is shown in Appendix D.

5.4 QA Review

Analytical methods were chosen based on PNNL's previous experience with the matrices from the HTL and CHG processes. Each section below is a description of the measurement methods and includes target analytes, detection limits, where the analyses were performed, and references. Upon receipt of the data, Leidos verified data from handwritten log books to Excel spreadsheets, confirmed electronic calculations, and reviewed instrument quantitation reports. Sample duplicates were collected for each method/matrix combination to evaluate precision. Internal laboratory duplicate results have also been reviewed for precision. Data has been reported using the significant figures received from PNNL. In cases where precision did not meet the criteria stated in the QAPP, results with one fewer significant figure are listed in Tables 5-3 to 5-11.

Table 5-11. Raney Nickel Sulfur Removal / Ruthenium on Graphite Characterization^a.

Measurement	Fresh Catalyst		Primary Sludge (WERF2-CHG)		Secondary Sludge (WERF3-CHG)		Digested Solids (WERF4-CHG)	
	R-Ni	Ru/C	R-Ni	Ru/C	R-Ni	Ru/C	R-Ni	Ru/C
Metals								
Aluminum	250,000	65.8	255,000	149	350,000	310	285,000	148
Barium	< 30	170	< 30	43.7	< 45	140	< 35	156
Calcium	253	188	210	482	100	275	440	820
Cobalt	259	< 45	< 30	< 30	242	< 45	267	< 35
Copper	< 30	38.8	< 30	< 30	< 45	< 45	< 35	< 35
Iron	789	101	751	202	843	219	959	194
Magnesium	120	67.0	94.0	45.9	62.0	56.5	160	96
Nickel	490,000	< 45	472,000	291	527,000	630	550,000	350
Phosphorus	< 30	< 45	< 30	< 30	156	229	< 35	< 35
Potassium	80.6	2,990	60.2	1,700	115	5,400	130	2,100
Ruthenium	< 30	72,500	< 30	76,800	< 45	91,600	< 35	84,900
Silicon	100	79	2,100	61	378	< 45	3,000	140
Sodium	3,460	186	< 30	1,230	132	1,190	< 35	1,100
Sulfur	68.7	452	4,100	1,700	16,000	3,400	9,900	1,410
Titanium	28.3	120	< 30	65.1	< 45	77.2	22	66

^a All results reported in units of ppm (wt/wt)

5.4.1 Ammonia

Ammonia in aqueous matrices was determined in the PNNL laboratories using the Hach TNT832 method with a DR 2800™ Portable Spectrophotometer and is reported as nitrogen. The method references EPA 350.1, 351.1, and 351.2. One milligram per liter (mg/L) of ammonia-nitrogen is equivalent to 1.22 mg/L of ammonia.

The HTL aqueous sample duplicates for the primary sludge run (WERF-02, 13:20 set-aside), the secondary sludge run (WERF-03, 12:40 set-aside) and the digested solids run (WERF-04, 12:30 set-aside) had adequate precision (<5%RPD).

Precision for the CHG ammonia method was evaluated by the reproducibility of the measurements for each run and reported as percent relative standard deviation (%RSD). WERF2-CHG results had 5.8%RSD, WERF3-CHG results had 4.5%RSD, and WERF4-CHG results had 4.1%RSD.

Analysis of ammonia in the gas phase for both the HTL and CHG processes was unsuccessful. Carbon dioxide and methane elute close to the expected retention time of ammonia, obscuring the peak and making quantitation unachievable.

5.4.2 Anions

Aqueous samples were analyzed for chloride, phosphate, and sulfate using a Dionex Ion Chromatograph (IC), Model ICS-3000, in the PNNL laboratories. The laboratory analyzed the HTL aqueous product at dilution factors of 10 and 100. The results for the digested solids feed run (WERF-04) agree within $\pm 10\%$ for chloride and sulfate and the data reported is an average of the results from the two dilutions. The phosphate data reported is from the 1:10 dilution which resulted in a concentration close to the calibration verification sample that was analyzed. The data reported for the primary sludge feed run (WERF-02) is from the 1:10 dilution. The precision for the sample duplicates for the primary sludge feed run (WERF-02, 13:20 set-aside) and the digested solids feed run (WERF-04, 12:30 set-aside) were adequate with <10%RPD.

Anion data for the CHG samples were interpreted from the chromatograms and quantitation reports. Samples from the primary sludge feed run (WERF2- CHG) and the secondary sludge feed run (WERF3-CHG) were analyzed at 1:100 and 1:10 dilutions. Data from the 1:10 dilution was evaluated with reported concentrations close to the 10 mg/L verification standard analyzed. Chloride and phosphate were not detected at 4 mg/L. Samples from the digested solids feed run (WERF4-CHG) were analyzed without additional dilution. A detection limit of 4 mg/L was applied as referenced in the QAPP. Sample duplicates were analyzed on the post ion exchange CHG feed sample and the 4:15 aqueous set-aside from WERF3-CHG run. Precision was adequate with <10%RPD.

5.4.3 Chemical Oxygen Demand

Chemical Oxygen Demand (COD) was determined in the PNNL laboratories using Hach method 8000, Program 435 with a DR 2800™ Portable Spectrophotometer. The range of the method is 20-1,500 mg O₂/L of sample. The Hach method references Standard Method 5220D. Beginning of run (BOR) and end of run (EOR) feed samples for the digested solids (WERF-04) were analyzed for COD, both in duplicate. Precision of the analyses was 4.6%RSD. The EOR feed sample for WERF-02 was not analyzed, so data in Table 5-3 is the BOR sample only. Precision of the sample duplicates for the HTL aqueous product samples for the primary sludge (WERF-02 13:20 set-aside), the secondary sludge (WERF-03 12:40 set-aside) and the digested solids feed (WERF-04 12:30 set-aside) was acceptable with $\leq 5.0\%$ RPD.

The precision of the WERF2-CHG COD data was poor (96.8%RSD) when samples collected during the full steady state period (between 8/13/15 9:00 and 8/14/15 5:35) are included (concentrations decreasing from 144 to 12 mg O₂/L throughout the time period). The precision improves to 61%RSD when the time period is narrowed, starting at 8/13/15 15:00 (same end time). The concentration decreases from 46 to 12 mg O₂/L during the steady state period with an average of 25 mg O₂/L.

The precision of the WERF3-CHG COD data was adequate (12.9%RSD) for samples collected during steady state (between 8/19/15 16:20 and 8/21/15 4:15). The precision of the WERF4-CHG COD data was adequate (21.0%RSD) for samples collected during steady state (between 9/15/15 11:10 and 9/16/15 8:00).

5.4.4 Density and Kinematic Viscosity

Density measurements for BOR and EOR feedstock samples were calculated gravimetrically at PNNL using a graduated centrifuge cone. At a minimum, samples were aliquoted and weighted in duplicate. Precision for the measurements met the criterion of $\leq 10\%$. Due to high levels of gas in the primary sludge BOR feedstock which resulted in inaccurate data, the results presented in Table 5-3 are from the EOR feedstock only. Notations in the WERF-02 logbook indicated challenges with the EOR WERF-02 (primary sludge) feed sample density measurements. The density values given in Tables 5-3 and 6-1 represent the most accurate data PNNL obtained.

Density and kinematic viscosity measurements for the biocrude oil samples were performed at the PNNL laboratories using an Anton Paar SVM3000 Stabinger Viscometer. The procedure is based on ASTM D7042-04. Density and kinematic viscosity measurements were performed at 20°C and 40°C , respectively. A certified standard obtained from Cannon Instrument Company was used to verify the accuracy of the results.

Precision for the analyses of biocrude oil from the digested solids sample duplicate (WERF-04, 12:30 set-aside) was acceptable, with density yielding $0.25\% \text{RPD}$ and kinematic viscosity $2.6\% \text{RPD}$.

5.4.5 Dissolved Organics

Dissolved organics in the HTL aqueous product, the CHG feed (both before and after ion exchange), and the CHG aqueous product were analyzed by HPLC using a refractive index detector in the PNNL Laboratories. Calibration standards ranged from 0.1 to 2.0 wt% and were verified with an independently prepared standard. Compounds of interest included: acetaldehyde, acetic acid, acetone, 1,2-butanediol, butanoic acid, 1-butanol, 2-butanol, ethanol, ethylene glycol, formic acid, glycerol, glycolic acid, methanol, 2-methyl-1-propanol, p-cresol, 2-pentanone, phenol, 1,3-propanediol, propanoic acid, 1-propanol, 2-propanol, and propylene glycol. The reporting limit was 0.03 wt%. Precision of the HTL aqueous sample duplicates for the primary sludge (WERF-02 13:20 set-aside), secondary sludge (WERF-03, 12:40 set-aside), and the digested solids feed (WERF-04, 12:30 set-aside) processes was acceptable with $\leq 15\% \text{RPD}$.

A sample duplicate was analyzed for the WERF3-CHG post ion exchange feed sample. Precision was adequate for all compounds ($\leq 15\% \text{RPD}$) with the exception of acetone (37% RPD). The sample contained 0.045 wt% and the duplicate 0.031 wt%. The average of the two values is reported in Table 5-8. It should be noted that this result is slightly above the reporting limit of 0.03 wt%. All CHG aqueous product samples did not contain dissolved organics above this detection limit.

5.4.6 Elemental Analysis

Elemental analysis was performed by ALS Environmental Laboratory in Tucson, AZ. Carbon, hydrogen and nitrogen (CHN) were analyzed using ASTM D5291/D5373. Oxygen (O) followed ASTM D5373 (modified), and Sulfur (S) was conducted by ASTMD1552/D4239. A sample duplicate from the composite BOR and EOR feed sample for the digested solids (WERF-04) was submitted to the lab and analyzed for CHNOS. Precision, as measured by %RPD, was $< 5\%$.

A sample duplicate was analyzed on the 12:30 biocrude oil set-aside from the WERF-04 run. Precision met the QAPP criteria for the oil matrix of $\leq 30\%$ RPD. The laboratory analyzed all samples in duplicate with adequate precision ($< 10\%$ RPD) with the exception of the carbon analysis for the duplicate of the 12:30 aqueous set-aside of the WERF-04 process. The result for this sample was 1.08 wt% and was determined to be an outlier using the Grubbs' test.

A sample duplicate was analyzed on the post ion exchange feed for the CHG run using secondary sludge (WERF3-CHG). The precision of the nitrogen analysis between the sample and the sample duplicate was poor with 39%RPD. The laboratory analyzed all samples in duplicate; the carbon data for the post ion exchange feed for WERF3-CHG was evaluated to be an outlier at 0.87 wt% as compared to the sample result of 0.71 wt%. Precision of the hydrogen results were acceptable. A sample duplicate was also analyzed on the CHG aqueous product (8/21-4:15 sample) for the secondary sludge feed (WERF3-CHG). Precision met the requirements of the QAPP.

5.4.7 Gravimetric Analyses

Analyses for ash, dry solid content, and product weight were performed gravimetrically in the PNNL laboratories. Samples were dried at 105°C for dry solid content measurement and held at 750°C for two hours for the ash determination. Filtered oil solids were determined on the biocrude oil, following ASTM D7579-09, in the PNNL laboratory. An aliquot of the biocrude oil was filtered through a tared 1 µm glass filter, washed with 50% methylene chloride/methanol until the filtrate ran clear, and allowed to dry. The mass collected on the filter was compared to the mass of oil filtered. Three balances of different tolerances were used for the gravimetric analyses, each calibrated prior to use. For gravimetric analyses, the QAPP listed a data quality objective (DQO) for precision [measured by relative percent difference (%RPD)] of $\leq 10\%$ as measured by the analysis of duplicate samples.

The precision for the ash determination in the primary sludge feed (WERF-02) was 11.7%RSD calculated from the BOR and EOR feed samples, both analyzed in duplicate. This was slightly higher than the QAPP criteria of $\leq 10\%$ RSD. The BOR samples had higher ash content. PNNL noted that this was atypical; if a difference is seen between the BOR and EOR samples, the EOR tends to be higher. The precision for dry solid content was 0.77%RSD.

The precision for the ash determination in the secondary sludge feed (WERF-03) was 1.0%RSD, calculated from the BOR and EOR feed samples, both analyzed in duplicate. The precision for dry solid content was 0.78%RSD. The precision for the ash determination in the digested solids feed (WERF-04) was 0.34%RSD calculated from the beginning and end of run feed samples, both analyzed in duplicate. Similarly, the precision for dry solid content was 0.73%RSD.

The reproducibility of the ash analysis for the three biocrude oil samples from the primary sludge feed (WERF-02) was poor with 58%RSD. The specific values were 0.54 wt%, 0.29 wt%, and 0.16 wt%. Precision for the analysis of ash in biocrude oil from the digested solids run (WERF-04) was acceptable with 6.1 %RPD.

A sample duplicate was analyzed for filtered oil solids from the WERF-04, 12:30 biocrude oil set-aside. The precision was 24%RPD, above the QAPP criteria of 10%RPD.

5.4.8 Light Hydrocarbons and Permanent Gases

Two instruments were used for the analysis of gas samples. An INFICON Model 3000 Micro GC with a TCD was used for the online analysis of the HTL process gas stream. The instrument was calibrated with a gas standard and verified prior to daily use to ensure response within 5%RPD of calibration. Gas samples for the HTL process were analyzed every four minutes for approximately 1 or 1.5 hours during RLD mode using this GC. The average value of the data collected is reported in Table 5-7. The following compounds were of interest: 1,3-butadiene, n-butane, 1-butene, cis-2-butene, trans-2-butene, carbon dioxide (CO_2), carbon monoxide (CO), ethane, ethylene, hydrogen (H_2), hydrogen sulfide, isobutane, isobutene, isopentane, methane (CH_4), 2-methyl-2-butene, nitrogen (N_2), oxygen (O_2), n-pentane, 1-Pentene, cis-2-pentene, trans-2-pentene, and propane. The reporting limit for these samples was 0.01 vol%.

The precision of the data was measured by percent relative standard deviation (%RSD) of all data collected during steady state. Precision of the data from the primary sludge HTL run (WERF-02) was adequate, with all gases having $\leq 15\%$ RSD. Precision of the data from the HTL run with secondary sludge (WERF-03) data was less than 15%RSD with the exception of nitrogen (25.3%RSD), carbon monoxide (70.6%RSD), propane (17.2%RSD), isobutene (18.1%RSD), n-butane (15.3%RSD), isopentane (60.0%RSD), and n-pentane (83.5%RSD). Levels of nitrogen decreased throughout the 1 hour and 24 minute time duration, while levels of propane and the butanes increased. Concentrations of carbon monoxide and the pentanes followed no discernable pattern. Precision of the data for the digested solids feed run (WERF-04) was less than 15%RSD for all compounds with the exception of nitrogen (36%RSD). Nitrogen concentration decreased throughout the hour that samples were collected from 1.3 vol% to 0.47 vol%.

A Carle GC-TCD using manual injections was used for the analysis of CHG process stream gas samples, timed to match the collection of CHG aqueous product samples. The gases of interest included: carbon dioxide, ethane, ethylene, hydrogen, methane, nitrogen, and oxygen. The reporting limit for the samples was 0.01 vol%. Results are found in Table 5-10. Four injections from the WERF2-CHG process were analyzed spanning a time frame of eight hours. The precision of the data was adequate ($\leq 15\%$ RSD) for all gases with the exception of hydrogen (18.2%RSD) and oxygen (17.2%RSD). Eight injections from the WERF3-CHG process were analyzed spanning a time frame of approximately 30 hours. Nitrogen concentrations decreased from 30 vol% to 5.7 vol% during this time period (46%RSD) while carbon dioxide concentrations fluctuated between 0.14 and 0.29 vol% resulting in a precision of 27%RSD. Five injections from the WERF4-CHG process were analyzed spanning a time frame of 21 hours. The precision of the data was adequate ($\leq 15\%$ RSD) for all gases with the exception of oxygen which varied between non-detect (≤ 0.01 vol%) and 0.25 vol% (26%RSD).

5.4.9 Metals

Samples for metals were analyzed by Inductively Coupled Plasma (ICP) – Optical Emission Spectrometry (OES) using a Perkin Elmer 7300DV OES in the PNNL laboratories. The PNNL method is based on ASTM D7692-11. Sludge feedstock, biocrude oil, and HTL solid phase product were digested in nitric acid. Results for silicon and zirconium may be biased low due to incomplete dissolution in nitric acid. Dilutions of aqueous samples were done with nitric acid. Element of interest included: aluminum (Al), arsenic (As), barium (Ba), cadmium (Cd),

calcium (Ca), chromium (Cr), cobalt (Co), copper (Cu), gold (Au), iron (Fe), lead (Pb), magnesium (Mg), manganese (Mn), molybdenum (Mo), nickel (Ni), palladium (Pd), phosphorus (P), platinum (Pt), potassium (K), rhenium (Re), rhodium (Rh), ruthenium (Ru), silicon (Si), silver (Ag), sodium (Na), strontium (Sr), sulfur (S), tin (Sn), titanium (Ti), tungsten (W), vanadium (V), yttrium (Y), zinc (Zn), and zirconium (Zr). Reporting limits for aqueous samples were 1.0 ppm (wt/vol) and for solid samples was between 25 and 50 ppm (wt/wt).

Precision of the sampling and analysis procedures were measured by the analysis of sample duplicates. The reproducibility of the results for the digested solids feed samples was greater than the QAPP criteria of $\leq 25\%$ RPD for Silicon (65%RPD) and Zirconium (106%RPD). Data for these elements are reported to two significant figures.

The laboratory digested and analyzed each biocrude oil sample in duplicate. Results for silicon show variability greater than 25%. Therefore, silicon data for the biocrude oil samples were reported with two significant figures. Precision for the laboratory duplicate analysis for the following elements in the analysis of the WERF-03 trap oil was greater than 25%RPD: magnesium, manganese, sodium, nickel, phosphorus and silicon.

Sample duplicates were analyzed for the aqueous product from the 13:20 set-aside from the primary sludge HTL test (WERF-02), the aqueous product from the 12:40 set-aside from the secondary sludge HTL test (WERF-03), and the aqueous product from the 12:30 set-aside from the digested solids test (WERF-04). A sample duplicate was analyzed on the filter solids from the WERF-04 run. The precision met criteria with all %RPD $< 25\%$.

The results of the aqueous product for the CHG test using the effluent from WERF-02 (primary sludge feed) had reproducibility greater than 25%RSD for multiple elements. Specifically results for potassium ranged from 35 ppm to 96 ppm, sodium ranged from 48 to 109 ppm, and silicon ranged from 16 to 39 ppm. With the exception of sulfur, the other elements were not detected at 1 ppm.

Precision of the duplicate analyses for the Raney nickel catalyst following the CHG test with primary sludge HTL effluent (WERF2-CHG) were acceptable except for calcium (59%RPD), sulfur (55%RPD), and silicon (62%RPD). Precision of the duplicate analyses for the ruthenium on graphite backing catalyst following the CHG process with primary sludge HTL effluent were acceptable except for silicon (74%RPD).

A sample duplicate was analyzed on the post ion exchange feed for the CHG test using secondary sludge HTL effluent (WERF3-CHG). All elements had acceptable precision. A sample duplicate was also analyzed on the CHG aqueous product (8/21-4:15 sample) for WERF3-CHG. Precision of aluminum was poor (120%RPD) and silicon was above the criteria in the QAPP with 36%RPD).

Aliquots of the Raney Nickel (R-Ni) used for sulfur removal and the ruthenium on graphite backing (Ru/C) were digested and analyzed in duplicate following each CHG test. Results above 25%RPD were observed for the WERF2-CHG test for calcium, silicon, and sulfur for the R-Ni and silicon for the Ru/C. Results above 25%RPD were observed for the WERF3-CHG test for aluminum, calcium, magnesium, and sulfur for the R-Ni and aluminum, barium,

nickel, and sulfur for the Ru/C. Results above 25%RPD were observed for the WERF4-CHG test for calcium, potassium, magnesium, and sulfur for the R-Ni and calcium, nickel, and silicon for the Ru/C.

Samples of fresh R-Ni and Ru/C were analyzed for metals. Results above 25%RPD were observed for magnesium in the Raney-Nickel and for barium, silicon, and titanium in the Ru/C catalyst.

5.4.10 Moisture

Moisture was determined by the Karl Fischer technique using Method ASTM D6869 at ALS Environmental Laboratories on the biocrude oil samples. The laboratory analyzed all samples in duplicate with adequate precision (<10%RPD). The sample duplicate was analyzed for the WERF-04 run, 12:30 set-aside. Results for the sample and its duplicate were identical.

5.4.11 pH

pH was measured in the PNNL laboratories using a pH meter calibrated with buffer solutions at pH 4, 7, and 10. Precision for the digested solids feed analysis was acceptable with 3.4%RPD. Precision for the analysis of the WERF-02 13:20 set-aside was 0.16%RPD. Precision for the WERF-03 duplicate samples (12:40 set-aside) was 0.25%RPD. Precision of the WERF-04 duplicate samples (12:30 set-aside) was 0.62%RPD. Precision of the CHG aqueous product pH measurements was acceptable with $\leq 1.5\%$ RPD

5.4.12 Siloxanes

Samples for siloxane analysis were collected in 1.4-L SUMMA[®] canisters and analyzed by Atmospheric Analysis and Consulting, Inc. in Ventura, California. Canisters were filled approximately half way, monitoring the progress on the vacuum gauge (30 in. Hg to 15 in. Hg). The laboratory followed EPA Method TO-15, putting the samples through a water and CO₂ management system and cryofocusing the gas onto a GC mass spectrometer (MS), analyzing in full scan mode. Compounds of interest included hexamethyldisiloxane (L2), hexamethylcyclotrisiloxane (D3), octamethyltrisiloxane (L3), octamethylcyclotetrasiloxane (D4), decamethyltetrasiloxane (L4), decamethylcyclopentasiloxane (D5), dodecamethylpentasiloxane (L5), trimethylsilanol, and tetramethylsilane. Calibration standards were not analyzed for trimethylsilanol and tetramethylsilane. These analytes were analyzed as tentatively identified compounds (TICs) in which the mass spectra from each sample was compared to the known spectra for the two compounds. The results for these two compounds are considered estimated. The laboratory reported the data in units of ppb which have been converted to mg Si/m³ using the molecular weight of each compound and the number of silicon atoms in the formula. These units are more representative of the mass of silica generated during combustion. With the exception of trimethylsilanol in the WERF1-CHG run, siloxanes were not found (detection limits are listed in the Appendices). As explained in Section 6.4.2, the results listed in Table 5-10 and Appendix C for siloxanes in the WERF4-CHG effluent were collected during the WERF1-CHG test.

The detection limits for the HTL WERF-04 sample were significantly higher than the other samples. For example, the detection limit for hexamethyldisiloxane was 6.6 mg Si/m³ in HTL WERF-04 as compared to 0.60 mg Si/m³ in HTL WERF-02 and < 0.1 mg Si/m³ for the CHG samples. Atmospheric Analysis and Consulting explained that the total volatile organic

compound (VOC) concentration in the HTL WERF-04 sample was higher than the others, requiring a larger dilution for quantitation of the internal standards and surrogate compounds.

5.4.13 Total Acid Number

Total Acid Number (TAN) was performed by ALS Environmental Laboratory following ASTM D3339 on biocrude oil samples. The laboratory analyzed all samples in duplicate with adequate precision (<10%RPD). The precision of the sample duplicate results for biocrude oil from the digested solids test (WERF-04, oil from 12:30 set-aside) was 0.3%RPD.

5.4.14 Total Organic Carbon

Samples for Total Organic Carbon (TOC) were analyzed by ALS Environmental Laboratory in Jacksonville FL following EPA Method 9060 for aqueous samples and ASTM Method D6316 for solid matrices. A sample duplicate from the composite BOR and EOR feed sample for the digested solids (WERF-04) was submitted to the lab and analyzed for TOC. Precision, as measured by %RPD, was <5%. Duplicate sample analysis was performed on the aqueous product of the 12:30 set-aside from the digested solids test (WERF-04). Results had 14.5% RPD, lower than the QAPP goal of ≤20%. All samples were analyzed in duplicate at the laboratory with ≤10% RPD. The laboratory also analyzed a matrix spike (MS) on the aqueous product of the 11:50 set-aside from the digested solids test and obtained 105% recovery. A matrix spike was done on the 13:20 aqueous set-aside from the secondary sludge HTL process and obtained 100% recovery.

The precision for the TOC measurement for the post ion exchange CHG feed from the primary sludge HTL aqueous product and the CHG aqueous products were acceptable with <20%RPD. Two set-asides from the CHG run with HTL primary sludge (WERF2-CHG) effluent were analyzed. One had 531 mg/L TOC and the second had <99 mg/L. This second concentration is evaluated to be an outlier when compared with all CHG aqueous product TOC measurements. It is included in the appendix table, but excluded from Table 5-9.

A sample duplicate was analyzed on the post ion exchange feed for the CHG run using secondary sludge. The precision of the TOC analysis was adequate with 3.9%RPD. A sample duplicate was also analyzed on the CHG aqueous product (8/21-4:15 sample) for the secondary sludge feed. Precision was 2.4%RPD.

CHAPTER 6.0

HTP TECHNICAL ANALYSIS

HTL and CHG tests with each of the three sludge feed types were all performed as part of this test program as planned. The set of HTL and CHG tests corresponding to the digested solids feed was repeated because of the incomplete HTL data set in the first test (WERF-01) caused by the unintended HTL system shutdown and the limited amount of liquid effluent available for the corresponding CHG test. The repeat HTL test with digested solids (WERF-04) was successfully completed, producing adequate quantity and quality of liquid effluent for the corresponding repeated CHG test. Only data from the repeated HTL and CHG digested solids tests were analyzed in this section.

As noted earlier, the bench-scale HTL and CHG systems at PNNL consist of separate equipment and are run independently of each other. Also, the PNNL CHG system operates at a different flowrate, more than an order of magnitude lower than the PNNL HTL system. This differs significantly from a commercial-scale design offered by Genifuel, where the HTL and CHG processes are integrated into a single operating system. As a result, the HTL and CHG data generated from this test program were mostly analyzed separately here, consistent with how it was generated, except where a result needed to be related back or projected to the potential operation of a commercial-scale system.

6.1 Sludge Feed Characteristics and Performance

No problems were observed with feeding any of the three sludges at the concentrations used in the HTL tests. In the four HTL tests conducted, the two cases where issues occurred were either due to operator error (WERF-01) or loss of mixing in the CSTR (WERF-03). Neither of these issues were directly related to or caused by the sludge feed being used.

In order to process sludge (or any) feed through the HTL process, it must be able to be pumped reliably and consistently. Based on past PNNL experience, this target feed concentration was anticipated to be in the range of 15–20 wt% solids, with the exact value depending on the nature of the particular feed material. The optimal concentration is the highest that can be pumped reliably, thereby generating the highest biocrude yield without sacrificing system mechanical efficiency. Both the digested solids and primary sludge concentrations were above this target range as shipped from Metro Vancouver. Because of limited time and budget in this test program, PNNL did not attempt to find the optimal concentration for these sludges and opted to dilute the feeds conservatively to ensure that the tests could be performed successfully. The secondary sludge was unable to be dewatered sufficiently to meet the target concentration range of solids. Though not ideal with respect to maximizing HTL product generation, the low secondary sludge concentration was not expected to have any impact on pumping.

Based on successful pumping of all three sludges and PNNL past experience, PNNL believes that all three sludges could have been processed successfully at higher concentrations than those tested in this test program, though it is not clear how much higher. In particular,

PNNL believes that the primary sludge was over diluted and might have been able to have been processed up to its first dilution at about 15 wt% solids. Any future testing with this technology and feeds should consider optimizing the feed concentration in order to maximize efficiency and product yields.

Table 6-1 summarizes key analytical data for the three sludge feeds used in the HTL tests. As expected, the digested solids feed had the highest ash concentration (28.0%) due to removal of some of the original organic content during anaerobic digestion. PNNL stated that this high ash content was within the range of ash processed successfully in the past with similar feeds. Primary sludge had the lowest ash concentration at 7.5%. Values of pH among the three feeds ranged from slightly acidic (5.0) for primary sludge to neutral (7.7) for digested solids. For comparison purposes, data for macro- and microalgae feed processed previously by PNNL are also shown in Table 6-1. The data is taken from the literature (Elliott et al., 2013 and Elliott et al., 2014) for algae strains tested that had feed properties (i.e., wt% solids, wt% ash) roughly comparable to that of the sludges processed in this test program.

Table 6-1. Key Sludge Feed Data.

Feed	wt% Solids ^a	Wt % Ash	Density (g/ml)	pH
Primary sludge (WERF-02)	11.9	7.5	1.04	5.09
Secondary sludge (WERF-03)	9.71	16.2	0.998	6.03
Digested solids (WERF-04)	16.0	28.1	1.05	7.73
Algae data for comparison				
<i>Saccharina</i> spp. (macroalgae) ^b	16.1	32.4	Not determined	5.12
<i>Nannochloropsis</i> sp. (microalgae) ^c	17.0	11.1	1.05	Not determined

^a As fed to HTL system

^b Data for feedstock #5 from Elliott et al., 2014

^c Data for Solix lipid extracted algae (LEA) from Elliott et al., 2013

Post-test inspections of the syringe pump and HTL system components did not reveal any evidence of corrosion, erosion, or feed pocketing in any of the tests. A small buildup of solids was found in the inlet line to the CSTR after the digested solids test, but this did not appear to impact flow during the test and was easily cleared. PNNL normally disassembles the system after each test to inspect for plugs and ensures full unimpeded water flow upon reassembly before performing a new test. Although there was an unusual strand of feed-related material pulled from the entrance of the PFR after the HTL test with secondary sludge (WERF-03), it is not clear if this was caused or affected by the solids buildup and lack of mixing in the CSTR during this test. PNNL has noted that the pump seals are particularly susceptible to feed-induced corrosion or erosion, and would have been evidenced by a leak near the pump, which was not observed during any testing. The lack of visible corrosion was likely helped by the absence of any extremes in pH of the feeds tested, though it is unlikely that any significant corrosion would have been observed in these relatively short tests. An interesting point to note is the order of magnitude increase in nickel concentration and higher chromium concentration in the solids (WERF-03) compared to that from the other two feeds. Nickel and chromium are the main components of Inconel, which is the material of construction of the CSTR vessel. PNNL has noted that the thread lubricant used to seal the CSTR and filter vessel contains nickel.

Syringe pumps are effective at delivering steady flows (or maintaining steady pressure) of feeds for materials that are otherwise difficult to pump reliably (such as slurries or sludges). Syringe pumps are not practical or cost efficient at large scales, however, so reliable feed pumping may still be an issue to explore for commercial-scale HTL systems. PNNL recognizes this issue and has recently investigated several types of positive displacement pumps by different vendors as possible candidates for pumping highly viscous fibrous biomass slurries in a pilot-scale HTL system (Berglin, et al., 2012). In general, particular attention needs to be paid during design to components and piping that contain slurries or sludges. One critical design consideration is that the piping and components need to be streamlined to eliminate dead spaces where solid material can accumulate (e.g., sudden line diameter reductions). Erosion/wear over time on pump components caused by feed solids can also be an issue of concern with slurries. On the positive side, the larger overall piping diameters and component size in a commercial HTL system could help reduce the potential for feed plugging, thus making it possible that a commercial-scale system could process a higher feed concentration (or at least no lower) than demonstrated at bench-scale in these tests. The existence and successful recent demonstration of a Genifuel pilot-scale system for an algae slurry feed to a private customer is encouraging with respect to identifying a design that can handle the added demands of slurry/sludge type feeds. According to Genifuel, initial flow problems experienced with the high pressure feed pump selected for their commercial system were traced to a manufacturer defect, which after correction caused no further problems.

6.2 Biocrude and Methane (CHG Gas) Yields

A biocrude or oil phase was successfully generated and isolated in HTL tests for all three sludge types. Table 6-2 summarizes key attributes of the biocrude generated for each sludge type, along with data from biocrude generated from the same macro- and microalgae species mentioned in Table 6-1 for comparison (Elliott et al., 2014 and Elliott et al., 2013). Note that the calculated biocrude flow rate is not measured but is calculated based on the total oil collected in the steady state set-asides divided by the total steady state time in Baseline mode.

Table 6-2. Key Biocrude Data.

Data	WERF-02 Biocrude	WERF-03 Biocrude	WERF-04 Biocrude	<i>Saccharina spp.</i> Biocrude ^a	<i>Nannochloropsis sp.</i> Biocrude ^b
wt% Carbon	66.6 wet	71.4	67.9	—	—
	76.5 dry	72.5	78.5	79.4	79.2
wt% Hydrogen	10.3 wet	8.68	9.74	—	—
	10.1 dry	8.7	9.51	8.0	10.0
H:C molar ratio	1.8 wet	1.4	1.7	—	—
	1.6 dry	1.4	1.4	1.2	1.5
wt% Oxygen	18.6 wet	7.32	17.4	—	—
	8.1 dry	6.5	6.21	8.3	5.7
wt% Nitrogen	3.7 wet	5.02	3.86	—	—
	4.3 dry	5.1	4.46	4.1	4.7
wt% Sulfur	0.55 wet	0.89	1.00	—	—
	0.63 dry	0.90	1.16	0.3	0.5
wt% Ash	0.3 wet	6.15	0.19	—	—
	0.38 dry	6.3	0.21	Not determined	Not determined
wt% Moisture	13.0	1.0 ^d	13.5	9.2	7.8
TAN (mg KOH/g)	65.0	44.8	36.0	36	Not determined
Density (g/ml)	1.000	0.984 ^e	1.013	1.03	0.95
Kinematic viscosity (cSt)	571	624 ^e	1160	1708	205

^a Data for feedstock #5 from Elliott et al., 2014

^b Data for Solix lipid extracted algae (LEA) from Elliott et al., 2013

^c Oxygen values shown here are calculated by difference. Based on past experience, PNNL has found that measured oxygen values in this matrix are of questionable accuracy at the observed moisture content, though no obvious inconsistencies were observed in the analytical results.

^d Measured after drying at 103°C

^e Measured on trap oil sample

The biocrudes generated from digested solids and primary sludge appear to be very similar with respect to elemental composition and physical properties, though the primary sludge biocrude has a higher TAN value and half the kinematic viscosity of digested solids biocrude. Both of these biocrudes were well-formed and easily separated from the aqueous phase product during testing. The secondary sludge biocrude results were difficult to assess. It was similar to the primary sludge and digested solids biocrudes in some respects but there were significant differences. The secondary sludge biocrude had a significantly lower moisture content and higher ash content than the others, though this was likely due to the fact that these analyses were performed on a dried biocrude sample. Also, much less biocrude was generated. The secondary sludge biocrude was much more difficult to separate from the aqueous product phase and initially did not appear to be separable at all. Initially it was thought that the behavior observed might have been due to an emulsion that could have formed if there was a high fatty acids content in the secondary sludge. To answer this question, Genifuel had dried feed samples for all three sludge types sent to the California Polytechnic State University in San Luis Obispo, CA, to perform a proximate analysis. This proximate analysis was different from the one performed by Metro Vancouver because this new one provided composition based on carbohydrate, protein, lipid, and ash content. The results of the analyses on each feed type tested are provided in Appendix E. The analyses showed that the more well-behaved primary sludge, not secondary sludge, had the highest concentration of both total lipids (which includes fatty acids) and fatty acid methyl esters (FAME; a derivative of fatty acids). With respect to the secondary sludge biocrude, only after considerable effort of rinsing and centrifuging the liquid product several times was a liquid-like oil product recovered. The properties cited of this biocrude may therefore have been affected by this additional separation work performed on the sample.

Due to the experimental difficulties that occurred during the HTL test with secondary sludge, including the loss of mixing and solids buildup in the CSTR, it is difficult to determine the cause of the issues associated with the secondary sludge biocrude separation. The question remains if its properties are inherent to the autoclaved secondary sludge feed as opposed to being reflective of the non-ideal operating conditions in this test. A repeat test with secondary sludge was unable to be performed within the limited budget of this test program. Factors that support the possibility that what was observed in the steady state set-asides was an artifact of the poor test conditions include the initially good appearance of separable oil that correlates to a time likely before mixing stopped and the quality and quantity of oil observed in the float traps. Factors that support the possibility that the difficulties seen with processing secondary sludge through HTL may be mostly feed related include the historic difficulties reported by WRRFs with breakdown of secondary sludge in anaerobic digestion, the difficulties seen in this test program and elsewhere with dewatering this material, the change in physical appearance after autoclaving (prior to shipment to PNNL), the difficulty in determining a mechanism to explain how the observed biocrude behavior could result from a loss of mixing, and the good mass balance closure at the current low biocrude yields. It is likely that the secondary sludge biocrude results observed in this test program were a combination of the sludge's inherent nature, effect of autoclaving, low solids concentration, and the experimental conditions (loss of mixing). Repeating this HTL test with proper mixing would allow a proper assessment of the biocrude quantity and quality from secondary sludge.

Comparing the dry biocrudes derived from sludge to the dry biocrudes derived from algae species shows that they are similar with respect to elemental composition and other key

attributes as shown in Table 6-2. The fact that biocrude can be produced from sludge which is of comparable quality to algae derived biocrude is encouraging and shows the value of sludge as a potentially viable HTL feed. Like algae and other common biomass derived biocrudes, however, the TAN values and oxygen content are too high for the sludge biocrudes to be utilized directly as a fuel except for relatively limited applications (e.g., in a burner with a stainless steel fuel nozzle tip or in engines designed to handle the corrosion from acidic species such as in bunker fuel or heavy fuel oil). Likewise, the sludge biocrudes could not be sent directly to a refinery because of the high TAN values. The exception would be for those refineries either large enough such that the biocrude would not be a significant percentage of (and could be blended with) the total petroleum being refined, or that already have the needed processes to handle biocrudes generated by HTP. In most cases, however, the sludge biocrudes as generated in these tests would likely need to undergo upgrading as an additional step before sending to a refiner. Genifuel claims that HTP biocrudes (without upgrading) are more similar to petroleum crude than any other form of bio-oil from other processes (e.g., fast pyrolysis).

Values of biocrude yield on a total mass basis and on a carbon basis for each sludge type are shown in Table 6-3. All yield values are given on a dry, ash free basis and defined as follows:

$$\text{Biocrude yield (total mass basis)} = \frac{\dot{m}_b * (1 - \text{biocrude \% moisture}) (1 - \text{biocrude \% ash})}{\dot{V}_s * \rho_s * (1 - \text{feed \% moisture}) (1 - \text{feed \% ash})} \times 100 \quad (\text{Equation 6-1})$$

$$\text{Biocrude yield (Carbon basis)} = \frac{(\dot{m}_b * \text{biocrude \% carbon})}{\dot{V}_s * \rho_s * (1 - \text{feed \% moisture}) * \text{feed \% carbon}} \times 100 \quad (\text{Equation 6-2})$$

where: \dot{m}_b = average mass flow rate of biocrude,

\dot{V}_s = average volumetric flow rate of sludge feed,

ρ_s = feed density.

Table 6-3. Biocrude Yield Values^a.

Test	% Yield (Total Mass Basis)	% Yield (Carbon Basis)
WERF-02 Biocrude	37.3	59.3
WERF-03 Biocrude	24.8	38.8
WERF-04 Biocrude	34.4	48.7
Algae data for comparison		
<i>Saccharina</i> spp. Biocrude ^b	27.1	45.3
<i>Nannochloropsis</i> sp. Biocrude ^c	53.2	Not determined

^a Dry, ash-free basis; normalized per mass balance value (see Section 6.3)

^b Data for feedstock #5 from Elliott et al., 2014

^c Data for Solix lipid extracted algae (LEA) from Elliott et al., 2013

All yield values in Table 6-3 are normalized by the appropriate mass balance value (see Section 6.3). As expected, the primary sludge had the highest biocrude yield of the three sludge types (37%) despite its relatively low organic (i.e., solids) content in the feed slurry. Surprisingly, the digested solids had a relatively high yield (34%) despite the fact that some of its original organic content had been depleted during anaerobic digestion. It should be noted, though, that the digested solids test (WERF-04) was performed without the spacer in the CSTR, thus having a larger reactor volume (1000 ml instead of 415 ml) and more time to react (i.e., larger space time) than the other HTL tests. The yield of biocrude from secondary sludge (25%)

was notably lower than the other two sludges. The significant drop in reaction temperature between the CSTR (top) exit and PFR entrance (down to 276°C instead of 350°C) due to the loss of mixing in the secondary sludge test may have had some effect on the lower yield, as well as the low solids concentration in the secondary sludge feed. It is important to note that these yield results were obtained for sludge feeds where the solids concentrations were not optimized (i.e., conservatively more dilute). Based on PNNL's experience with other feeds, a higher solids concentration in the feeds would be expected to result in higher yields.

Product gas concentrations from CHG tests are summarized in Table 6-4, along with total gas yield and methane yield values on a carbon basis. Gas concentrations shown in Table 6-4 are shown on an air-free basis. Notable amounts of nitrogen and oxygen were measured in the gas effluent of all CHG tests. These quantities decreased over time, even during the declared steady state periods. While PNNL has stated that the nitrogen and oxygen quantities are due to air contamination during manual gas sampling, these quantities are not in the expected 4/1 ratio found in air, with nitrogen being present instead in higher amounts. Nevertheless, without an obvious reason for the presence of either gas, they have been subtracted from the product gas in each test with remaining concentrations re-calculated. Methane is found to be the dominant product in all cases, except for WERF2-CHG, where a notable amount of CO₂ is seen. This is consistent with the pH value for the aqueous feed for WERF2-CHG (6.4) being lower than that for the other two feeds (8). PNNL has typically observed a roughly 60/40 split of CH₄ to CO₂ in previous tests with other CHG feeds derived from HTL of biomass. The higher pH values for WERF3-CHG and WERF4-CHG likely result in CO₂ conversion to bicarbonate, explaining its absence from the gas product.

Table 6-4. CHG Gas Product Data.

	WERF2-CHG	WERF3-CHG	WERF4-CHG
Volume%^a			
Methane	74.6	96.0	97.3
Carbon Dioxide	22.0	0.3	0.7
Hydrogen	1.5	3.1	1.9
Ethane	1.2	—	0.1
Propane	0.8	0.6	0.6
Wt% gas yield ^b (carbon basis)	63.4	62.0	65.8
Wt% CH ₄ yield ^b (carbon basis)	46.7	60.7	64.1

^a Air-free basis

^b Normalized per mass balance value (see Section 6.3)

Because most of the CHG feeds are water, the total gas yield and methane yield values are shown on a carbon basis only. These yield values are calculated as follows:

$$CHG \text{ Gas yield (Carbon basis)} = \frac{(\sum \%V_i * \dot{V}_g * v_{i,C}) * P * MW_C / (R * T)}{\dot{V}_{aq} * \rho_{aq} * \text{feed \% carbon}} \times 100 \quad (\text{Equation 6-3})$$

$$CHG \text{ Methane yield (Carbon basis)} = \frac{(\%V_{CH_4} * \dot{V}_g) * P * MW_C / (R * T)}{\dot{V}_{aq} * \rho_{aq} * \text{feed \% carbon}} \times 100 \quad (\text{Equation 6-4})$$

where: $\%V_i$ = measured volume fraction of carbon-containing species i in the product gas,

\dot{V}_g = volumetric flow of product gas,

$v_{i,C}$ = moles of carbon per mole of species i ,

P = pressure,

MW_C = molecular weight of carbon,

R = universal gas constant,

T = temperature,

\dot{V}_{aq} = average volumetric flow rate of CHG feed,

ρ_{aq} = CHG feed density.

The results show that 43-62 wt% of the residual HTL carbon in the CHG aqueous feed ends up in the gas phase, and 32-60 wt% of the carbon ends up as methane. Because of the significant carbon loss that occurred in the IX process performed before CHG to remove the sulfate (catalyst poison), it is possible that these methane yields could have been higher (see Section 6.4.1).

A combined yield of biocrude and methane product for a given sludge feed type is difficult to do for these tests. Because the HTL and CHG bench-scale systems are independent and run separately at PNNL, and because the HTL flow rates are roughly 40 times higher than CHG flow rates, there is no way to use both HTL and CHG data for the same calculation and get a meaningful value. However, if one hypothetically scales up the CHG feed rate to match the rate of aqueous HTL product and assumes the same distribution of CHG products as observed at the lower flow rates, one can extrapolate an equivalent amount of CH_4 product on the same basis as the biocrude production to produce a hypothetical yield. Values of this combined yield for each sludge type are calculated and shown in Section 6.3.

Table 6-5 contains estimated heating values for the biocrude and CHG gas products generated for each sludge feed. The biocrude heating values were calculated using the correlation developed by Channiwala and Parikh (2002):

$$HHV = 0.349*C + 1.1783*H + 0.1005*S - 0.1034*O - 0.0151*N - 0.0211*A \quad (\text{Equation 6-5})$$

where C, H, S, O, N, and A refer to the weight percent of carbon, hydrogen, sulfur, oxygen, nitrogen, and ash, respectively. Equation (6-5) calculates the heat content as the high heating value (HHV) in units of MJ/kg. The equation was developed from a large database and is stated to be applicable for a wide variety of gas, liquid, and solid fuels including biomass materials. The equation is valid over a wide composition range as well: $0.00 < C < 92.25\%$, $0.43 < H <$

25.15%, 0.00 < O < 50.00%, 0.00 < N < 5.60%, 0.00 < S < 94.08%, 0.00 < A < 71.4%. The elemental analysis of the biocrude generated in this test program all fall within this range. The HHVs for the digested solids and primary sludge derived biocrudes are approximately the same at 38 MJ/kg, with the secondary sludge derived biocrude having a slightly lower value at 35 MJ/kg. For perspective, these values are close but below the HHV for petroleum crude oil (typically about 45.5 MJ/kg). The HHVs for the sludge derived biocrudes are comparable in magnitude to butanol (37.3 MJ/kg) and methyl tert-butyl ether (MTBE) (38.0 MJ/kg).

Table 6-5. Calculated High Heating Values of HTL Biocrude and CHG Product Gas.

Feed	Sludge ^a		HTL Biocrude ^a		CHG Product Gas	
	MJ/kg	BTU/lb	MJ/kg	BTU/gal	MJ/m ³ at 0°C	BTU/ft ³ at 60°C
Primary sludge	20.7	8900	37.8	135,713	30.8	782
Secondary sludge	19.6	8413	34.8	123,068	38.7	983
Digested solids	16.8	7229	38.0	137,795	39.1	993

^aDry basis

The heating value of the CHG product gas was calculated as a weighted average of the HHV values of the pure components based on the measured composition in each test. All values listed are at standard conditions of 1 atm and 0°C. The HHVs for gas from WERF3-CHG and WERF4-CHG (originally derived from secondary sludge and digested solids, respectively) were relatively close to each other at about 39 MJ/m³. These values are similar to that of natural gas (40.6 MJ/m³ at 0°C) and very close to the HHV of pure methane (39.7 MJ/m³ at 0°C), which is not surprising given that most of the product gas for these tests was comprised of methane. The HHV for gas from WERF2-CHG (originally derived from primary sludge) had a lower value (31 MJ/m³), mainly due to the higher percentage of CO₂ in the gas product, due in turn to the lower pH of the aqueous phase in that test.

6.3 Mass Balances

Calculated values of all HTL feed and product flow rates, as well as the total mass balance for the HTL tests performed are included in Table 6-6. The HTL mass balance calculation for the PNNL bench-scale system is unusual because the three product phases are sampled at different times rather than all being sampled at the same time. This is due to the unique constraints of the bench-scale system operation. The steady state organic and aqueous liquid phases are quantified during Baseline mode, the steady state product gas phase is quantified during RLD mode, and the product solids are quantified at the end of the test when the filter vessel and CSTR are accessed. Thus, to calculate a mass balance, all product quantities need to be converted to a flow rate, which is done by dividing the measured quantities of each product by the corresponding accumulation time. For liquid products, this time corresponds to the total collection time for the number of steady state set-asides (a multiple of 40 minutes per set-aside). For gases, it is the steady state period during RLD over which the total gas flow from the WTM and gas samples are taken. For solids, it is the total time on feed, as it is assumed that the solids recovered at the end of the test accumulated at a steady rate while processing feed. This approach assumes that the calculated flow rates are steady over the entire steady state operation of the test including periods where a particular phase is not sampled.

The HTL total mass balance is calculated according to the following equation, with all components being mass flow rates:

$$HTL \text{ total mass balance} = \frac{\text{Biocrude} + \text{Aqueous} + \text{Gas} + \text{Solids}}{\text{Feed}} \times 100 \text{ (Equation 6-6)}$$

Mass balance values for all of the HTL tests ranged from 101% to 107%, and all were within the target range of $\pm 15\%$ of closure.

Table 6-6. HTL Flow Rates and Total Mass Balance.

Stream	Primary Sludge (WERF-02)	Secondary Sludge (WERF-03)	Digested Solids (WERF-04)
Feed (g/hr)	1541	1499	1570
Dry, Ash-free Feed (g/hr)	168.8	122.0	181.1
Biocrude (g/hr)	73.4	33.5	77.3
Dry, Ash-free Biocrude (g/hr)	63.6	31.1	66.7
Aqueous Effluent (g/hr)	1424	1471	1478
Solids (g/hr)	17.4	29.8	88.9
Gas Effluent (g/hr)	37.2	11.5	29.6
Mass Balance (%)	101	103	107

The carbon mass balances for all HTL tests, along with mass flow rates on a carbon basis are provided in Table 6-7. The carbon balance is calculated according to the following equation, with %C values measured on a weight basis:

$$HTL \text{ carbon balance} = \frac{(mass \text{ flow} * \% \text{C})_{biocrude} + (mass \text{ flow} * \% \text{C})_{aqueous} + (mass \text{ flow} * \% \text{C})_{solids} + (\sum \% V_i * \dot{V}_g * v_{i,C} * P * \dot{M}W_C / (R * T) * 100)}{\dot{V}_s * \rho_s * \% C_{dry \text{ feed} \text{ solids}} * (1 - feed \% moisture)} \text{ (Equation 6-7)}$$

where: $\% V_i$ is the measured volume fraction of carbon-containing species i in the HTL product gas,

\dot{V}_g is the volumetric flow of HTL product gas,

$v_{i,C}$ is the moles of carbon per mole of species i ,

P is the pressure,

MW_C is the molecular weight of carbon,

R is the universal gas constant,

T is the temperature,

\dot{V}_s is the average volumetric flow rate of HTL sludge feed,

ρ_s is the feed density,

$\% C_{dry \text{ feed} \text{ solids}}$ is the measured carbon weight percentage of the feed solids.

Table 6-7. HTL Carbon Flow Rates and Carbon Balance.

Stream	Primary Sludge (WERF-02)	Secondary Sludge (WERF-03)	Digested Solids (WERF-04)
Feed (g/hr)	87.3	63.5	97.3
Biocrude (g/hr)	48.8	23.9	52.5
Aqueous Effluent (g/hr)	17.9	26.2	27.8
Solids (g/hr)	5.0	8.0	18.0
Gas Effluent (g/hr)	10.6	3.5	9.5
Carbon Balance (%)	94	97	111

Carbon mass balance values are all within the target range. Similar to the total mass balance values, the carbon balance for WERF-04 (111%) is higher than expected. The fact that both the total mass and carbon balances for this test are on the high side suggest a possible discrepancy with one of the overall flow rates, but no definitive reason has been provided by PNNL.

The CHG total mass balance and individual mass flow rates for each CHG test are shown in Table 6-8. The CHG mass balances are also performed in terms of feed and product flow rates, but the calculations are more straightforward since total liquid and gas product are quantified over the full test duration and are sampled at the same times. Note that no solids were found in the precipitator in any of the CHG tests, so that the only products in these tests were liquid and gaseous. The CHG total mass balance is calculated according to the following equation, with all components being mass flow rates:

$$CHG \text{ total mass balance} = \frac{\text{Aqueous product + Gas}}{\text{Aqueous Feed}} \times 100 \quad (\text{Equation 6-8})$$

Mass balance values for all of the CHG tests ranged from 88% to 95%, and all were within the target range of $\pm 15\%$ of closure.

Table 6-8. CHG Flow Rates and Total Mass Balance.

Stream	Primary Sludge (WERF2-CHG)	Secondary Sludge (WERF3-CHG)	Digested Solids (WERF4-CHG)
Feed (g/hr)	39.59	43.78	41.15
Aqueous Effluent (g/hr)	36.68	41.40	36.00
Gas Effluent (g/hr)	0.188	0.254	0.304
CH ₄ in gas effluent (g/hr)	0.100	0.247	0.291
Mass Balance (%)	93	95	88

The carbon mass balances for all CHG tests, along with mass flow rates on a carbon basis are provided in Table 6-9. The carbon balance is calculated according to the following equation, with %C values measured on a weight basis:

$$CHG \text{ carbon balance} = \frac{(mass \text{ flow} * \% C)_{aqueous \text{ product}} + (\sum \% V_i * \dot{V}_g * v_{i,C}) * P * MW_C / (R * T)}{\dot{V}_{aq} * \rho_{aq} * \% C_{aqueous \text{ feed}}} \times 100 \quad (\text{Equation 6-9})$$

where: %V_i is the measured volume fraction of carbon-containing species i in the CHG product gas,

\dot{V}_g is the volumetric flow of CHG product gas,

v_{i,C} is the moles of carbon per mole of species i,

P is the pressure,

MW_C is the molecular weight of carbon,

R is the universal gas constant,

T is the temperature,

\dot{V}_{aq} is the average volumetric flow rate of CHG feed,

ρ_{aq} is the feed density,

%C_{aqueous feed} is the measured carbon weight percentage of the CHG aqueous feed.

Table 6-9. CHG Carbon Flow Rates and Carbon Balance.

Stream	Primary Sludge (WERF2-CHG)	Secondary Sludge (WERF3-CHG)	Digested Solids (WERF4-CHG)
Feed (g/hr)	0.24	0.31	0.39
Aqueous Effluent (g/hr)	0.06	0.12	0.12
Gas Effluent (g/hr)	0.102	0.189	0.223
CH ₄ in gas effluent (g/hr)	0.075	0.185	0.218
Carbon Balance (%)	68	99	88

Two of the three CHG test carbon balance values were within the target range. The carbon balance for WERF2-CHG was unusually low (67%) and the only value outside the target range. Since the total mass balance for this test was much better at 93%, it would seem that any possible errors would be associated with carbon concentration measurements (since carbon balance terms are essentially the product of a flow rate and carbon concentration for each phase). PNNL has suggested that the carbon concentration of the feed is likely too high based on the low COD measurements in the aqueous product but also the low gas flow rate. However, carbon concentrations for the feed and aqueous product were both measured by the same lab and showed consistency among duplicate measurements. The amount of carbon in the gas phase of WERF2-CHG was lower than in the other CHG tests (about 50% instead of 75%), but PNNL has stated that the WTM and GC were both working properly. It should be noted that because of the low flow rates used in CHG tests, a small change in any carbon concentration measurement can have a significant effect on the balance.

A total mass balance for the combined HTL and CHG process is difficult to perform because the two PNNL bench-scale systems are operated independently and at different flow rates. In addition, no input and output data were recorded for the unanticipated ion exchange (IX) step that had to be performed on HTL aqueous product to remove sulfate before feeding through the CHG system. Nevertheless, it is possible to estimate a combined system overall mass balance if it is assumed that the full HTL aqueous product flow is sent to the CHG system, the mass loss in the IX process is negligible (because the HTL aqueous product is mostly water which is not lost), and that the measured CHG liquid and gas product quantities are scaled by the ratio of the HTL aqueous product flow (from Table 6-6) to the actual CHG feed flow (from Table 6-8). Thus, the combined total mass balance would be as follows:

$$\text{Combined total mass balance} = \frac{\text{Biocrude} + \text{HTL Gas} + \text{HTL Solids} + \text{scaled CHG Gas} + \text{scaled CHG Aqueous}}{\text{Sludge Feed}} \times 100 \quad (\text{Equation 6-10})$$

with

$$\text{scaled CHG aqueous flow} = \text{actual CHG aqueous effluent flow} \times \frac{\text{HTL aqueous effluent flow}}{\text{actual CHG feed flow}} \quad (\text{Equation 6-11})$$

The scaling factor for the primary sludge tests would be 1424/39.59 = 36.0. Similarly, the scaling factors for secondary sludge and digested solids tests are 33.6 and 35.9, respectively. The resulting flow rates are shown in Table 6-10, along with the corresponding mass balance values. All of the balance values range between 94-98%. Even at scaled CHG values, the biocrude

quantity generated is significantly more than methane gas on a weight basis and is the dominant fuel product.

Table 6-10. Estimated Combined HTL-CHG Process Total Mass Balance.

Stream	Primary Sludge (WERF-02)	Secondary Sludge (WERF-03)	Digested Solids (WERF-04)
HTL Feed (g/hr)	1541	1499	1570
HTL Solids (g/hr)	17.4	29.8	88.9
HTL Gas Effluent (g/hr)	37.2	11.5	29.6
Biocrude (g/hr)	73.4	33.5	77.3
CHG Gas Effluent (scaled) (g/hr)	6.8	8.4	10.8
CHG Aqueous Effluent (scaled) (g/hr)	1319	1391	1293
Mass Balance (%)	94	98	96

An estimated combined process carbon balance can also be calculated based on the same idea. In this case, the carbon loss observed by PNNL to occur in the IX process can also be taken into account. This can be done using the values of elemental carbon concentration measured for the HTL aqueous product before and after the IX process. Resulting flow rates and carbon balance values are shown in Table 6-11. Combined process carbon balance values range between 91-109%. By normalizing each flowrate by the appropriate individual HTL or CHG carbon balance values (from Table 6-7 or 6-9), an estimated combined process biocrude and methane yield on a carbon basis can be calculated. These values are also shown in Table 6-11. As stated in Section 6.2, the carbon loss that occurred during the IX step prior to CHG tests, likely results in a lower methane contribution to the combined yields shown in Table 6-11 than would otherwise be expected.

Table 6-11. Estimated Combined HTL-CHG Process Carbon Balance.

Stream	Primary Sludge (WERF-02)	Secondary Sludge (WERF-03)	Digested Solids (WERF-04)
HTL Feed (g/hr)	87.3	63.5	97.3
HTL Solids (g/hr)	5.0	8.0	18.0
HTL Gas Effluent (g/hr)	10.6	3.5	9.5
Biocrude (g/hr)	48.8	23.9	52.5
IX Carbon Loss ^a (g/hr)	8.8	15.1	13.9
CHG Aqueous Effluent (scaled) (g/hr)	2.3	4.3	4.3
CHG Gas Effluent (scaled) (g/hr)	3.8	6.8	7.8
CH ₄ in CHG gas effluent (scaled) (g/hr)	2.8	6.7	7.6
Carbon Balance (%)	91	97	109
Combined Biocrude + CH₄ Yield (%)^b	65	51	56

^a Determined from difference between Pre-IX carbon (HTL aqueous effluent flow from Table 6-6 multiplied by Pre-IX % C from Table 5-8) and Post-IX carbon (HTL aqueous effluent flow multiplied by Post-IX % C).

^b Calculated using biocrude values normalized by the HTL carbon mass balance value (from Table 6-7) and methane normalized by the CHG carbon mass balance value (from Table 6-9).

While not the main focus in this study, it is interesting to look at elemental balances for key species other than carbon. These other elemental balances were calculated similar to Equations 6-7 and 6-9, except with the measured elemental concentration of the species of interest instead of carbon. For HTL tests, elemental balances were calculated for nitrogen, phosphorus, and sulfur. Nitrogen and phosphorus in particular are of interest for use of this technology at wastewater treatment facilities because of the effect of these elements on water pollution and the associated regulatory limits on discharge of species containing these elements. HTL nitrogen balances were reasonably good (i.e., close to 100%), ranging from 102-111%.

Phosphorus and sulfur balances were not very good, however, ranging from only 46-78% for P and 66-73% for S. These low mass balance closures for P and S were not unexpected, as PNNL has stated that the P and S balances in all HTL tests are typically low. A possible reason for this observation may be related to the way the system is run. During normal operation, phosphorus and sulfur-containing salts (e.g., phosphates and sulfates) precipitate out of solution due to their generally low solubilities near the critical point and accumulate in the filter vessel (and in the CSTR as seen when there is a loss of mixing). Once the test is over, the system is allowed to cool with continued water flow for several hours. As the water temperature drops, any phosphate or sulfate salts in the system will start to go back in solution and would leave the system unrecovered, resulting in less solids in the filter vessel by the time the system is shutdown and opened up for examination. The same would be true for any salt buildup elsewhere in the system. Thus, the missing P and S mass might be accounted for in the lost amount of solids and would explain why these elemental balances are usually low while carbon balances show good closure.

In CHG tests, the only other elemental balance performed was for nitrogen. Values for WERF3-CHG and WERF4-CHG were low at 77% and 86%, respectively. The value for WERF2-CHG, however, was high at 127%. This was the same test that had the unusually low carbon balance value of 67%, indicating again a likely problem with elemental analyses for this test.

6.4 Effluent Quality

The following subsections discuss observations and results related to the HTL and CHG product phases other than biocrude.

6.4.1 CHG Aqueous Phase Product

In the combined HTL-CHG process offered by Genifuel, the CHG aqueous effluent is the liquid phase end product of the process, and is what gets discharged to the environment or recycled for another use. In the current test program, an additional step of ion exchange had to be added between the HTL and CHG steps. This was necessary to remove the relatively high concentrations of sulfate from the HTL aqueous effluent observed with each of the three sludge feeds in order to prevent poisoning of the CHG catalyst. This ion exchange step (not originally anticipated) added delays to the testing and additional complexity to the analysis, and is not representative of what would be performed in a commercial-scale system for sulfate removal. Tables 6-12 through 6-16 summarize key analytical data for the aqueous phase as measured for HTL effluent product, prior to IX, after IX, and as CHG effluent product for carbon, sulfur/sulfate, phosphorus/phosphate, nitrogen, and COD, respectively. COD values for sludge feed are also included in Table 6-16 for comparison.

Table 6-12. Summary of Aqueous Phase Carbon Data^a.

Sludge Feed	Post-HTL		Pre-IX		Post-IX		Post-CHG	
	%C	TOC	%C	TOC	%C	TOC	%C	TOC
Primary	1.26	11,700	1.88	17,100	0.64	5470	0.16	530
Secondary	1.78 ^b	15,940 ^b	1.92	NA ^c	0.705	6320	0.28	971
Digested Solids	1.88	17,000	1.82	15,100	0.94	8680	0.32	1130

^a TOC units are in ppm

^b Adjusted from analytical results of combined phase liquid product (due to oil inseparability) to remove calculated biocrude portion.

^c Not analyzed

In theory, data from the HTL aqueous phase product should be the same as pre-IX data, as they are the same material differing only in the time of their analysis. Post-HTL and pre-IX COD analyses (differing in time by several weeks) are generally in agreement, as well as that for carbon, sulfur, and phosphorus where available, confirming no change in sample composition over time under refrigeration.

Table 6-13. Summary of Aqueous Phase Sulfate and Total Sulfur Data^a.

Sludge Feed	Post-HTL		Pre-IX		Post-IX		Post-CHG	
	SO ₄	S	SO ₄	S	SO ₄	S	SO ₄	S
Primary	60.2	102	NA ^b	NA ^b	< 4.0	21.7	5.80	2.67
Secondary	161	157	NA ^b	NA ^b	< 4.0	46.0	< 4.0	< 1.0
Digested Solids	200	280	283	187	< 4.0	36.6	< 4.0	< 1.0

^a SO₄ and S units are in ppm

^b Not analyzed

Table 6-14. Summary of Aqueous Phase Phosphate and Total Phosphorus Data^a.

Sludge Feed	Post-HTL		Pre-IX		Post-IX		Post-CHG	
	PO ₄	P	PO ₄	P	PO ₄	P	PO ₄	P
Primary	24.6	11.9	NA ^b	NA ^b	< 4.0	< 1.0	< 4.0	< 1.0
Secondary	714	290	NA ^b	NA ^b	4.38	2.21	< 4.0	< 1.0
Digested Solids	72	33.1	47.1	33.8	< 4.0	< 1.0	< 4.0	< 1.0

^a PO₄ and P units are in ppm

^b Not analyzed

Table 6-15. Summary of Aqueous Phase Nitrogen, Ammonia, and pH Data^a.

Sludge Feed	Post-HTL			Pre-IX		Post-IX			Post-CHG		
	%N	NH ₃	pH	%N	NH ₃	%N	NH ₃	%N	NH ₃	pH	
Primary	0.26	1330	6.42	< 0.05	NA ^b	0.08	NA ^b	0.11	2080	9.30	
Secondary	0.66 ^c	4520	8.04	< 0.05	NA ^b	0.30	NA ^b	0.36	5520	9.35	
Digested Solids	0.57	4960	8.01	0.58	NA ^b	0.36	NA ^b	0.35	5430	9.13	

^a NH₃ units are in ppm

^b Not analyzed

^c Adjusted from analytical results of combined phase liquid product (due to oil inseparability) to remove calculated biocrude portion.

Table 6-16. Summary of Aqueous Phase COD Data^a.

Sludge Feed	HTL Feed	Post-HTL	Pre-IX	Post-IX	Post-CHG
Primary	187,000	41,000	40,800	20,300	54
Secondary	153,000	73,000	72,300	21,700	25
Digested Solids	203,000	48,200	49,900	23,700	19

^a COD units are in ppm

Average COD and TOC data for feed and aqueous products over the course of HTL and CHG testing clearly indicate a reduction in organic content of the aqueous phase for all three sludge feeds. COD values are reduced by about four orders of magnitude and TOC values by about two orders of magnitude. COD values of the CHG aqueous effluent product in particular were so low (19-54 ppm) as to be near the limit of reliable measurement for the method of analysis. Of some concern, however, is the fact that TOC values for the CHG aqueous effluent (530-1130 ppm) do not reflect the same level of conversion as their corresponding COD values. A rough rule of thumb suggests that the ratio of COD to TOC for a sample should be about 3, whereas COD/TOC values for these tests range between 0.02 and 0.1. Note that COD/TOC values for upstream measurements such as post-HTL aqueous phase and pre- and post-IX are all in the range of 3. Note also that TOC values in the CHG effluent are higher than COD values,

which is just the opposite everywhere else, and that the highest TOC measurement corresponds to the lowest COD measurement. All of the above suggests that either TOC or COD values for the CHG effluent may be in error. ICP and HPLC analyses of all CHG aqueous effluents indicated no metals or organic species of concern above detection limit.

Figure 6-1 shows the variation in individual sample COD values over the course of each CHG test starting from the point when steady state was declared (which is the origin on the time axis in this graph). COD values for the WERF3-CHG and WERF4-CHG tests are fairly steady and well-represented by the average COD values for these tests in Table 6-16. COD values for the WERF2-CHG test, however, continue to decrease significantly until a little over 10 hours after steady state was declared before leveling off. This trend suggests that steady state may have been declared too early in the WERF2-CHG test, at least with respect to COD data. While the WERF2-CHG test had the shortest duration at steady state of the three CHG tests, data in Table 4-7 shows that it had the longest total operating time on feed. The reason for the longer operating time on feed prior to declaring steady state in WERF2-CHG was due to difficulties with and the ultimate replacement of the BPR valve in this test.

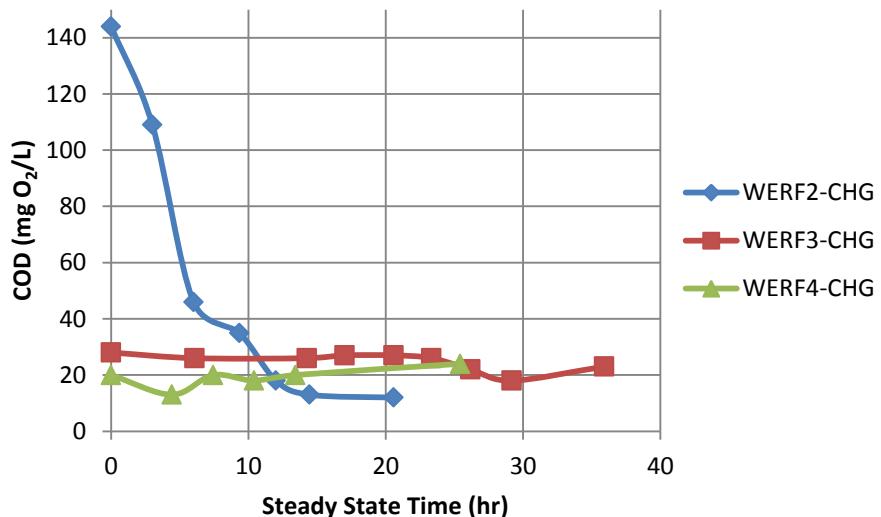


Figure 6-1. COD Values in CHG Aqueous Product as a Function of Elapsed Steady State Time.

Comparison of sulfate and total sulfur concentrations in the post-HTL aqueous effluent shows that sulfate constitutes between 20-33% of the total sulfur present, indicating the presence of other sulfur-containing compounds. Comparison of the post-HTL or pre-IX sulfate concentrations to their post-IX values in Table 6-13 suggests that the IX step was effective at removing most of this species. PNNL has stated that sulfate concentrations in the CHG feed should be less than 10 ppm. Post-IX concentrations of sulfate from the non-optimized IX step were all below the detection limit of 4 ppm, with total sulfur ranging from 22-46 ppm. These concentrations had no obvious impact on CHG operation or methane formation, although data from the CHG catalyst analysis shows that sulfur uptake and poisoning of the catalyst did occur in all tests (see Section 6.4.3). One undesirable side effect of the IX step was a loss of organic material. Elemental carbon and TOC analyses on pre- and post-IX samples show a drop in organic carbon by a factor of between 2-3 in all cases. This likely reduced the potential for methane production in all the CHG tests. The IX step also increased the pH of the aqueous phase fed to the CHG system, likely accounting for the reduced amount of CO₂ in the CHG gas effluent compared to that normally seen with other feeds.

In order to further evaluate the quality of the CHG aqueous effluent, the composition can be compared to regulatory limits for WRRF water discharge. This regulatory information was provided by several WRRF Steering Committee members that responded to a request made during this project. Data provided by the Tohopekaliga Water Authority (FL), City of Calgary, City of Orlando, and Metro Vancouver are shown in Table 6-17. As can be expected, values for certain limits vary from plant to plant depending on the specific location and local requirements, but the general categories of concern are consistent: Biochemical Oxygen Demand (BOD), total suspended solids (TSS) content, total nitrogen (TN) (and variations of this), total phosphorus (TP), and various indicators of bacteria count (i.e., sterility). Of these categories, the bacteria-related ones and associated indicators of disinfection (Cl content) are not relevant to CHG effluent because the combined HTL-CHG process, with operation under near-critical conditions for residence times on the order of tens of minutes, essentially functions as an autoclave with respect to microbial activity. TSS was not measured as part of the analytical work performed in this study on CHG effluent.

This leaves BOD, TN, and TP requirements to compare to measured data in this study. While BOD was also not measured in this study, it is an indicator of organic content similar to COD, except that it measures oxidation performed by biological species as opposed to abiotic chemical oxidation. Thus, BOD values are typically smaller than COD values. A rough rule of thumb relating the two quantities is that the ratio of COD/BOD is 2.1. Data for both HTL and CHG aqueous effluent to compare to the water discharge requirements can be found in Tables 6-14, 6-15, and 6-16. Upon making this comparison, none of the HTL aqueous effluents appear to meet any of the BOD, TN, or TP requirements. CHG aqueous effluent, on the other hand, appears to meet BOD and TP requirements for some of the WRRFs in Table 6-17, and is relatively close for those cases where it does not meet the requirements. Values for TN and NH₃ for CHG aqueous effluent, however, are about three orders of magnitude above the limits. Based on this limited comparison, CHG effluent quality might be sufficiently clean for direct discharge from a WRRF provided that a method for nitrogen removal (e.g., by air stripping) is added. As an alternative, the aqueous product may have value for its nitrogen content as a fertilizer. This is what is often done with systems designed for algae feeds, where the CHG aqueous effluent is sent to the algae growth ponds to utilize the nutrients.

It should be noted that other non-technical factors such as permitting, process control, or economic issues may play a bigger role in determining the ultimate fate of the aqueous effluent from an installed HTL-CHG system. It may be easier, for example, to simply recycle the CHG effluent back to the plant headworks and not have to deal with direct discharge. However, noting how close the data comes to meeting water discharge requirements is of value for providing another measure of the capabilities of the HTL-CHG technology.

If the CHG effluent is not discharged to the environment or otherwise utilized, it may make sense to consider whether the CHG step is needed at all. In this case, the HTL aqueous effluent could be sent back to the plant headworks. Since the quantity of gas production from CHG is less than that of biocrude from HTL (even when the CHG is scaled to the same rate as HTL aqueous phase production), most of the energy recovery is from the biocrude. As demonstrated in these tests, CHG functions primarily as a polishing step. If the effluent quality is not important, however, CHG may not be needed. An HTL-only system would reduce system

Table 6-17. WRRF Water Discharge Limits.

Analysis	City of Calgary			Metro Vancouver		City of Orlando		Tohopekaliga Water Authority (FL)
	Bonnybrook	Fish Creek	Pine Creek	Wastewater Systems Effluent Regulations (Federal)	Annacis Island (Provincial)	Iron Bridge	Water Conserv II	South Bermuda
BOD ₅ ^a	-	-	-	-	-	-	-	≤ 60.0 mg/L
cBOD ^b	< 15 mg/L	< 20 mg/L	< 15 mg/L	≤ 25 mg/L	≤ 45 mg/L	4.28 mg/L	20.0 mg/L	
TSS	< 20 mg/L	< 25 mg/L	< 15 mg/L	≤ 25 mg/L	≤ 45 mg/L	5.0 mg/L	5.0 mg/L	≤ 5 mg/L
pH	-	-	-	-	-	6.0 – 8.5	6.0 – 8.5	6.0 – 8.5
Total N	-	-	< 15 mg/L	-	-	2.31 mg/L	10.0 mg/L	≤ 20.0 mg/L
Total Kjeldahl N	-	-	-	-	-	2.14 mg/L	-	-
Total N, NO ₃ (as N)	-	-	-	-	-	-	-	≤ 12.0 mg/L
Ammonia-N	< 5 mg/L or < 10 mg/L	-	< 5 mg/L or < 10 mg/L	-	-	-	-	-
Ammonia (NH ₃)	-	-	-	< 1.25 mg/L	-	-	-	-
Total P	< 1 mg/L	< 1 mg/L	< 0.5 mg/L			0.2 mg/L	0.2 mg/L	
Total Residual Cl ^c	-	-	-	≤ 0.02 mg/L	< 0.1 mg/L	-	-	≤ 1.0 mg/L
Fecal Coliform	< 200 CFU/100 ml ^d	< 200 CFU/100 ml ^d	< 200 CFU/100 ml ^d	-	-	< 1 (75% of time), not to exceed 25	< 1 (75% of time), not to exceed 25	≤ 25 #/100 ml

^a 5-day Biochemical Oxygen Demand

^b carbonaceous Biochemical Oxygen Demand

^c For disinfection

^d CFU = colony-forming unit

complexity and cost. However, sending HTL aqueous effluent back to the headworks would introduce phenolic/aromatic compounds generated during HTL that the wastewater treatment process is not used to or not designed to handle, though there would be significant dilution involved in this action. In this case, the CHG process would need to be retained.

6.4.2 Siloxane Analysis of CHG Gas Phase

For WRRFs that utilize anaerobic digestion, siloxanes in the biogas produced are a particular problem. Siloxanes are compounds that contain the basic functional group of two silicon atoms bonded to an oxygen atom, thus being the silicon analog to an ether. They are man-made compounds that are utilized predominantly in the cosmetics and personal hygiene products industries. As a result, residues often end up in wastewater and processed at WRRFs. In the anaerobic digesters, siloxanes partition into the gas phase, or biogas. When this biogas is burned in an engine to recover its fuel value, the siloxanes are oxidized to silica. The silica is not only abrasive to engine parts but also can plate out on engine surfaces, forming a hard, insulating layer that impedes heat transfer.

Due to these issues with siloxanes in biogas, the Project Steering Committee requested that gas phases be analyzed for siloxanes. The gas phase product was analyzed from a total of five HTL and CHG tests. Since the CHG product gas could be used as a fuel due to its high methane content, the CHG tests corresponding to all three sludge feed types were sampled and analyzed for siloxanes (note that the digested solids CHG test that was sampled was WERF1-CHG instead of WERF4-CHG because it was not clear at the time of sampling whether the failed digested solids HTL test would be repeated). The remaining two samples were taken from the HTL product gas for the test with digested solids and with primary sludge (to represent pre-digester sludge). For analysis, the laboratory chosen by Silicon Valley Clean Water WRRF to analyze its biogas was utilized, along with the same siloxane analytical method and procedures used for biogas. This procedure analyzes for seven specific siloxane species and two siloxane precursors:

- ◆ Hexamethyldisiloxane (L2)
- ◆ Hexamethylcyclotrisiloxane (D3)
- ◆ Octamethyltrisiloxane (L3)
- ◆ Octamethylcyclotetrasiloxane (D4)
- ◆ Decamethyltetrasiloxane (L4)
- ◆ Decamethylcyclopentasiloxane (D5)
- ◆ Dodecamethylpentasiloxane (L5)
- ◆ Trimethylsilanol
- ◆ Tetramethylsilane

Results from the siloxane analyses are provided in Table 6-18. For comparison, the siloxane concentration limits in the inlet fuel specified for two common brands of gas engines (GE Jenbacher and MWM/Caterpillar) are also provided in Table 6-18. Concentrations were below detection limit for all species in all tests except for one (trimethylsilanol) in WERF1-CHG, which was only slightly above the detection limit. In all but one test, the detection limits were all well below (1-2 orders of magnitude) the limits for the two gas engine brands. The digested solids HTL test (WERF-04) had a relatively high detection limit compared to the other four samples due to a higher volatile organic compound background concentration than in other

samples, forcing a higher dilution and corresponding detection limit. Though the reason for the higher detection limit was unrelated to the siloxane concentration, this detection limit was still just below one of the engine limits. Note that because of its high CO₂ content and low fuel value, HTL product gas would not be utilized by a gas engine. HTL product gas was analyzed only to assess whether it was a sink for siloxane compounds. The overall results show that siloxanes do not appear to partition into the HTL or CHG gas phases, and should not be a concern for use of CHG product gas in gas engines.

Table 6-18. Summary of Gas Phase Siloxane Concentrations.

Test	Feed	Siloxane Concentration ^{a, b}
WERF-02	Primary sludge	All species < 263 ppb
WERF-04	Digested solids	All species < 2886 ppb
WERF1-CHG	HTL aqueous phase from digested solids (first test)	All species < 22.7 ppb except trimethylsilanol = 43.3 ppb
WERF2-CHG	HTL aqueous phase from primary sludge	All species < 43 ppb
WERF3-CHG	HTL aqueous phase from secondary sludge	All species < 40 ppb
Gas Engine Fuel Specifications^c		
GE Jenbacher (without oxidation catalyst)		< 3 ppm
MWM/Caterpillar (with oxidation catalyst)		< 800 ppb

^a Siloxane species analyzed for: hexamethylidisiloxane (L2), hexamethylcyclotrisiloxane (D3), octamethyltrisiloxane (L3), octamethylcyclotetrasiloxane (D4), decamethyltetrasiloxane (L4), decamethylcyclopentasiloxane (D5), dodecamethylpentasiloxane (L5), trimethylsilanol, and tetramethylsilane

^b Equivalent concentrations in units of mg Si/m³ are provided in Appendices A, B, and C

^c Source: Vandenburg (2012)

To better understand where siloxanes may be going in HTL and CHG tests, it is helpful to consider the total silicon values measured in each phase via ICP. Total Si data are also provided in Table 6-19. Given the fact that Si concentrations in each HTL phase are similar (in the range of 50-400 ppm) but that the aqueous product phase has the highest flow rate, most of the silicon appears to partition into the aqueous phase. The same is true in CHG tests. This partitioning of Si compounds primarily into the aqueous product phases rather than gas phases would clearly be preferred and would be a notable advantage of hydrothermal processing over anaerobic digestion.

Table 6-19. Summary of Total Si Data.

Stream	Total Si (ppm)		
	Primary Sludge Feed	Secondary Sludge Feed	Digested Solids Feed
HTL Feed	190	280	270
Biocrude	55	20,900	390
HTL Solids	80.5	206	82.9
HTL Aqueous Phase	260	190	301
CHG Feed (Post-IX)	7.9	40	139
CHG Aqueous Phase	24	17	53

6.4.3 HTL Solids

The HTL system is designed to take advantage of the low solubility of inorganic salts in the typical operating regime near the critical point of water to collect, concentrate, and remove them from the process flow. This is to prevent downstream fouling of the CHG catalyst. All solids recovered during testing were found mainly in the HTL filter vessel (or in the CSTR in the case of WERF-03 where mixing was lost). While a separator exists prior to the CHG reactor as a secondary means to ensure solids collection, no solids were found there in any of the CHG tests.

The digested solids feed produced the highest quantity of solids and the primary sludge feed produced the lowest quantity of solids during testing. This is consistent with the ash content and source of these feeds in the WRRF. Even with the highest amount of solids accumulation, none of the tests required blowdown of the filter vessel during operation, which the PNNL system design is capable of doing if necessary. At a high enough flow rate and long enough period of operation, one would expect that blowdown would eventually be required in the bench-scale system design.

Analysis of the solids produced in the HTL tests is summarized in Table 5-6. Of those species positively identified, two species (barium and chromium) are on the list of metals regulated by the U.S. EPA according to the Toxicity Characteristic Leaching Procedure (TCLP) test. A TCLP test is used to simulate leaching of solids within a landfill environment and is used to determine if a solid sample is considered hazardous for disposal purposes. Exceeding TCLP regulatory levels for any listed chemical species requires disposal of the solids as hazardous waste. Barium concentrations ranged from 579 -844 ppm over all HTL tests, while chromium concentrations ranged from 309-1070 ppm. The presence of these TCLP metals in the HTL solids alone does not indicate whether the solids are hazardous, since it is the concentration that would end up in the leachate that is regulated. However, the detection of these species in the solids may justify the performance of a TCLP test, which is the only way to determine whether or not the solids would be considered hazardous. Because nickel was also detected in the HTL solids, it is likely that both the Ni and Cr come from corrosion of high nickel alloy components (such as the Inconel CSTR) used in the heated portion of the HTL system, though some of the Ni may have come from the nickel-based anti-seize compound used by PNNL used on the sealing gasket in the CSTR. Because of the inherently variable nature of the sludge feed, the composition of the solids removed would be expected to vary over time.

As mentioned earlier, one particular species that PNNL actively tries to remove as a solid is sulfate. All sulfur-containing materials will negatively impact the Ruthenium catalyst used in the CHG reactor. The Raney nickel used in the entrance to the reactor is able to remove any reduced sulfur compounds, but it is not as effective for oxidized sulfur as in sulfate. PNNL utilizes the inherently low solubility of many inorganic salts in the near-critical and supercritical region to their advantage as a way of removing sulfate in the HTL system. The reason for this drop in salt solubility (which is related to the corresponding high solubility and reactivity of organic species that form biocrude) is related to the changing polarity of the water solvent as it approaches and exceeds its critical point. As temperature increases and density decreases, water begins to lose its hydrogen bonding, which directly affects its solvating power. This dramatic change in the nature of water is represented by the variation in the value of its dielectric constant and dissociation constant as shown in Figure 6-2 at the same fixed pressure as the current HTL tests. The dielectric constant of water decreases steadily with increasing temperature from a value of 80 under ambient conditions to a value of 14-21 between 300-350°C, which is equivalent to the solvent power of acetone and cyclohexanol at ambient conditions. The dissociation constant initially increases but then sharply decreases with increasing temperature by several orders of magnitude, showing the inability of water at the higher temperatures to stabilize ionic species.

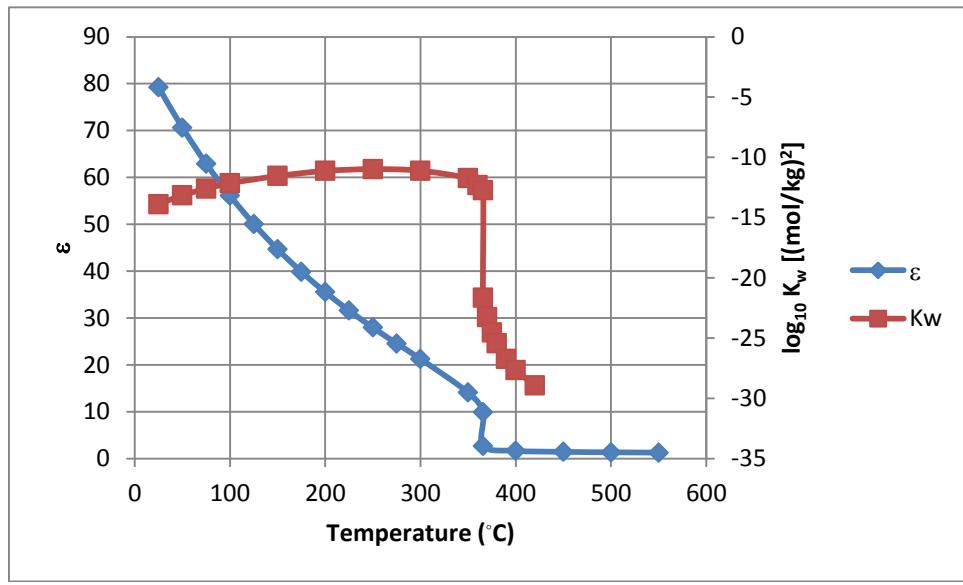


Figure 6-2. The Dielectric Constant (ϵ) and Dissociation Constant or Ion Product (K_w) of Water at 200 bar (2900 psi).

Note that water is a vapor at temperatures above 365.7°C at this pressure.

Data is taken from Uematsu and Franck (1980) and Tanger and Pitzer (1989).

PNNL has stated that the sulfate concentration in the aqueous phase HTL product/CHG feed needs to be at or below 10 ppm to avoid catalyst poisoning/fouling. Concentrations up to 100 ppm may be tolerated, but will require frequent catalyst replacement to the point where the process economics become significantly impacted. While all ionic species have solubilities on the order of 100 ppm or less under supercritical conditions, it is less predictable in the near critical region where HTL operates. Not all sulfates have concentrations low enough at the typical 300-350°C HTL operating temperature to meet the 10 ppm target. The HTL test results (Table 6-13) show sulfate concentrations in the HTL aqueous phase all above 100 ppm. During this test program, PNNL utilized ion exchange to reduce the sulfate concentrations prior to processing through CHG. This lowered the sulfate concentrations down to just below 10 ppm. This was enough to successfully process the aqueous phase through the CHG system for the relatively short time of operation in the bench-scale tests, though there were signs of catalyst poisoning occurring (see Section 6.5). However, ion exchange resulted in significant carbon loss and would likely be impractical and expensive to perform at the commercial scale. The goal would be to achieve greater removal of sulfate in the HTL system to avoid any additional post-HTL treatment prior to CHG.

How much sulfate is removed under HTL conditions depends on the cations available in the sludge feed, their quantity relative to the sulfate concentration in the feed, the corresponding solubility under operating conditions, and competition from other anions (such as phosphate). From ICP data for the sludge feeds (Table 5-3), Ca, Fe, Al, Cu, Mg, K, and Na are all species that could pair with sulfate, with Ca and Fe being present in the highest concentrations. Based on the ICP data for the HTL solids recovered, high concentrations of Ca, Fe, Al, and Mg indicate that these species did form insoluble salts. The fact that P is present in the solids at a concentration an order of magnitude higher than S indicates that there may not have been enough cations at the right solubility to remove all of the sulfate present (though it is desirable to remove phosphate too since it can also foul the CHG catalyst).

One way to potentially improve sulfate removal is to increase the HTL temperature in order to further drop its solubility. Although the target temperature of the filter vessel section of the PNNL HTL system was intended to be 350°C, it ranged only between 300-330°C in this test program. Maintaining the filter vessel temperature (and the rest of the reactor system) at 350-360°C would likely result in increased precipitation of sulfate (and other salts). This would be the simplest and most straightforward way to reduce sulfate concentrations in the HTL system design. Whether this increase in temperature alone would be sufficient to reduce sulfate concentrations down to the desired value is unknown, since it will depend on the particular salt species and concentrations present in the sludge feed and their specific solubilities. In separate tests with algae feed for a commercial client using a pilot-scale system, Genifuel has stated that it achieved comparatively more solids precipitation operating at 360°C than was observed in these bench-scale tests with sludge feed at PNNL. Operation above 360°C would not be recommended despite the further decrease in salt solubility on average with increasing temperature. Operating in the vicinity of the critical temperature (374°C) results in excessive instabilities in physical properties for stable operation. Operation at supercritical temperatures would also not be viable, as it would favor formation of gaseous products such as syngas instead of the desired liquid biocrude.

If increased temperature alone is insufficient for reducing sulfate concentrations down to the desired value, another option is to alter the feed chemistry to provide more cations that could pair with sulfate. This approach has already been used with supercritical water oxidation technology as a means to control salt composition and precipitation (Hazlebeck, 2001), although for limiting salt precipitation as opposed to encouraging it. The key aspect of this approach is finding an inexpensive additive that would have the desired < 10 ppm solubility at 350°C but also be sufficiently soluble under ambient conditions to blend homogeneously with the sludge feed. The additive would need to be added in a form where the associated anion does not negatively and inadvertently impact operation.

Of the additive possibilities, the alkali metals such as sodium and potassium have solubilities that are too high (still in single digits of weight percent) at 350°C to be of use (Figure 6-3). Alkaline metals such as calcium or magnesium may be a possibility. CaSO₄ in particular has a sufficiently low enough solubility, reaching a value of 10 ppm at about 230°C. The ideal candidate would have a high ambient solubility to ensure a homogeneous distribution in the feed but a low solubility (e.g., 10 ppm or less) at the reactor operating temperature. While many Ca salts have low solubility at ambient conditions, species such as Ca(NO)₃ or CaCl₂ do not and therefore are possible candidates for introducing Ca into the system. Given the nature of this application for use at a WRRF, however, adding more nitrogen to the feed may not be desirable, and adding more Cl could increase corrosion risks. Pairing Ca with an organic ligand is one way to add Ca without impacting operation, as the organic portion would in principle be converted to biocrude. Ethylene diamine tetraacetic acid (EDTA) is an example of a readily available organic ligand that could be used since its calcium salt (CaNa₂EDTA) is fully soluble at ambient conditions. A downside to EDTA is that it is somewhat expensive and contains nitrogen. Calcium oxide (lime) is a readily available compound that does not introduce undesirable elemental species, but it is only slightly soluble in ambient water. The fact that lime has the ability to remain in suspension may still make it worthy to consider.

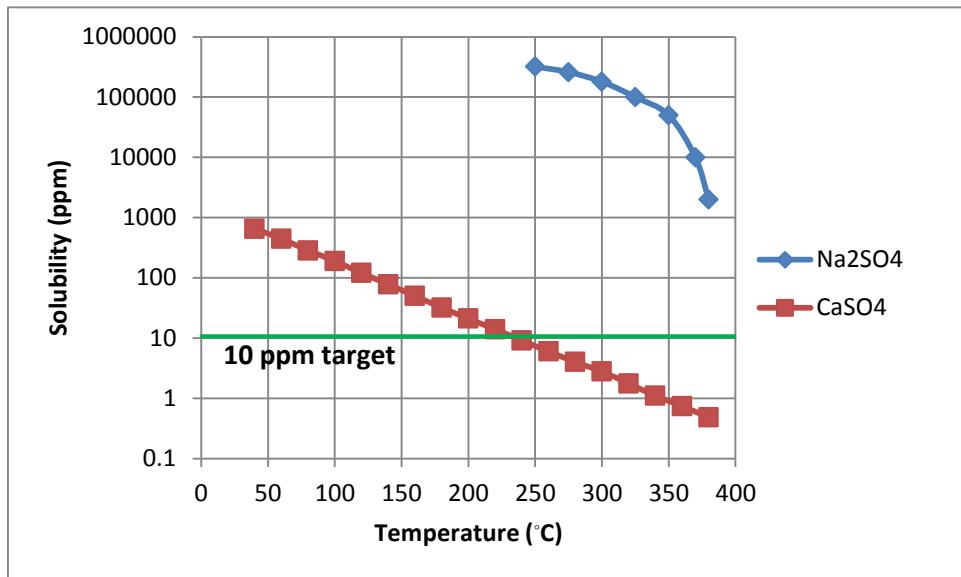


Figure 6-3. Salt Solubility in High Temperature Water.
Data from Marshall (1975), Martynova (1976), Ravich and Borovaya (1964), and Cobble and Lin (1989).

Genifuel and PNNL have recently begun development of an additive approach for sulfate removal, as presented in a recent patent (Elliott and Oyler, 2013). This patent proposes use of calcium ascorbate as the additive. Solubility data provided for sodium sulfate heated to a temperature of 350°C shows a sulfate concentration of 308 ppm, but when calcium ascorbate is added, the sulfate concentration drops to 22 ppm. Because of the inherent variability of sludge feeds, additives may not be needed if the viable cation species are present in sufficient quantities. The results of the present bench-scale tests indicate that an additive option needs to be available for a commercial-scale system and tailored to the feed by periodic monitoring of its composition. This approach will require empirical testing to find the optimal additive and should be verified with sludge feed at an appropriate scale before use.

The need to precipitate sulfate salts and consequent promotion of conditions to do so in the HTL reaction zone carries its own inherent risk of potential system plugging if solids precipitate in the wrong location. There does not appear to be a strong history of this occurring in the PNNL bench-scale system in previous testing. However, the buildup of solids in the CSTR in response to the loss of mixing, the snake-like plug found at the entrance to the PFR, and poor system performance during the HTL test with secondary sludge indicates that plugging can be a potential problem if conditions deviate from normal. The presence of solids in the CSTR at the end of the repeated digested solids test indicates that solids accumulation over time may also impact performance even under standard conditions. This risk of solids accumulation could be mitigated somewhat in a larger-scale system by the larger overall piping diameters and component sizes and the associated higher flow rates. Under normal operating conditions, PNNL appears to rely on a sufficiently high turbulent flow, generated in part by mixing in the CSTR, to mitigate the risk of solids settling out prior to reaching the filter vessel. In this respect, the approach is similar to the high velocity approach that has been used in the past in some tubular SCWO reactor systems (Marrone et al., 2004).

Past tests by both Genifuel and PNNL have utilized several different reactor combinations including the CSTR and PFR in series as used in the current tests, dual stirred

reactors in series, and use of only a single PFR. The CSTR/PFR combination as utilized in this test program allows the benefits of homogenization, gradual heatup, and enhanced mixing that the CSTR provides along with a guaranteed minimum residence time provided by the PFR. This reactor design approach can work, as was demonstrated, but the design needs to ensure that potential dead zones where solids could accumulate and/or bridge are avoided, and process conditions during operation must be closely monitored to ensure sufficient flow is maintained. The use of CSTRs over PFRs provides lower risk of plugging but has the downside of not all feed having the same fixed residence time. The residence time concern can be reduced by the use of multiple CSTRs in series. In a recent pilot-scale system built for a commercial client, Genifuel utilized two CSTRs in series. The use of CSTRs could also provide another point for controlled solids accumulation without interfering with the main process flow if operated similar to a reverse flow tank reactor (Hong et al., 1989). In this case, both feed and effluent flow would enter and exit through the top of the CSTR rather than feed entering the bottom as in the current design. Though Genifuel believes that the mixing achievable with two CSTRs provides superior results to that attained with a PFR, Genifuel would still consider use of a hybrid CSTR/PFR system in future applications since the reactor choice will depend on the needs and behavior associated with the specific feed and situation.

6.4.4 HTL Effluent Gas Product

The HTL gas product consists mostly of CO₂ (resulting from the water gas shift and decarboxylation reactions that occur during liquefaction), with trace amounts of other hydrocarbon species and H₂. It does not have any value as a fuel. There is concern with the level of hydrogen sulfide (H₂S) detected in the HTL tests with all three sludge types. The measured H₂S concentrations in these tests (0.33% vol, 0.40% vol, and 1.53% vol for primary sludge, secondary sludge, and digested solids tests, respectively) are well above the typical alarm limits for exposure of about 10 ppm. The presence of H₂S in the HTL product gas will require that a method be determined to reduce or remove the compound from the product gas prior to venting. This additional step will add to the process cost. Genifuel has stated that at the concentrations indicated, they would use air mixing to reduce the H₂S concentration.

6.5 CHG Catalyst Performance

There were no obvious problems with either the Raney nickel (reduced sulfur stripping material) or ruthenium catalyst in any of the CHG tests performed. In all tests, methane was the dominant gaseous product, as desired, with no drop-off in concentration observed up through the last sample taken. This corresponds to exposure of the Raney nickel and catalyst to 31-49 hours of feed over the three CHG tests performed representing the HTL aqueous product at steady state (52-85 hours if including the startup CHG feed representing HTL aqueous product before steady state).

For this test program, the Raney nickel and Ruthenium catalyst were replaced fresh for each test and inspected at the end of each test. The catalytically active form of the Ruthenium is its reduced state, which is pyrophoric. When still active catalyst is removed from the reactor and exposed to air, it reacts with the air, exhibiting a red glow as it starts to burn the graphite base. According to PNNL staff, these observations are what signify that the catalyst is still effective at the end of a test.

PNNL reported that after each test, the catalyst was active. However, ICP analysis of the recovered catalyst from each test show sulfur concentrations at the thousands of ppm level

(Table 6-20). Based on PNNL past experience, these sulfur concentrations suggest that catalyst poisoning was occurring, since sulfur concentrations for non-poisoned catalyst should be generally less than about 1000 ppm for a duration similar to that of these CHG tests. This would suggest that the ion exchange step utilized was not sufficient to avoid catalyst poisoning even with sulfate concentrations reduced to below the 10 ppm target. Based on the limited testing performed, it is unclear how much longer the catalyst would last beyond that tested before needing to be replaced. However, signs of poisoning after a relatively short duration of testing as in this test program provides additional incentive to improve the method used for sulfate removal from the CHG feed. The alternative would be to plan on frequent periodic replacement of the catalyst at commercial-scale with these feeds.

Table 6-20. Summary of Total Sulfur and Phosphorus Concentrations on CHG Catalyst After Each Test.

	WERF2-CHG		WERF3-CHG		WERF4-CHG	
	Raney Ni	Ru/C	Raney Ni	Ru/C	Raney Ni	Ru/C
Total Sulfur	4100	1700	16,000	3400	9900	1410
Total Phosphorus	< 30	< 30	156	229	< 35	< 35

Even if the sulfur poisons can be sufficiently removed/reduced from the CHG feed, it is unclear from the short duration testing whether the organic species in the CHG feed might slowly deactivate the catalyst over time by coking. The current test program was not designed to answer this question, but it would be another important point to assess in determining catalyst lifetime and any CHG feed pretreatment requirements. Genifuel claims that PNNL has never seen catalyst coking in previous tests with other feeds when operating at the correct temperature, but that would need to be verified at sufficiently long durations (e.g., several hundred hours) with the current feeds.

6.6 System Performance

While the PNNL bench-scale system tested as part of this test program is not fully representative of a commercial-scale HTL-CHG system, there are certain aspects of operation which are relevant to evaluating system performance. Measured quantities of biocrude per each set-aside are one indicator of the time needed to achieve steady state and the stability of the system once at steady state in the HTL system. Biocrude production rates for each HTL test as a function of time are shown in Figure 6-4. In most cases, PNNL declared steady state at a point 3-4 hours after the start of feed. Based on the measured rates of biocrude production, it may have taken slightly longer for steady state to be reached. For the digested solids and primary sludge tests, biocrude rates continued to fluctuate or rise during the first one or two set-asides after steady state was declared but appeared to level off by the last two set-asides. Operation in Baseline mode for a few more hours may have resulted in a more accurate steady state, and at least for the primary sludge test, may have resulted in a higher average biocrude yield. Biocrude values for the secondary sludge test appear to be more consistent during steady state, but these values are based on the analysis of only one set-aside due to the difficulty in oil separation in this test.

The CHG system in general took a much longer time to reach steady state than the HTL system, primarily due to the slower flow rate. Based on liquid and gas analytical data, the declared start of steady state for some of these tests may have been a little too soon also. For example, in WERF2-CHG, COD values in the aqueous effluent continued to decrease up to six hours after the declared start of steady state before appearing to level off. In WERF3-CHG,

unexplained N₂ concentration in the gas effluent continued to decrease for a significant portion of steady state. This may in part explain the long duration of these tests.

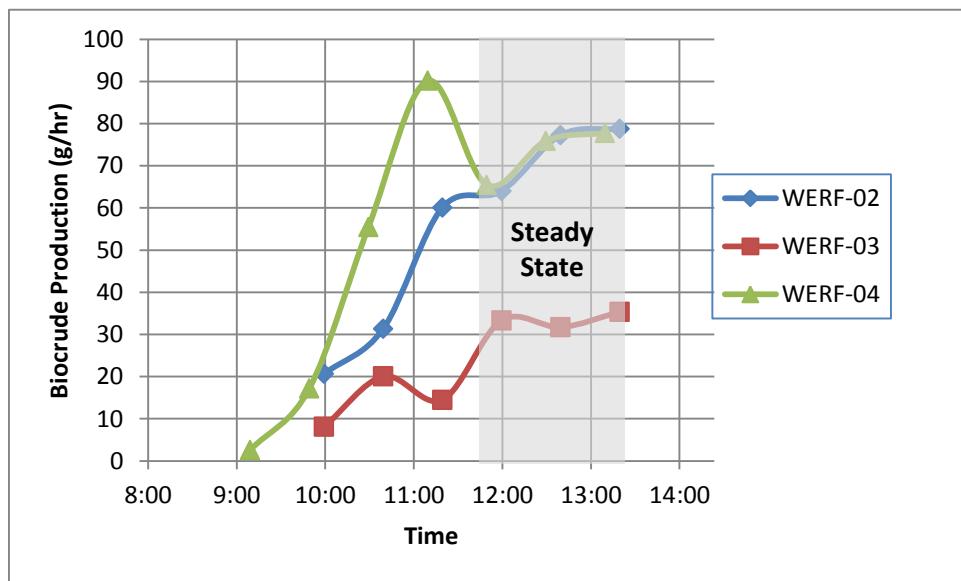


Figure 6-4. HTL Biocrude Production Rates Over Time.

Temperatures in the heated section of the HTL system showed a wider range than would be expected during testing. The average temperature difference across the CSTR and PFR alone in the primary sludge and digested solids tests was about 35°C. This span increased to about 55°C in the digested solids test when including the heated filter vessel. The secondary sludge test had an average temperature difference across the CSTR and PFR of about 82°C, though temperature measurements in the CSTR were likely impacted by an insulating layer of solids buildup due to loss of mixing and may therefore be somewhat artificial. These temperature differences are significant enough that they may impact reaction conversion. The biggest temperature differences occurred between the CSTR, PFR, and filter vessel, suggesting significant heat loss from the connecting fittings and piping. The HTL system appeared to be well insulated and lined with heating tape, but this may not be sufficient based on temperature data from these tests. Maintaining consistent temperatures closer to the target 350°C should result in better biocrude yields and better solids removal efficiency due to the lower solubility at higher temperatures. CHG temperatures were much closer to target with less deviation, though the heated reactor section is smaller and simpler (i.e., less components).

From a mechanical stability perspective, both systems behaved reasonably well. The most significant equipment problem observed with the HTL system was the detachment of the CSTR impeller from the stirring rod and consequent loss of mixing. Despite the impact of the event on performance, the problem was relatively easy to fix. In the CHG system, the most significant problem that occurred were several instances of plugging of the BPR, which needed to be replaced several times over the course of testing. As planned, maintainability and availability of the bench-scale system were not evaluated due to the relatively short operational time and the significant differences between the bench-scale design and potential commercial-scale systems.

With respect to reproducibility, HTL data is limited to data gathered in consecutive steady state set-asides spanning a total of two hours, or gaseous data spanning a separate steady state period of 1-1.5 hours. Data was generally consistent over their respective periods of operation, though more stable near the end of the steady state Baseline period (as discussed above) for liquid collection. The relatively short and separate HTL steady state periods for liquid, gas, and solid samples makes it difficult to fully assess long-term reproducibility. This would need to be demonstrated from longer term operation with samples for each phase taken at the same time, or from replicate tests. While CHG tests had steady state periods of longer duration, all three aqueous phase set-asides had to be combined to have enough feed to perform a sufficiently long enough CHG test, rather than processing each aqueous set-aside consecutively in series as originally intended. This eliminated the opportunity to look at reproducibility in CHG tests.

WERF-01 and WERF-04 were replicates in some respect since they were performed with the same digested solids feed. However, WERF-01 ended prematurely when the HTL system shutdown due to operator error. Only a single sample was obtained that may or may not have been at steady state. The corresponding CHG test had to be performed mixing all of the initial unsteady state aqueous phase HTL product with that from the single steady state sample to have enough feed to perform a CHG test. WERF-04 and WERF4-CHG lasted their full duration with a complete set of samples taken, and provide a much more credible picture of digested solids performance. The biocrude yield from WERF-01 (31%) and gas yield from WERF1-CHG (27%) are notably lower than their WERF-04 and WERF4-CHG counterparts, possibly reflecting the lower organic concentrations in the limited amount of feed reflecting full steady state. Other data from WERF-01 and WERF1-CHG, such as elemental analyses and physical properties such as density and pH, are in better agreement with data from WERF-04 and WERF4-CHG.

CHAPTER 7.0

ECONOMIC POTENTIAL

Consistent with the nature and scope of these proof-of-concept tests, a full economic analysis of the HTL-CHG system was not planned. The PNNL bench-scale HTL and CHG systems used for this test program have been designed for research and are neither energy efficient nor do they fully represent the configuration and economic aspects of a commercial-scale system as would be supplied by Genifuel. A full economic analysis would require detailed capital and operating cost data (including utilities and labor) for a specific location and WRRF design. This level of analysis is both beyond the scope and budget of this study and is not appropriate or reliable for the first time bench-scale tests performed with these sludge feeds (though it may be relevant as a next step based on this study's results). Nevertheless, from the bench-scale data that was collected, observations made during testing, and information provided by WRRFs on sludge disposal options, insight is provided in this section on some potential economic impacts of the HTL-CHG technology at commercial-scale.

7.1 Implications from Tests Results

All three sludge feeds were able to be pressurized and pumped through the HTL system without difficulty in this test program. While syringe pumps would not be used in a commercial-scale system, there were no obvious issues with any of the sludge feeds that suggest these feeds could not be pumped at a larger scale or would require specialized equipment beyond pumps capable of handling feed slurries. Opportunity exists to optimize the sludge solids concentration for all three feeds to further improve biocrude yields (and increase reactor volume utilization). In particular, secondary sludge needs to be further concentrated. It has been stated that this is possible with more robust dewatering processes (e.g., larger scale centrifuge). The literature of one vendor (Havrin, no date) claims that secondary sludge can be concentrated up to 18% solids with its decanter centrifuge. Several other sources claim that secondary sludge can be effectively treated by standard mechanical dewatering equipment such as belt presses and centrifuges (e.g., WEF, 2010). From a technology standpoint, centrifuges are well known in the wastewater treatment industry, especially for digested solids or biosolids concentration. However, adequate dewatering of secondary sludge should be demonstrated because nothing attempted in this test program appeared to be successful in dewatering secondary sludge to the same extent as the other sludges tested or to the desired target range (15-20 wt% solids). This is important because the solids concentration impacts the biocrude yield, which directly affects the economics of the HTL. Successful dewatering demonstration will help determine the particular equipment and specific operating conditions necessary to achieve the target solids concentration. No additional pre-treatment appears to be necessary to process sludge through HTL.

During normal operation, there was relatively little system fouling or plugging observed in the HTL reactor configuration of CSTR and PFR in series. However, with a high solids feed such as sludge, the margin of error is small when conditions deviate from normal, as evidenced by the solids buildup in the CSTR and at the PFR entrance in the secondary sludge test where mixing stopped near the beginning of the test. While larger size piping and cross-sectional areas

provide greater margin against solids buildup, anything that disrupts the required turbulence and high flow may result in excess solids accumulation prior to the filter vessel. This is of particular concern if additives are used to better ensure precipitation of sulfate at reactor temperatures. Excessive solids buildup would result in downtime due to system shutdown and maintenance (e.g., to open up and clear out the system).

When functioning properly, all solids should accumulate in the filter vessel. The test durations in this program were not long enough to reach a point where the filter would need to be cleared by blow down of solids and/or backflush. Thus, it is not known from the current tests what the frequency of filter cleaning would be with these sludge feeds. While the provision exists for solids blow down from the filter vessel in the present design, frequent filter cleanings could impact operational time and economics at commercial-scale. If the blowdowns are too frequent, the filter vessel needs to be larger.

The most valuable products from hydrothermal processing of sludge are the biocrude generated from HTL and methane gas from CHG. Of the two, the biocrude is the more important, since it is generated in higher quantities (even when the CHG flow is normalized with the HTL liquid effluent flow). As discussed in Section 6.2, the biocrude produced in these tests has about 76-84% of the heating value (HHV) of crude oil. This means that it would take about 1.2-1.3 times the amount of biocrude generated from sludge to provide the equivalent amount of energy as standard petroleum crude oil. This heating value comparison is one factor to consider when attempting to quantify the value of biocrude. Because of the high acid number and percent oxygen in biocrude compared to petroleum crude oil, the biocrude value would be further decreased. Determining exactly how much the biocrude value is decreased relative to petroleum crude is difficult due to the limited data available in this area. One study assigned a 15% discount for pyrolysis oils derived from biomass relative to the price of crude oil (Badger et al. 2011). Because of its claim that HTL oil is superior to pyrolysis oil, Genifuel believes that any discount should be less than 10%. A comparison of the price of Venezuelan crude (a low quality petroleum crude often compared to biocrudes derived from biomass) to standard petroleum crude over the past year also shows about a 15% difference in price. However, the actual price of biocrude is highly variable and will depend on what is negotiated between the buyer and generator, subject to the factors described above.

To realize the value of the biocrude produced, a WRRF has several options:

1. Upgrade the biocrude and sell it to a refinery (or find a refinery that can already upgrade it).
2. Upgrade the biocrude and utilize it on-site as boiler fuel.
3. Sell the biocrude as generated to a refinery.
4. Utilize the biocrude as generated on-site.

Upgrading the biocrude would remove the oxygen and reduce the acid number to produce an oil quality that is similar to petroleum crude. This would make it more valuable to a refinery or easier to burn on-site without equipment materials constraints, but would add the cost of upgrading to that of running the HTL-CHG process. At the oxygen concentrations measured in the biocrudes generated in this test program (Table 5-4), it would be possible to upgrade via conventional hydrotreating. This hydrotreating would require multiple reactors with limited temperature increases between the reactors. Utilizing the biocrude as produced avoids the cost of upgrading, but restricts how it could be used. The biocrude generated in this test program (as

with most biocrudes derived from biomass) would likely not be accepted by a conventional refinery unless the refinery were large enough that it could be blended with the incoming crude oil feed without significant impact on the overall composition of the petroleum crude, or already has the equipment to upgrade. Burning the biocrude as generated onsite is the simplest option and the easiest to assess a value to the biocrude (i.e., equivalent to the amount of conventional fuel that does not need to be purchased). However, burning the biocrude on-site would likely require a one time cost upgrade to more expensive materials of construction for the existing burners to accommodate the high TAN values in the biocrude (TAN values in crude oil above 1.0 mg KOH/g are considered high).

The CHG product gas derived from secondary sludge and digested solids (WERF3-CHG and WERF4-CHG) had compositions very similar to natural gas. Natural gas has a typical composition of 87-96 vol% CH₄, 1.8-5.1 vol% C₂H₆, 0.1-1.5 vol% C₃H₈, 0.1-1.0 vol% CO₂, and trace-0.02 vol% H₂. The typical HHV of natural gas ranges from 36-41 MJ/m³. Comparing the CHG product gas composition and calculated HHVs in Tables 6-4 and 6-5 with these values, WERF3-CHG and WERF4-CHG differ mainly in having a slightly higher H₂ concentration, which is likely due to the large concentration of water present as the reaction medium and the effect of the water gas shift reaction. Product gas derived from primary sludge had a notably higher CO₂ concentration, which reduced the HHV. By using the price of natural gas and scaling by the HHV relative to natural gas, a value could be assigned to the CHG product gas. Because of the relatively low quantities of CHG product gas generated compared to that of biocrude, the most likely use of CHG product gas is as a replacement for fuel gas on-site at the WRRF as opposed to offsite sale. Thus, the real value of the CHG product gas is by the reduction of natural gas that needs to be purchased by the plant.

Both the biocrude and CHG product gas generated from the HTL-CHG process may have additional value with respect to greenhouse gas (GHG) emissions and carbon offsets. With global efforts currently underway to control GHGs, the HTL-CHG process offers the economic advantage of off-setting fossil fuel requirements through its production of biocrude (from this study, about 80% of the energy value of petroleum crude) and methane. This is significant because in some areas (e.g., British Columbia and Alberta, Canada), industries are under a carbon tax and have a high incentive to displace fossil fuels with renewable fuels, with the value of carbon set at \$30/metric ton or more. Also, some organizations (e.g., Google, Inc.) have adopted “green” policies and are willing to pay a premium to reduce their GHG emissions or buy carbon offsets. To get an accurate assessment of the full GHG reduction/carbon offset potential of the HTL-CHG process would require also quantifying the energy input to the process, which can only come from operation of a more representative system to what would be utilized at a WRRF, not the bench-scale system of the present study. Performing a GHG emission and carbon offset analysis as part of future, larger-scale tests is recommended.

There are three main process effluents requiring disposal – CHG aqueous product, HTL effluent gas, and HTL solids. As discussed in Section 6.4.1, the CHG aqueous product should meet WRRF discharge requirements except for nitrogen and pH. The pH values were high (> 9) in these tests, but this was likely a result of having to perform the ion exchange for sulfate removal. However, pH adjustment is relatively easy to achieve, though there would be a cost associated with the acid required for neutralization. Nitrogen removal would require an additional process step (e.g., air stripping) and would be more costly to implement. It may also

be possible to capture the nitrogen rather than waste it. As an example, membrane systems are currently being developed and tested in WRRFs to capture ammonia (Govind, no date). If successful, nitrogen capture could generate another revenue stream while eliminating nitrogen from the plant. Recycling of CHG aqueous effluent back to the WRRF headworks would eliminate the need for any further treatment of this stream and the need for disposal. In this case, because the CHG process functions mainly as a polishing step, one might also consider eliminating CHG and recycling the HTL aqueous product to save further cost. HTL effluent gas has no real value but must be treated to reduce or remove the H₂S content before the gas can be safely released to the atmosphere or otherwise disposed.

HTL solids are mostly inorganic in composition and would need to be disposed. However, the solids disposal quantities from HTL are much smaller compared to sludge quantities if all of the sludge were disposed instead of processing via HTL. Based on current test results when comparing the solids produced relative to the sludge feed, the HTL process reduced the amount of solid material to be disposed by 94-99% (Table 7-1). Note that since sludge is sent offsite for disposal at a solids concentration comparable to that tested (see Section 7.2), it is valid to compare the weight of HTL solids to the full weight of the sludge feed when determining the percentage of weight reduction. The low value corresponds to the digested solids feed, which already has a higher ash content because of the preceding anaerobic digestion process. As discussed in Section 6.4.3, analysis of the HTL solids from this test program indicated the presence of the TCLP regulated metals barium and chromium. The chromium may be from corrosion of high nickel alloy process equipment. The source of barium is unknown and may have come with the batch of sludge feeds that were provided at the time they were collected. A TCLP test would need to be performed to determine if the HTL solids would need to be disposed as hazardous waste, which would increase the cost of their disposal. Because of the inherently variable nature of wastewater, solids concentrations would need to be analyzed periodically to ensure continued compliance with respect to regulated species.

Table 7-1. Solids Reduction and Ash Concentration Data from HTL Tests.

	Primary Sludge (WERF-02)	Secondary Sludge (WERF-03)	Digested Solids (WERF-04)
Sludge Feed (g/hr)	1541	1499	1570
Sludge Ash (wt%)	7.5	16.2	28.1
HTL Solids (g/hr)	17.4	29.8	88.9
HTL Solids Ash (wt%)	64.4	64.5	73.3
HTL Solids Weight Reduction (%)	99	98	94

Based on the COD and TOC reductions achieved in the current tests, the CHG Ruthenium-based catalyst appears to be effective for aqueous feeds derived from HTL tests with all three wastewater sludges. Based on the high concentrations of sulfur found on the Raney nickel after each test, this (reduced) sulfur stripping material also appears to have been effective, though it is unclear if the Raney nickel was fully saturated. Both Raney nickel and Ruthenium have been used for sulfur removal and methane generation, respectively, in previous sub- and supercritical treatment processes for a wide range of biomass. Sulfur concentrations on the catalyst after each test, however, indicate that sulfur poisoning was occurring, even with sulfate concentrations in the CHG feed reduced by ion exchange to less than 10 ppm. It is not clear whether the sulfur compounds getting through to the catalyst were reduced sulfur compounds or sulfates, and thus whether the sulfate limit was too high or if there was an insufficient amount of

Raney nickel for these feeds. While system performance appeared to be unaffected by the poisoning up to the maximum feed time run in these tests (about 85 hours) at the feed rate tested (~ 40 ml/hr), it is not known how much longer the catalyst would be effective and thus how frequent the catalyst would need to be replaced. While Raney nickel is relatively inexpensive (\$33/lb as recently purchased by Genifuel), the Ruthenium catalyst is more expensive (\$114/lb for last purchase by Genifuel). PNNL has stated that having to replace the catalyst more than once or twice a year would be uneconomical.

A more practical means of sulfate removal than ion exchange needs to be developed for commercial-scale operation, though this may be as simple as operating at a high enough temperature (e.g., 350–360°C). In addition, longer duration tests are needed to determine the Raney nickel and catalyst lifetime/replacement frequencies, and any additional controls on sulfur if necessary in order to verify the economic viability of the CHG process with sludge feeds.

One aspect that was not specifically addressed in the current test program but is of great interest to WRRFs is the fate of trace organic contaminants in the HTL-CHG process. These trace organic contaminants found in wastewater consist of flame retardants, antimicrobial agents, hormones, pharmaceuticals, and pesticides. Most of these species are present at low concentrations, but are of increasing concern for regulators based on their impact when released back into the environment. Some specific examples of these contaminants are nonylphenol (surfactants that are suspected endocrine disruptors), acetaminophen (a ubiquitous analgesic), estrone (a hormone that can affect wildlife reproductive systems), and malathion (a pesticide). These chemical species are often large molecules, sometimes containing a number of heteroatom species such as chlorine, fluorine, bromine, phosphorus, sulfur and/or nitrogen. Many of these chemical species are also difficult to completely destroy by conventional means such as anaerobic digestion in the typical wastewater treatment process.

In hydrothermal processes with added oxidant that operate in the supercritical regime, such as SCWO, there is a large data base that shows that these trace organic contaminants are completely destroyed (Tester et al., 1993). The relatively milder conditions of HTL and CHG are designed generally not to destroy but to reform organic species into more useful substances (as demonstrated in this test program). While not fully destroyed, the original molecular structure of large molecules such as these trace contaminants are often broken up in HTL and CHG to a sufficient degree that the remaining molecular fragments no longer resemble or have the same undesirable chemical properties of the original compound. However, because of the milder temperatures and smaller data base available, this cannot be said for certain with all contaminant species. Verification of the elimination of problematic trace contaminants in CHG effluent would be an additional significant economic advantage to the use of HTL-CHG technology at WRRFs. Future work should focus on identification of the most critical trace contaminants to the wastewater industry and demonstration of their fate after HTL-CHG via analysis for these species.

It is worth noting that incorporation of HTP technology into a WRRF design would require mechanical dewatering of the sludge prior to HTP treatment, in contrast to plants with anaerobic digestion where dewatering follows the treatment (Figure 7-1). Mechanical dewatering of undigested sludge (rather than digested sludge) is an area with which the wastewater industry has limited experience and would create a new centrate or filtrate stream of unknown

composition that would have to be recycled back to the headworks. In order to ensure that the filtrate stream composition can be handled and is compatible with plant operation if an HTL-CHG system were to be installed, the filtrate will need to be characterized. Future work should include sampling and analysis of the expected filtrate resulting from dewatering of undigested sludge via a representative technology to address this data gap.

Wastewater Treatment with Hydrothermal Processing

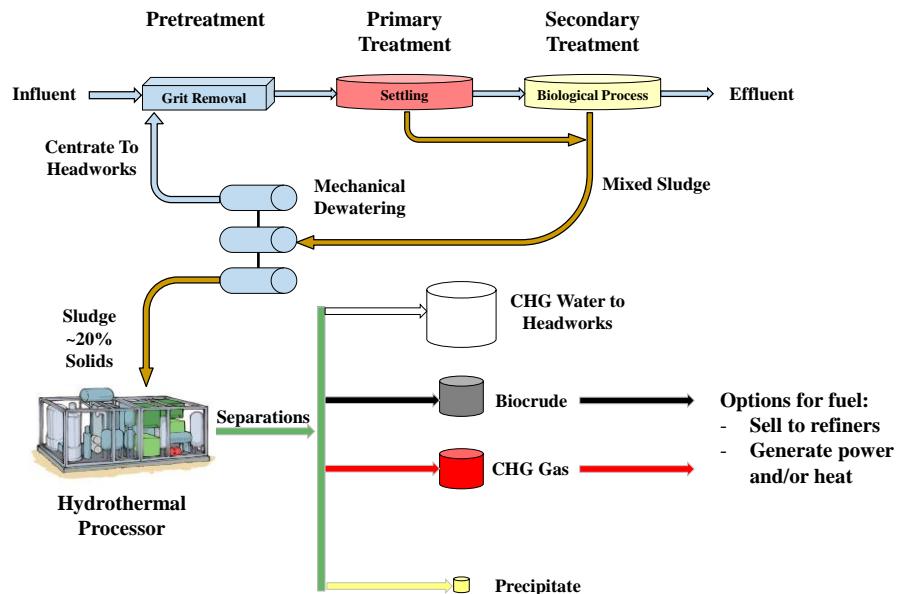


Figure 7-1. Proposed WRRF Process with Incorporated HTP Technology.

7.2 WRRF Sludge Disposal

While energy recovery in the form of biocrude and methane are an important advantage of hydrothermal processing offered by the Genifuel system, another advantage is the potential to minimize off-site waste solids disposal costs. To understand current methods of handling sludge at WRRFs, information was provided by several WRRF Steering Committee members. Data was provided by the Tohopekaliga Water Authority (FL), City of Calgary, City of Orlando, Metro Vancouver, and Santa Rosa Water, and is summarized in Table 7-2. The table shows the types of sludge that are handled at each plant, the method and ultimate fate of disposal, and the cost to prepare and dispose of the sludge.

Even among the five WRRFs that provided information, there is significant variability in the types of sludge and methods of handling, even for different plants within the same organization. Some of this variability reflects the nature of the local wastewater input, different state or provincial requirements, and regional preferences/culture. However, for all five facilities, sludge is ultimately shipped off-site at a cost ranging between \$21-102/wet ton or \$121-645/dry ton (ignoring the compost disposal option). Thus, there is the potential for significant cost savings if the volume of solids requiring disposal (and associated preparation work) can be reduced. Note that the solids concentration in sludge shipped offsite for several plants.

Table 7-2. Current Methods of WRRF Sludge Disposal.

Agency	No. of Plants	Sludge Type and Avg. Conc.	Disposal Method	Disposal Cost (\$/ton) ^a		Sludge Disposed (tons/yr) ^a		Annual Cost (\$MM/yr) ^a
				Wet ^b	Dry	Wet ^b	Dry	
City of Calgary	3	Digested, Land App.: 6-7 wt% Beneficial Use ^c 17-18 wt%	Pumped to lagoon, then shipped off-site for land application and beneficial use	Land App.: \$20.8 Beneficial Use: \$96.5	Land App.: \$320 Beneficial Use: \$551	Land App.: 184,615 Beneficial Use: 45,714	Land App.: 12,000 Beneficial Use: 8000	Land App.: \$3.84 Beneficial Use: \$4.41
Metro Vancouver	4	Digested, 15-50 wt%	Largely dewatered and shipped off-site for land reclamation, soil fabrication, or soil fertilization (landfill as contingency)	\$34 -102	\$121-364 ^d	68,629	19,216 ^d	\$2.33-7.00
City of Orlando	2	Iron Bridge: Undigested 21.3 wt%	Dewatered, lime stabilized, and shipped off-site for land application	\$60	\$283	48,764	10,386	\$2.94
		Water Conserv II: Digested 13.1 wt%	Dewatered and shipped off-site for land application	\$81	\$645	19,111	2,411	\$1.56
Santa Rosa Water	1	Digested, 14-16 wt%	Dewatered and shipped off-site to one of three options: compost, land application, or landfill	Compost: \$150 Land App.: \$29 Landfill: \$42	Compost \$1000 Land App.: \$193 Landfill: \$280	27,000	4050	Compost \$4.05 Land App.: \$0.78 Landfill: \$1.13
Tohopekaliga Water Authority	1	Waste Activated Sludge, 14 wt%	Dewatered and shipped off-site. (washed grit and screenings disposed in dumpster)	\$45	\$321	44,700	6118	\$1.97

^a All costs are in U.S. dollars, at exchange rate of \$C1 = \$US 0.75. All weights are in short tons (2000 lbs).

^b Based on avg. sludge concentration cited

^c Examples of beneficial use include marginal land reclamation and biomass plantation

^d Based on 28% solids sludge concentration

(6-21 wt%) is roughly in the same range as the sludge feed concentrations tested in this test program (9-16 wt%). Based on the 94-99% solids reduction demonstrated in this test program (Table 7-1) and the disposal costs provided by the participating WRRFs (from \$780 thousand up to \$4.4 million), there could be a significant reduction in the annual sludge disposal costs.

The information in Table 7-2 suggests that whether sludge is digested or not is not the most significant factor in determining the sludge disposal cost. If one ranks all of the disposal costs shown in Table 7-2, the two cases representing undigested sludge (Orlando and Tohopekaliga) are in the middle of the range. In this case, the plant size and number, extent of dewatering, and specific disposal option probably play a larger role in determining the disposal cost than if the sludge is digested or not. This is shown by the significant difference in cost among the three options (compost, land application, and landfill) shown in the data provided by Santa Rosa Water.

One plant (Orlando) specifically shows the difference in overall cost between disposal of undigested and digested sludge at two of its plants. In this case, the price of digested sludge disposal (in terms of dollars per ton) is higher than that for undigested sludge. Orlando personnel stated that the additional \$362/dry ton for digested sludge disposal is due to the cost of anaerobic digestion and the cost of treating a high ammonia side stream. Plants with anaerobic digestion have added costs due to operation of the digestion process, but would in theory have to dispose of a lower quantity of solids and would recover valuable fuel from biogas. This can be seen with the Orlando data, where the cost per ton is higher for digested sludge but the overall disposal cost for digested sludge is lower because of the smaller quantity. In terms of total annual cost (i.e., dollars), this translates into almost double the amount spent to dispose of undigested sludge relative to digested sludge for Orlando.

Because of the depleted organic content of the feed and lower quantity of sludge to dispose, the prevailing thought has been that the HTL-CHG process would be less economically viable at a plant with anaerobic digestion. However, based on the surprisingly high biocrude yield from digested solids in the current tests and the limited data set of sludge disposal costs, installation of a HTL-CHG system at a plant with anaerobic digestion may be viable, though it can't be known for sure without doing a full economic analysis.

As seen in this test program and discussed in Section 6.4.3, the HTL process does not completely eliminate solids, but it can reduce the amount of solids considerably by converting the organic fraction to liquid biocrude, methane, or carbon dioxide primarily, and concentrating the remaining inorganic fraction. In this test program, the amount of solids was reduced by 94-99%. The increase in the inorganic or ash content of the HTL solids may change some of the disposal options available compared to those for the higher organic content sludge. Also, the higher concentration of any regulated species in the HTL solids (e.g., TCLP metals) may impose added disposal costs if their presence results in the solids being classified as hazardous (i.e., failing a TCLP test). In most cases, regulated species present in the HTL solids come from the original sludge and wastewater and are unaffected by the HTL process other than being concentrated. An exception would be increases in certain species such as nickel and chromium which can be indicative of corrosion of high temperature materials of construction in the HTL process. The amount of corrosion will vary with that of the sludge feed composition. However,

there are ways of minimizing corrosion in hydrothermal systems that can be implemented if corrosion becomes a problem (Marrone and Hong, 2009).

Due to the variability in WRRF configurations and requirements, potential solids disposal cost savings from implementation of a HTL-CHG system can only be determined with a full economic analysis performed for each plant location. However, based on the sludge disposal costs surveyed, the typical quantities of sludge generated at WRRFs, future tighter regulatory and environmental trends for waste disposal, and the volume reduction of solids demonstrated in this test program, the potential for significant solids disposal cost savings with implementation of HTL-CHG technology justifies further investigation.

CHAPTER 8.0

HTP LESSONS LEARNED

Some of the more significant lessons learned as a result from testing and the potential paths forward are summarized in Table 8-1. All of these issues were discussed in more detail in Chapter 6. Most of these issues should be addressed or their proposed resolutions demonstrated in pilot-scale testing of a Genifuel HTL-CHG system, which should be the next step in this program. The current proof-of-concept test program has demonstrated that sludge can be successfully processed to form biocrude at a sufficient yield to warrant further investigation. Testing with a larger scale, integrated, and more representative system to that which could be installed at a WRRF would also allow one to gather important data on long-term operation and energy usage, which are critical to understanding the full cost/benefit analysis with this feedstock.

Table 8-1. Lessons Learned from HTL-CHG Bench-scale Tests.

Lessons Learned	Potential Path Forward
Secondary sludge is difficult to dewater.	Perform additional dewatering tests with secondary sludge (e.g., using a large-scale centrifuge) and/or find an optimal and representative combination of primary and secondary sludge that can be successfully dewatered to the 15-20 wt% solids range.
There was difficulty in generating separable biocrude from secondary sludge.	Rerun test under proper operating conditions to determine whether results are inherent to this feed or not (can be done in larger scale test).
Solids buildup can occur and possibly impact biocrude formation when turbulent flow/mixing is insufficient in the HTL system.	Evaluate and demonstrate sufficient mixing design for larger scale systems.
Additional sulfur/sulfate needs to be removed from the aqueous phase upstream of the CHG system to avoid CHG catalyst poisoning.	Design, test, and evaluate a method for better sulfate removal in the HTL system. Start with maintaining reactor at correct temperature.
Biocrude oxygen and TAN levels are too high relative to petroleum crude oil. Upgrading must be performed on biocrude, or use on-site as is with upgraded burner material of construction if necessary.	Upgrade samples of biocrude from sludge to determine effectiveness, characterize the final product, and compare to petroleum crude.
Siloxanes appear to stay in the aqueous phase as opposed to the gas phase in the HTL and CHG effluent.	No further work necessary.
CHG liquid effluent is capable of meeting most discharge standards except nitrogen.	Confirm bench-scale observations at larger-scale and evaluate/test methods to treat liquid effluents to meet discharge requirements for a specific location.

Genifuel has previously built larger HTL-CHG systems (including a pilot-scale unit for algae feed for a recent customer), but not for sludge feed. The current bench-scale test results indicate that a larger scale system for sludge should not require any fundamental design differences. Because of the inherently variable nature of wastewater, a HTL-CHG system for sludge may have to accommodate a wide variety of feed conditions. Current test results show that HTL-CHG should be applicable at least for primary sludge and digested solids. Though results with secondary sludge were unfortunately inconclusive as to the ease of generating a separable and good quality biocrude, it is likely that most WRRFs without anaerobic digestion

would process a single sludge stream from the secondary clarifiers consisting of a combination of the same material that would be found in primary and secondary sludge instead of processing either of these individually. In this case, the effective dilution of secondary sludge by the better behaved primary sludge might result in a material that is easier to handle and process than pure secondary sludge.

Other potential scale-up issues include heat and mass transfer limitations, operation of the HTL and CHG processes in series as a true integrated system, and achieving continuous, automated HTL liquid product phase separation. The latter two issues have not been demonstrated to date. The impact of heat and mass transfer limitations increases with increasing size and are off-set to some extent by the enhanced transport properties and higher density of near-critical water. However, eventually the CSTR vessel size and corresponding wall thickness to hold pressure may become large enough to affect heat transfer. In this case, Genifuel has indicated that it would propose having a train of smaller systems or vessels running in parallel to produce the required net throughput.

With respect to system limitations, the feed needs to be as concentrated as possible (to maximize the quantity of biocrude produced) but still easily pumpable. This is true of all hydrothermal systems and while this was known prior to the current test program, it remains an important and valid constraint. All sludges tested in this test program were below their optimal concentration in order to ensure successful processing. Actual economically viable operation will require determination of the optimal feed concentration. Based on the current test results, additional system limitations include the need to further reduce sulfate concentrations in the HTL aqueous product to avoid CHG catalyst poisoning, and the need to maintain turbulent/well mixed conditions in the HTL reactor section to keep solids sufficiently suspended.

CHAPTER 9.0

SUMMARY AND CONCLUSIONS

Based on the data gathered and observations made during the proof-of-concept, bench-scale HTL and CHG tests with wastewater sludges, the following summary/conclusions can be made:

1. The HTL process is capable of generating separable biocrude from primary sludge and digested solids at yields (34-37%) that are significant with respect to potential revenue to a project, even with feed concentrations that have not been optimized with respect to solids concentration. Based on PNNL tests with other feeds, higher solids concentrations in the feed would be expected to generate higher yields.
2. The HTL process may be capable of generating separable biocrude from secondary sludge, but test results were inconclusive due to equipment failure that occurred during the test. Initial indications of a separable liquid biocrude changed to a solids-like organic phase that was difficult to separate during steady state after mixing stopped in the CSTR. It is not clear to what extent the equipment problems, low feed solids concentration, and autoclaving (constraint of PNNL testing) influenced these observations or by what mechanism. In the absence of these test or program related issues, it is possible that secondary sludge could behave similarly to the other sludge feeds tested. However, if these test observations are inherent to the nature of the secondary sludge, a separation method would need to be developed at commercial scale.
3. Unlike primary sludge, secondary sludge was difficult to dewater beyond 11 wt% solids with the methods tried in this study. While this observation is consistent with the reputation of secondary sludge in the wastewater treatment industry, there is sufficient vendor data to suggest that secondary sludge can be mechanically dewatered up to at least 18 wt% solids with appropriate equipment. Also, unlike primary sludge, autoclaving appears to have a significant degrading effect on the physical structure of secondary sludge (though no autoclaving would be necessary in a commercial-scale HTP system).
4. No significant equipment changes were needed to process sludge feed at the concentrations tested. The feed concentrations (which ranged from 9.7 – 16.0 wt% solids) were not optimized. It is likely that the HTL system could have processed higher concentrations than that tested but it is not clear how much higher as the solids concentration limits were not determined by these tests. Minor quantities of fouling were observed during testing, but the system is susceptible to solids buildup if there is insufficient turbulence to suspend the solids until reaching the filter vessel.
5. Biocrude quality appears to be comparable to that derived from other biomass feeds (e.g., algae) and needs to undergo upgrading for reduction of oxygen content and TAN values to generate a refinery-compatible feed (unless a refiner is capable and willing to perform the upgrading).

6. Good mass balance closure (to within \pm 15%, as was the objective) was achieved for all total mass and carbon balances across each system except in one case.
7. Ninety four samples were collected from the HTL and CHG processes to characterize the feedstock samples and product streams. Eighteen measurement methods were used by four laboratories for a total of approximately 2,500 analytical data results. With minor exceptions, these results had adequate precision and accuracy and can be used for an evaluation of the technologies.
8. CHG aqueous feed in all cases had to be processed through an ion exchange column for removal of high sulfate concentrations (catalyst poison) in the HTL aqueous product. As implemented for this test program, the ion exchange process impacted the composition of the CHG feed (e.g., pH increase, significant carbon loss) and is not representative of how sulfate removal would or should be performed in a commercial-scale system. An improved method for sulfate removal needs to be demonstrated.
9. CHG product gas consisted mostly of methane, showed no unusual components, and had a calculated heating value similar to natural gas. The high methane content (75-97 vol%) may have partly been an artifact of testing, as the amount of carbon dioxide in the gas phase was directly affected by the increased pH of the aqueous feed caused by the ion exchange step. On a mass and energy basis, less CHG product gas was generated than HTL biocrude.
10. Siloxane concentrations in the CHG product gas were below detection limits in most cases, and well below the fuel inlet composition limits established by several engine manufacturers. Most silicon appears to partition into the HTL and CHG aqueous phase product.
11. The CHG process is capable of producing aqueous effluent that is sufficiently clean to meet all bacteria-related regulatory limits for water discharge from several WRRFs. The CHG aqueous effluent in these tests also met or came close to meeting BOD and total phosphorus discharge limits, but not total nitrogen. An additional nitrogen removal step would be needed to consider direct discharge of CHG effluent along with treated WRRF effluent. An alternative to avoid this additional step would be to return the CHG aqueous product to the WRRF headworks, or sell it as fertilizer for its nitrogen content. In the former case, the impact of adding nitrogen to the headworks will need to be carefully assessed for treatment and cost impacts.
12. The CHG Ru/C catalyst and Raney nickel guard bed performed well during testing, but sulfur levels measured on the catalyst and guard solids at the end of each test indicated that poisoning was occurring. The catalyst and guard bed life times beyond the maximum time exposed to feed in these tests (85 hours) and the frequencies of replacement with these sludge-derived aqueous feeds is uncertain. Because of the high catalyst cost (\$114/lb for Ru/C and \$33/lb for Raney Ni), further sulfur content reduction upstream of CHG will be necessary to minimize the frequency of catalyst replacement.
13. The CHG process functions primarily as a polishing stage for the effluent water, as well as a method to obtain more fuel value from additional methane produced and possibly to recover

plant nutrients. If aqueous effluent from hydrothermal processing is not intended to be discharged to the environment (e.g., if it is recycled back to the plant headworks), the CHG process may not be necessary or may not justify the added operational expense for the above listed benefits (improved effluent quality, the amount of methane produced, and/or value of nutrients recovered). In this case, it may make sense to consider utilizing only the HTL process.

14. Based on the demonstrated yields and the amount of solids reduction observed relative to typical WRRF sludge quantities, there is potential for cost savings (in terms of fuel displacement and disposal costs) from implementation of hydrothermal processing.
15. The overall results of this proof-of-concept test program are sufficiently promising to justify further investigation of the HTL-CHG technology for application to WRRF sludge.

CHAPTER 10.0

RECOMMENDATIONS

Based on the results of this proof-of-concept bench-scale test program for HTL-CHG of wastewater sludge, a number of recommendations can be made. In general, it should be noted that while some of the specific recommendations are either related to or a result of issues that occurred during the bench-scale testing, the team does not believe that more bench-scale tests are necessary for this technology and application. The intent would be to resolve or further explore any of the outstanding issues from the current test program during the recommended future pilot-scale testing (see #2 below). The recommendations for future work are as follows:

1. Determine the optimal sludge feed concentration for each sludge type through HTL. This includes verification/demonstration of sufficient dewatering of secondary sludge. The optimization should be based on the expected pump type to be utilized in a commercial-scale system.
2. Perform long-term operation tests on a single, integrated HTL-CHG system at pilot-scale that is representative of the equipment and design that would be installed at a WRRF. If possible, these tests could be performed at a WRRF location. Such tests should be performed with both an optimized, plant representative combination of primary/secondary sludge mixed feed and with digested solids feed. The tests should be of sufficient duration to demonstrate and assess continuous HTL biocrude/aqueous phase product separation, HTL solids removal, and CHG catalyst performance, and to identify at a high level key reliability and availability values and maintenance (RAM) requirements. Tests should be performed in triplicate to verify reproducibility of results. Upgrading of the biocrude produced should also be performed to assess its quality and value compared to petroleum crude. Performing these tests on a system built and installed directly at a utility would have the advantage of allowing observation of both equipment operation and integration into an actual operating environment.
3. Repeat HTL tests with (non-autoclaved) secondary sludge to confirm biocrude yield and phase separability results under proper functioning experimental conditions. This could be done during pilot-scale tests described in Recommendation #2.
4. Determine the most representative combination of primary and secondary sludge concentrations for WRRFs that do not utilize anaerobic digestion and perform HTL and CHG tests on this combined sludge feed. This could be done during pilot-scale tests described in Recommendation #2.
5. Demonstrate better temperature control and monitoring over the HTL reactor components. Temperature variations of 40°C or more as seen in these bench-scale tests will have a noticeable effect on salt solubility and precipitation. Reactor system temperatures should be kept as uniformly close to the target 350°C value as possible (or

slightly higher) to not only maintain more consistent operating conditions but also to maximize product solids (e.g., sulfate) removal prior to CHG.

6. Develop and demonstrate an effective method to remove sulfate species from HTL effluent to a sufficiently low concentration to avoid the need for ion exchange and poisoning of the downstream CHG catalyst. This method may be as simple as maintaining consistent operation at the standard HTL temperature (i.e., 350-360°C) for decreased sulfate solubility and increased precipitation, and should be investigated first. An additional option to explore if temperature alone is insufficient is the use of chemical additives. The additives should be chosen to be compatible with sludge feed and to further reduce sulfate concentration via precipitation under HTL reaction conditions without plugging or interfering with system fluid flow.
7. Determine the CHG ruthenium catalyst replacement frequency with sludge-derived aqueous feeds after adequate means of sulfate removal have been established. Also, assess the amount and impact (if any) of catalyst coking during future long-term operating tests (see Recommendation #2).
8. Perform an energy balance on an integrated, representative pilot-scale system (in conjunction with the recommended long-term operating tests in Recommendation #2). This will allow a relevant and more accurate assessment of the energy input requirements.
9. Produce enough biocrude (without upgrading) to do a burner test and possibly a small internal combustion or diesel engine test (e.g., 10 hp, four-stroke engine) to assess the viability for use of biocrude on-site for power or steam production. A check of engine manufacturers for materials compatibility should be done before any test.
10. Perform a TCLP test on HTL solids to determine proper classification for disposal. This could be done during pilot-scale tests described in Recommendation #2 using a sludge feed composition representative of that intended to be processed at a WRRF.
11. In collaboration with WRRF facilities, identify trace organic contaminants (e.g., antimicrobials, flame retardants, hormones, pharmaceuticals, surfactants, pesticides) of highest concern and/or difficulty to eliminate by present means for the wastewater industry. In future HTL-CHG tests (such as the pilot-scale tests in Recommendation #2), analyze both the sludge feeds and CHG effluent for these contaminants in order to determine/verify their fate during hydrothermal processing. If necessary, a test feed could be spiked with a known amount of a particular contaminant for a more controlled test.
12. Characterize the filtrate resulting from dewatering of undigested sludge (prior to HTP) in order to ensure compatibility of this new filtrate stream with WRRF operation when recycled back to the headworks.
13. Identify interested WRRF facilities and perform a detailed site-specific economic analysis to assess the economic viability for a full-scale installation of a HTL-CHG system. This analysis should include estimating the value of biocrude produced via HTL

and the costs to upgrade it. In the analysis, consideration of various options (e.g., recycling of CHG aqueous effluent versus collection for sale as a liquid fertilizer) should also be considered to determine the optimal configuration.

14. Perform a full analysis of the GHG reduction potential and associated value of carbon offsets from a representative scale HTL-CHG system (this can be done as part of the recommended long-term operating tests in Recommendation #2).

APPENDIX A

WERF-02

PRIMARY SLUDGE FEEDSTOCK ANALYTICAL DATA

Appendix A: HTL WERF-02 (Primary Sludge Feedstock) Complete Data Set

Note: Cells in yellow indicate planned analyses per the QAPP (test plan)

Method/Analyte	HTL Feedstock				HTL Biocrude					HTL Aqueous				HTL Solid	
	BOR	EOR	Average	Units	12:00	12:40	13:20	Average	Units	12:00	12:40	13:20	Average	Units	Units
Moisture					14.1	10.2	14.7	13.0	wt%						
TAN					64.8	67.1	63.0	65.0	mg KOH/g						
Viscosity					605	558	550	571	cSt						
Ammonia as Nitrogen										NA	1,330	1,320	1,330	mg/L	
ANIONS										58.0	60.4	60.7	59.7	mg/L	
Chloride										23.6	24.3	25.9	24.6	mg/L	
Phosphate										57.9	60.3	62.3	60.2	mg/L	
Sulfate										41,000	41,200	40,700	41,000	mg O ₂ /L	
COD	187,000	187,000	mg O ₂ /L												
DISSOLVED ORGANICS										0.083	0.085	0.091	0.086	wt%	
Glycolic acid										0.049	0.05	0.05	0.050	wt%	
Glycerol										<0.03	<0.03	<0.03	<0.03	wt%	
Formic acid										0.34	0.35	0.35	0.35	wt%	
Acetic Acid										<0.03	<0.03	<0.03	<0.03	wt%	
Ethylene Glycol										0.12	0.12	0.12	0.12	wt%	
Propylene Glycol										<0.03	<0.03	<0.03	<0.03	wt%	
1,3-Propanediol										<0.03	<0.03	<0.03	<0.03	wt%	
Acetaldehyde										<0.03	<0.03	<0.03	<0.03	wt%	
Propanoic Acid										<0.03	<0.03	<0.03	<0.03	wt%	
Methanol										0.12	0.12	0.12	0.12	wt%	
1,2-Butanediol										<0.03	<0.03	<0.03	<0.03	wt%	
Ethanol										<0.03	<0.03	<0.03	<0.03	wt%	
Butanoic Acid										<0.03	<0.03	<0.03	<0.03	wt%	
2-Propanol										<0.03	<0.03	<0.03	<0.03	wt%	
Acetone										0.13	0.13	0.13	0.13	wt%	
1-Propanol										<0.03	<0.03	<0.03	<0.03	wt%	
2-Butanol										0.063	0.060	0.059	0.061	wt%	
2-Methyl-1-propanol										<0.03	<0.03	<0.03	<0.03	wt%	
1-Butanol										<0.03	<0.03	<0.03	<0.03	wt%	
2-Pentanone										<0.03	<0.03	<0.03	<0.03	wt%	
Phenol										<0.03	<0.03	<0.03	<0.03	wt%	
p-Cresol										0.033	<0.03	0.04	0.034	wt%	
Dry Solid Content	11.8%	11.9%	11.9%	wt%											
pH	5.13	5.05	5.09							6.39	6.44	6.43	6.42		
TOC	44.6	44.6	wt%							11,300	11,900	11,900	11,700	mg/L	26.6 wt%
Product Weight														129 g	

Note: Cells in yellow indicate planned analyses per the QAPP (test plan)

Method/Analyte	HTL Gas			
	Minimum	Maximum	Average	Units
GAS ANALYSIS				
H2 - Hydrogen	0.93	1.13	0.95	vol%
O2 - Oxygen	0.01	0.01	< 0.01	vol%
N2 - Nitrogen	0.48	0.79	0.54	vol%
CH4 - Methane	1.17	1.31	1.20	vol%
CO - Carbon Monoxide	0.00	0.00	< 0.01	vol%
CO2 - Carbon Dioxide	92.8	95.4	95.1	vol%
Ethylene	0.12	0.15	0.12	vol%
C2 - Ethane	0.51	0.60	0.54	vol%
H2S - Hydrogen Sulfide	0.30	0.36	0.33	vol%
Propane	0.37	0.45	0.42	vol%
Isobutane	0.01	0.01	< 0.01	vol%
n-Butane	0.16	0.20	0.18	vol%
trans-2-Butene	0.00	0.00	< 0.01	vol%
1-Butene	0.10	0.12	0.11	vol%
Isobutene	0.00	0.00	< 0.01	vol%
ds-2-Butene	0.14	0.17	0.15	vol%
Isopentane	0.00	0.00	< 0.01	vol%
n-Pentane	0.047	0.055	0.050	vol%
1,3-Butadiene	0.00	0.00	< 0.01	vol%
trans-2-Pentene	0.00	0.00	< 0.01	vol%
2-Methyl-2-butene	0.047	0.060	0.052	vol%
1-Pentene	0.10	0.13	0.11	vol%
cis-2-Pentene	0.03	0.04	0.04	vol%
Ammonia (gas)	NA	NA	NA	vol%
SILOXANES				
Hexamethylcyclotrisiloxane (L2)			< 0.60	mg Si/m ³
Hexamethylcyclotrisiloxane (D3)			< 0.91	mg Si/m ³
Octamethylcyclotrisiloxane (L3)			< 0.91	mg Si/m ³
Octamethylcyclotetrasiloxane (D4)			< 1.21	mg Si/m ³
Decamethyltetrasiloxane (L4)			< 1.21	mg Si/m ³
Decamethylcyclopentasiloxane (D5)			< 1.51	mg Si/m ³
Dodecamethylpentasiloxane (L5)			< 1.51	mg Si/m ³
Trimethylsilanol*			< 0.3	mg Si/m ³
Tetramethylsilane*			< 0.3	mg Si/m ³
	* Analyzed as a tentatively identified compound (TIC). Result is estimated.			

Note: Cells in yellow indicate planned analyses per the QAPP (test plan)

Method/Analyte	CHG Feed			CHG Aqueous								CHG Sulfur Removal/Catalyst			
	Pre Ion Exchange	Post Ion Exchange	Units	8/13/15 9:00	8/13/15 12:00	8/13/15 15:00	8/13/15 18:20	8/13/15 21:00	8/13/15 23:26	8/14/15 5:35	Average	Units	R-Ni	Ru/C	Units
Ammonia as Nitrogen				—	1,915	2,250	2,110	2,005	2,035	2,170	2,080	mg/L			
ANIONS															
Chloride	—	< 4.0	mg/L	—	—	< 4.0	< 4.0	—	—	< 4.0	< 4.0	mg/L			
Phosphate	—	< 4.0	mg/L	—	—	< 4.0	< 4.0	—	—	< 4.0	< 4.0	mg/L			
Sulfate	—	< 4.0	mg/L	—	—	< 4.0	5.80	—	—	< 4.0	5.80	mg/L			
COD	40,800	20,300	mg O ₂ /L	144	109	46	35	18	13	12	54	mg O ₂ /L			
DISSOLVED ORGANICS															
Glycolic acid	<0.03	0.09	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
Glycerol	0.05	0.05	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
Formic acid	<0.03	<0.03	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
Acetic Acid	<0.03	0.35	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
Ethylene Glycol	<0.03	<0.03	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
Propylene Glycol	<0.03	<0.03	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
1,3-Propanediol	<0.03	<0.03	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
Acetaldehyde	<0.03	<0.03	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
Propanoic Acid	<0.03	0.12	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
Methanol	0.05	<0.03	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
1,2-Butanediol	<0.03	<0.03	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
Ethanol	<0.03	<0.03	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
Butanoic Acid	<0.03	<0.03	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
2-Propanol	<0.03	<0.03	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
Acetone	0.04	0.13	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
1-Propanol	<0.03	<0.03	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
2-Butanol	<0.03	0.06	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
2-Methyl-1-propanol	<0.03	<0.03	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
1-Butanol	<0.03	<0.03	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
2-Pentanone	<0.03	<0.03	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
Phenol	<0.03	<0.03	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
p-Cresol	0.03	0.034	wt%	< 0.03	—	< 0.03	< 0.03	—	—	< 0.03	< 0.03	wt%			
pH	6.44	9.25		9.17	9.29	9.59	9.26	9.37	9.23	9.20	9.30				
TOC	17,100	5,470	mg/L			531	NA			< 99	530	mg/L			

Appendix A: CHG WERF-02 (Primary Sludge Feedstock) Complete Data Set

Note: Cells in yellow indicate planned analyses per the QAPP (test plan)

Method/Analyte	CHG Gas						
	8/13/15 15:28	8/13/15 18:20	8/13/15 21:03	8/13/15 23:48	8/14/15 5:40-9:37	Average	Units
GAS ANALYSIS							
H2 - Hydrogen	1.2	1.4	1.8	1.6		1.5	vol%
O2 - Oxygen	0.36	0.36	0.37	0.50		0.4	vol%
N2 - Nitrogen	1.54	1.53	1.60	1.75		1.61	vol%
CH4 - Methane	72.3	72.5	73.4	75.6		73.5	vol%
CO2 - Carbon Dioxide	22.6	22.2	21.0	20.8		21.7	vol%
Ethylene	< 0.01	< 0.01	< 0.01	< 0.01		< 0.01	vol%
C2 - Ethane	1.37	1.25	1.12	1.01		1.19	vol%
Ammonia	NA	NA	NA	NA			
SILOXANES							
Hexamethylcyclotrisiloxane (L2)					< 0.0988		mg Si/m ³
Hexamethylcyclotrisiloxane (D3)					< 0.1482		mg Si/m ³
Octamethylcyclotrisiloxane (L3)					< 0.1482		mg Si/m ³
Octamethylcyclotetrasiloxane (D4)					< 0.1976		mg Si/m ³
Decamethyltetrasiloxane (L4)					< 0.1976		mg Si/m ³
Decamethylcyclopentasiloxane (D5)					< 0.247		mg Si/m ³
Dodecamethylpentasiloxane (L5)					< 0.247		mg Si/m ³
Trimethylsilanol*					< 0.0494		mg Si/m ³
Tetramethylsilane*					< 0.0494		mg Si/m ³
* - Analyzed as a tentatively identified compound (TIC). Result is estimated.							

APPENDIX B

WERF-03

SECONDARY SLUDGE FEEDSTOCK
ANALYTICAL DATA

Note: Cells in yellow indicate planned analyses per the QAPP (test plan)

Method/Analyte	HTL Feedstock				HTL Biocrude				HTL Aqueous				HTL Solid		
	BOR	EOR	Average	Units	Trap 2 Oil	12:40 Solids	Units	12:00	12:40	13:20	Average	Units	CSTR Wash	Snake	Units
Ash	16.2%	16.3%	16.2%	wt%dry	0.46	6.15	wt%						64.52	1.67	wt%
Density	0.9929	1.0039	0.998	g/mL@ 20°C	0.9846	NA	g/mL@ 40°C								
ELEMENTAL ANALYSIS															
Carbon	43.6	43.6	wt%	56.6	71.4	wt%	NA	NA	2.62	2.62	wt%	26.9	—	wt%	
Hydrogen	6.55	6.55	wt%	10.7	8.68	wt%	NA	NA	12.1	12.1	wt%	3.22	—	wt%	
Nitrogen	7.90	7.90	wt%	3.55	5.02	wt%	NA	NA	0.72	0.72	wt%	1.49	—	wt%	
Oxygen	29.0	29.0	wt%	11.0	7.32	wt%						20.5	—	wt%	
Sulfur	0.72	0.72	wt%	0.76	0.89	wt%						0.69	—	wt%	
Filterable Solids				0.25	NA	wt%									
METALS															
Ag - Silver	< 50	< 50	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	< 50	< 50	ppm	
Al - Aluminum	3,330	3,330	ppm (wt/wt)	77.8	107	ppm	NA	1.69	1.73	1.71	ppm (wt/vol)	13,600	540	ppm	
As - Arsenic	< 50	< 50	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	< 50	< 50	ppm	
Au - Gold	< 50	< 50	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	< 50	< 50	ppm	
Ba - Barium	170	170	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	667	< 50	ppm	
Ca - Calcium	9,030	9,030	ppm (wt/wt)	< 50	57.1	ppm	NA	1.61	1.53	1.57	ppm (wt/vol)	46,000	702	ppm	
Cd - Cadmium	< 50	< 50	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	< 50	< 50	ppm	
Co - Cobalt	< 50	< 50	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	< 50	< 50	ppm	
Cr - Chromium	50.0	50.0	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	1,070	78	ppm	
Cu - Copper	590	590	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	2,510	131	ppm	
Fe - Iron	26,200	26,200	ppm (wt/wt)	79.0	111	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	34,700	2,680	ppm	
K - Potassium	4,280	4,280	ppm (wt/wt)	134	136	ppm	NA	280	269	275	ppm (wt/vol)	1,700	158	ppm	
Mg - Magnesium	2,920	2,920	ppm (wt/wt)	29	72.0	ppm	NA	1.26	1.33	1.29	ppm (wt/vol)	12,400	424	ppm	
Mn - Manganese	250	250	ppm (wt/wt)	29	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	1,060	54	ppm	
Mo - Molybdenum	< 50	< 50	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	< 50	< 50	ppm	
Na - Sodium	890	890	ppm (wt/wt)	62	251	ppm	NA	102	100	101	ppm (wt/vol)	528	79.1	ppm	
Ni - Nickel	< 50	< 50	ppm (wt/wt)	23	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	8,570	183	ppm	
P - Phosphorus	33,300	33,300	ppm (wt/wt)	73	< 45	ppm	NA	290	291	290	ppm (wt/vol)	60,600	2,820	ppm	
Pb - Lead	< 50	< 50	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	< 50	< 50	ppm	
Pd - Palladium	< 50	< 50	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	< 50	< 50	ppm	
Pt - Platinum	< 50	< 50	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	< 50	< 50	ppm	
Re - Rhenium	< 50	< 50	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	< 50	< 50	ppm	
Rh - Rhodium	< 50	< 50	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	< 50	< 50	ppm	
Ru - Ruthenium	< 50	< 50	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	< 50	< 50	ppm	
S - Sulfur	6,420	6,420	ppm (wt/wt)	2,600	8,240	ppm	NA	162	151	157	ppm (wt/vol)	4,840	2,800	ppm	
Si - Silicon	280	280	ppm (wt/wt)	210	20,900	ppm	NA	192	192	190	ppm (wt/vol)	206	246	ppm	
Sn - Tin	< 50	< 50	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	< 50	< 50	ppm	
Sr - Strontium	110	110	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	380	73.4	ppm	
Ti - Titanium	94.1	94.1	ppm (wt/wt)	< 50	46.7	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	78	74.3	ppm	
V - Vanadium	< 50	< 50	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	< 50	< 50	ppm	
W - Tungsten	< 50	< 50	ppm (wt/wt)	< 50	NA	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	< 50	< 50	ppm	
Y - Yttrium	< 50	< 50	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	< 50	< 50	ppm	
Zn - Zinc	530	530	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	2,950	81	ppm	
Zr - Zirconium	51.4	51.4	ppm (wt/wt)	< 50	< 45	ppm	NA	< 1.0	< 1.0	< 1.0	ppm (wt/vol)	< 50	< 50	ppm	

Appendix B: HTL WERF-03 (Secondary Sludge Feedstock) Complete Data Set

Note: Cells in yellow indicate planned analyses per the QAPP (test plan)

Method/Analyte	HTL Feedstock				HTL Biocrude			HTL Aqueous					HTL Solid			
	BOR	EOR	Average	Units	Trap 2 Oil	12:40 Solids	Units	12:00	12:40	13:20	Average	Units	CSTR Wash	Snake	Units	
Moisture					28.6	1.0	wt%									
TAN					38.3	44.8	mg KOH/g									
Viscosity					624	NA	cSt									
Ammonia as Nitrogen								4,440	4,610	4,520	4,520	mg/L				
ANIONS																
Chloride								NA	102	NA	102	mg/L				
Phosphate								NA	714	NA	714	mg/L				
Sulfate								NA	161	NA	161	mg/L				
COD	149,000	158,000	153,000	mg O ₂ /L				74,200	71,000	73,700	73,000	mg O ₂ /L				
DISSOLVED ORGANICS																
Glycolic acid								NA	<0.03	<0.03	<0.03	wt%				
Glycerol								NA	0.05	0.05	0.05	wt%				
Formic acid								NA	<0.03	<0.03	<0.03	wt%				
Acetic Acid								NA	0.32	0.32	0.32	wt%				
Ethylene Glycol								NA	<0.03	<0.03	<0.03	wt%				
Propylene Glycol								NA	<0.03	<0.03	<0.03	wt%				
1,3-Propanediol								NA	<0.03	<0.03	<0.03	wt%				
Acetaldehyde								NA	<0.03	<0.03	<0.03	wt%				
Propanoic Acid								NA	0.12	0.12	0.12	wt%				
Methanol								NA	<0.03	<0.03	<0.03	wt%				
1,2-Butanediol								NA	<0.03	<0.03	<0.03	wt%				
Ethanol								NA	<0.03	0.03	0.03	wt%				
Butanoic Acid								NA	0.06	0.06	0.06	wt%				
2-Propanol								NA	<0.03	<0.03	<0.03	wt%				
Acetone								NA	0.06	0.06	0.06	wt%				
1-Propanol								NA	<0.03	<0.03	<0.03	wt%				
2-Butanol								NA	<0.03	<0.03	<0.03	wt%				
2-Methyl-1-propanol								NA	<0.03	<0.03	<0.03	wt%				
1-Butanol								NA	<0.03	<0.03	<0.03	wt%				
2-Pentanone								NA	<0.03	<0.03	<0.03	wt%				
Phenol								NA	<0.03	<0.03	<0.03	wt%				
p-Cresol								NA	0.04	0.04	0.04	wt%				
Dry Solid Content	9.66%	9.76%	9.71%	wt%												
pH	6.18	5.88	6.03					8.03	8.07	8.03	8.04					
TOC	40.9	40.9	40.9	wt%				NA	NA	23,500	23,500	mg/L	26.0	—	wt%	
Product Weight													225	3.02	g	

Note: Cells in yellow indicate planned analyses per the QAPP (test plan)

Method/Analyte	HTL Gas			
	Minimum	Maximum	Average	Units
Ammonia (gas)	NA	NA	NA	
GAS ANALYSIS				
H2 - Hydrogen	1.22	1.61	1.49	vol%
O2 - Oxygen	0.01	0.01	0.01	vol%
N2 - Nitrogen	6.21	13.8	8.9	vol%
CH4 - Methane	2.05	2.80	2.50	vol%
CO - Carbon Monoxide	< 0.01	0.13	0.08	vol%
CO2 - Carbon Dioxide	75.0	78.9	77.9	vol%
Ethylene	0.69	0.83	0.78	vol%
C2 - Ethane	0.40	0.63	0.52	vol%
H2S - Hydrogen Sulfide	0.37	0.46	0.40	vol%
Propane	0.36	0.61	0.47	vol%
Isobutane	0.01	0.02	0.02	vol%
n-Butane	0.25	0.38	0.31	vol%
trans-2-Butene	< 0.01	< 0.01	< 0.01	vol%
1-Butene	0.30	0.40	0.37	vol%
Isobutene	< 0.01	< 0.01	< 0.01	vol%
cis-2-Butene	0.59	0.70	0.65	vol%
Isopentane	0.04	0.39	0.15	vol%
n-Pentane	0.02	0.13	0.06	vol%
1,3-Butadiene	< 0.01	< 0.01	< 0.01	vol%
trans-2-Pentene	< 0.01	< 0.01	< 0.01	vol%
2-Methyl-2-butene	0.17	0.25	0.21	vol%
1-Pentene	0.27	0.38	0.33	vol%
cis-2-Pentene	0.10	0.14	0.12	vol%

Appendix B: CHG WERF-03 (Secondary Sludge Feedstock) Complete Data Set

Note: Cells in yellow indicate planned analyses per the QAPP (test plan)

Method/Analyte	CHG Feed			CHG Aqueous									CHG Sulfur Removal/Catalyst				
	Prelon Exchange	Postlon Exchange	Units	8/19/15 16:20	8/19/15 22:25	8/20/15 6:35	8/20/15 9:20	8/20/15 12:55	8/20/15 15:40	8/20/15 18:30	8/20/15 21:30	8/21/15 4:15	Average	Units	R-Ni	Ru/C	Units
ELEMENTAL ANALYSIS																	
Carbon	1.92	0.705	wt%	—	—	0.27	—	—	0.30	—	—	0.29	0.28	wt%			
Hydrogen	11.2	11.6	wt%	—	—	11.6	—	—	11.2	—	—	11.1	11.3	wt%			
Nitrogen	<0.05	0.3	wt%	—	—	0.38	—	—	0.35	—	—	0.36	0.36	wt%			
METALS																	
Ag - Silver	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Al - Aluminum	—	< 1.0	ppm (wt/vol)	—	—	1.9	—	—	3.4	—	—	3.2	2.8	ppm (wt/vol)	350,000	310	ppm (wt/wt)
As - Arsenic	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Au - Gold	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Ba - Barium	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	140	ppm (wt/wt)
Ca - Calcium	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	100	275	ppm (wt/wt)
Cd - Cadmium	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Co - Cobalt	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	242	< 45	ppm (wt/wt)
Cr - Chromium	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Cu - Copper	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Fe - Iron	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	843	219	ppm (wt/wt)
K - Potassium	—	328	ppm (wt/vol)	—	—	309	—	—	328	—	—	338	325	ppm (wt/vol)	115	5,400	ppm (wt/wt)
Mg - Magnesium	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	62.0	56.5	ppm (wt/wt)
Mn - Manganese	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Mo - Molybdenum	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Na - Sodium	—	84.3	ppm (wt/vol)	—	—	83.3	—	—	84.2	—	—	87.3	84.9	ppm (wt/vol)	132	1,190	ppm (wt/wt)
Ni - Nickel	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	527,000	630	ppm (wt/wt)
P - Phosphorus	—	2.21	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	156	229	ppm (wt/wt)
Pb - Lead	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Pd - Palladium	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Pt - Platinum	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Re - Rhenium	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Rh - Rhodium	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Ru - Ruthenium	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	91,600	ppm (wt/wt)
S - Sulfur	—	46	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	16,000	3,400	ppm (wt/wt)
Si - Silicon	—	40	ppm (wt/vol)	—	—	15	—	—	20	—	—	17	17	ppm (wt/vol)	378	< 45	ppm (wt/wt)
Sn - Tin	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Sr - Strontium	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Ti - Titanium	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	77.2	ppm (wt/wt)
V - Vanadium	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
W - Tungsten	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Y - Yttrium	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Zn - Zinc	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)
Zr - Zirconium	—	< 1.0	ppm (wt/vol)	—	—	< 1.0	—	—	< 1.0	—	—	< 1.0	< 1.0	ppm (wt/vol)	< 45	< 45	ppm (wt/wt)

Note: Cells in yellow indicate planned analyses per the QAPP (test plan)

Method/Analyte	CHG Feed			CHG Aqueous										CHG Sulfur Removal/Catalyst			
	Pre Ion Exchange	Post Ion Exchange	Units	8/19/15 16:20	8/19/15 22:25	8/20/15 6:35	8/20/15 9:20	8/20/15 12:55	8/20/15 15:40	8/20/15 18:30	8/20/15 21:30	8/21/15 4:15	Average	Units	R-Ni	Ru/C	Units
Ammonia as Nitrogen				5070	5700	5640	5680	5,200	5,400	5,640	5,830	5,510	5,520	mg/L			
ANIONS																	
Chloride	—	< 4.0	mg/L	—	—	< 4.0	—	—	< 4.0	—	—	< 4.0	< 4.0	mg/L			
Phosphate	—	4.38	mg/L	—	—	< 4.0	—	—	< 4.0	—	—	< 4.0	< 4.0	mg/L			
Sulfate	—	< 4.0	mg/L	—	—	< 4.0	—	—	< 4.0	—	—	< 4.0	< 4.0	mg/L			
COD	72,300	21,700	mg O ₂ /L	28	26	26	27	27	26	22	18	23	25	mg O ₂ /L			
DISSOLVED ORGANICS																	
Glycolic acid	<0.03	<0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
Glycerol	0.05	0.04	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
Formic acid	<0.03	<0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
Acetic Acid	0.32	0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
Ethylene Glycol	<0.03	<0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
Propylene Glycol	<0.03	<0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
1,3-Propanediol	<0.03	<0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
Acetaldehyde	<0.03	<0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
Propanoic Acid	0.12	<0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
Methanol	<0.03	0.21	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
1,2-Butanediol	<0.03	<0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
Ethanol	<0.03	0.04	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
Butanoic Acid	0.06	<0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
2-Propanol	<0.03	<0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
Acetone	0.06	0.04	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
1-Propanol	<0.03	<0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
2-Butanol	<0.03	<0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
2-Methyl-1-propanol	<0.03	<0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
1-Butanol	<0.03	<0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
2-Pentanone	<0.03	<0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
Phenol	<0.03	<0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
p-Cresol	0.04	<0.03	wt%	—	—	<0.03	—	—	<0.03	—	—	<0.03	<0.03	wt%			
pH	8.05	9.35		9.36	9.33	9.35	9.34	9.35	9.34	9.35	9.36	9.34	9.35	9.35			
TOC	—	6,320	mg/L	—	—	963	—	—	969	—	—	981	971	mg/L			

Appendix B: CHG WERF-03 (Secondary Sludge Feedstock) Complete Data Set

Note: Cells in yellow indicate planned analyses per the QAPP (test plan)

Method/Analyte	CHG Gas										Average	Units
	8/19/15 16:21	8/19/15 22:27	8/20/15 6:37	8/20/15 9:20	8/20/15 12:58	8/20/15 15:44	8/20/15 18:33	8/20/15 21:33	8/21/15 4:05			
GAS ANALYSIS												
H2 - Hydrogen	3.01	3.07	3.32	3.06	2.84	2.93	2.55	3.09	2.75	2.96	vol%	
O2 - Oxygen	0.40	0.36	0.30	0.39	0.37	0.39	0.35	0.36	0.32	0.36	vol%	
N2 - Nitrogen	30	18	19	18	15	12	9.4	7.9	5.7	15	vol%	
CH4 - Methane	66.18	77.38	76.50	78.01	81.40	84.20	86.90	87.92	90.39	81.0	vol%	
CO2 - Carbon Dioxide	0.1	0.3	0.2	0.2	0.2	0.3	0.2	0.2	0.3	0.2	vol%	
Ethylene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	vol%	
C2 - Ethane	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	vol%	
Ammonia	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA		
SILOXANES (8/21/15 04:20 to 09:05)												
Hexamethylcyclotrisiloxane (D2)									< 0.0919		mg Si/m³	
Hexamethylcyclodotrisiloxane (D3)									< 0.138		mg Si/m³	
Octamethylcyclotrisiloxane (L3)									< 0.138		mg Si/m³	
Octamethylcyclotetrasiloxane (D4)									< 0.184		mg Si/m³	
Decamethyltetrasiloxane (L4)									< 0.184		mg Si/m³	
Decamethylcyclopentasiloxane (D5)									< 0.23		mg Si/m³	
Dodecamethylpentasiloxane (L5)									< 0.23		mg Si/m³	
Trimethylsilanol*									< 0.046		mg Si/m³	
Tetramethylsilane*									< 0.046		mg Si/m³	

* - Analyzed as a tentatively identified compound (TIC). Result is estimated.

APPENDIX C

WERF-04

DIGESTED SOLIDS FEEDSTOCK
ANALYTICAL DATA

Appendix C: HTL WERF-04 (Digested Solids Feedstock) Complete Data Set

Note: Cells in yellow indicate planned analyses per the QAPP (test plan)

Method/Analyte	HTL Feedstock				HTL Biocrude						HTL Aqueous						HTL Solid	
	BOR	EOR	Average	Units	11:10	11:50	12:30	13:10	Average	Units	11:10	11:50	12:30	13:10	Average	Units		Units
Moisture					—	13.5	14.2	12.8	13.5	wt%								
TAN					—	37.4	35.4	35.3	36.0	mg KOH/g								
Viscosity					1,420	1,100	1,110	1,020	1,160	cSt								
Ammonia as Nitrogen											4,810	5,050	4,990	4,970	4,960	mg/L		
ANIONS											—	96	95	93	94	mg/L		
Chloride											—	65	77	75	72	mg/L		
Phosphate											—	200	199	200	200	mg/L		
Sulfate																		
COD	208,600	198,400	203,000	mg O ₂ /L							45,200	49,500	49,000	49,200	48,200	mg O ₂ /L		
DISSOLVED ORGANICS											—	<0.03	<0.03	<0.03	<0.03	wt%		
Glycolic acid											—	0.06	0.06	0.06	0.06	wt%		
Glycerol											—	<0.03	<0.03	<0.03	<0.03	wt%		
Formic acid											—	0.37	0.38	0.38	0.38	wt%		
Acetic Acid											—	<0.03	<0.03	<0.03	<0.03	wt%		
Ethylene Glycol											—	0.09	0.10	0.10	0.09	wt%		
Propylene Glycol											—	<0.03	<0.03	<0.03	<0.03	wt%		
1,3-Propanediol											—	<0.03	<0.03	<0.03	<0.03	wt%		
Acetaldehyde											—	<0.03	<0.03	<0.03	<0.03	wt%		
Propanoic Acid											—	<0.03	<0.03	<0.03	<0.03	wt%		
Methanol											—	<0.03	<0.03	<0.03	<0.03	wt%		
1,2-Butanediol											—	<0.03	<0.03	<0.03	<0.03	wt%		
Ethanol											—	0.04	0.03	0.05	0.04	wt%		
Butanoic Acid											—	<0.03	<0.03	<0.03	<0.03	wt%		
2-Propanol											—	<0.03	<0.03	<0.03	<0.03	wt%		
Acetone											—	0.17	0.17	0.19	0.18	wt%		
1-Propanol											—	<0.03	<0.03	<0.03	<0.03	wt%		
2-Butanol											—	<0.03	<0.03	<0.03	<0.03	wt%		
2-Methyl-1-propanol											—	<0.03	<0.03	<0.03	<0.03	wt%		
1-Butanol											—	<0.03	<0.03	<0.03	<0.03	wt%		
2-Pentanone											—	0.05	0.06	0.05	0.05	wt%		
Phenol											—	<0.03	<0.03	<0.03	<0.03	wt%		
p-Cresol											—	0.08	0.08	0.08	0.08	wt%		
Dry Solid Content	15.9%	16.1%	16.0%	wt%							—	7.96	8.07	8.01	8.01	wt%		
pH	7.60	7.86	7.73								—	17,100	17,800	16,200	17,000	mg/L	19.2	wt%
TOC	35.3	35.3	wt%								—					637	g	
Product Weight																		

Note: Cells in yellow indicate planned analyses per the QAPP (test plan)

Method/Analyte	HTL Gas			
	Minimum	Maximum	Average	Units
GAS ANALYSIS				
H2 - Hydrogen	1.19	1.25	1.22	vol%
O2 - Oxygen	< 0.01	< 0.01	< 0.01	vol%
N2 - Nitrogen	0.47	1.35	0.82	vol%
CH4 - Methane	5.92	6.37	6.17	vol%
CO - Carbon Monoxide	< 0.01	< 0.01	< 0.01	vol%
CO2 - Carbon Dioxide	84.4	85.7	85.0	vol%
Ethylene	0.38	0.41	0.40	vol%
C2 - Ethane	0.89	1.06	0.99	vol%
H2S - Hydrogen Sulfide	1.43	1.61	1.53	vol%
Propane	1.06	1.34	1.23	vol%
Isobutane	0.05	0.06	0.06	vol%
n-Butane	0.65	0.85	0.77	vol%
trans-2-Butene	0.22	0.30	0.26	vol%
1-Butene	0.39	0.48	0.43	vol%
Isobutene	< 0.01	< 0.01	< 0.01	vol%
cis-2-Butene	0.21	0.33	0.28	vol%
Isopentane	0.25	0.34	0.30	vol%
n-Pentane	0.04	0.06	0.05	vol%
1,3-Butadiene	< 0.01	< 0.01	< 0.01	vol%
trans-2-Pentene	< 0.01	< 0.01	< 0.01	vol%
2-Methyl-2-butene	0.30	0.39	0.36	vol%
1-Pentene	0.04	0.05	0.05	vol%
cis-2-Pentene	0.07	0.09	0.08	vol%
Ammonia (gas)	NA	NA	NA	
SILOXANES				
Hexamethyldisiloxane (L2)			<6.63	mg Si/m ³
Hexamethylcyclotrisiloxane (D3)			<9.95	mg Si/m ³
Octamethyltrisiloxane (L3)			<9.95	mg Si/m ³
Octamethylcyclotetrasiloxane (D4)			<13.3	mg Si/m ³
Decamethyltetrasiloxane (L4)			<13.3	mg Si/m ³
Decamethylcyclopentasiloxane (D5)			<16.6	mg Si/m ³
Dodecamethylpentasiloxane (L5)			<16.6	mg Si/m ³
Trimethylsilanol*			<3.3	mg Si/m ³
Tetramethylsilane*			<3.3	mg Si/m ³
* - Analyzed as a tentatively identified compound (TIC). Result is estimated				

Appendix C: CHG WERF-04 (Digested Solids Feedstock) Complete Data Set

Note: Cells in yellow indicate planned analyses per the QAPP (test plan)

Method/Analyte	CHG Feed			CHG Aqueous								CHG Sulfur Removal/Catalyst		
	Pre Ion Exchange	Post Ion Exchange	Units	9/15/15 6:35	9/15/15 11:00	9/15/15 14:00	9/15/15 17:00	9/15/15 20:00	9/16/15 8:00	Average	Units	R-Ni	Ru/C	Units
ELEMENTAL ANALYSIS														
Carbon	1.82	0.94	wt%	—	0.32	—	0.32	—	0.33	0.32	wt%			
Hydrogen	10.7	11.6	wt%	—	11.8	—	11.7	—	11.2	11.6	wt%			
Nitrogen	0.58	0.36	wt%	—	0.36	—	0.38	—	0.32	0.35	wt%			
METALS														
Ag - Silver	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Al - Aluminum	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	285,000	148	ppm (wt/wt)
As - Arsenic	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Au - Gold	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Ba - Barium	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	156	ppm (wt/wt)
Ca - Calcium	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	440	820	ppm (wt/wt)
Cd - Cadmium	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Co - Cobalt	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	267	< 35	ppm (wt/wt)
Cr - Chromium	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Cu - Copper	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Fe - Iron	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	959	194	ppm (wt/wt)
K - Potassium	136	141	ppm (wt/vol)	—	118	—	141	—	142	133	ppm (wt/vol)	130	2,100	ppm (wt/wt)
Mg - Magnesium	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	160	96	ppm (wt/wt)
Mn - Manganese	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Mo - Molybdenum	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Na - Sodium	79.4	104	ppm (wt/vol)	—	74.5	—	94.0	—	90.2	86.2	ppm (wt/vol)	< 35	1,100	ppm (wt/wt)
Ni - Nickel	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	550,000	350	ppm (wt/wt)
P - Phosphorus	33.8	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Pb - Lead	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Pd - Palladium	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Pt - Platinum	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Re - Rhenium	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Rh - Rhodium	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Ru - Ruthenium	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	84,900	ppm (wt/wt)
S - Sulfur	187	36.6	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	9,900	1,410	ppm (wt/wt)
Si - Silicon	270	139	ppm (wt/vol)	—	50.8	—	53.4	—	56.2	53	ppm (wt/vol)	3,000	140	ppm (wt/wt)
Sn - Tin	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Sr - Strontium	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Ti - Titanium	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	22	66	ppm (wt/wt)
V - Vanadium	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
W - Tungsten	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Y - Yttrium	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Zn - Zinc	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)
Zr - Zirconium	< 1.0	< 1.0	ppm (wt/vol)	—	< 1.0	—	< 1.0	—	< 1.0	< 1.0	ppm (wt/vol)	< 35	< 35	ppm (wt/wt)

Note: Cells in yellow indicate planned analyses per the QAPP (test plan)

Method/Analyte	CHG Feed			CHG Aqueous							CHG Sulfur Removal/Catalyst			
	Pre Ion Exchange	Post Ion Exchange	Units	9/15/15 6:35	9/15/15 11:00	9/15/15 14:00	9/15/15 17:00	9/15/15 20:00	9/16/15 8:00	Average	Units	R-Ni	Ru/C	Units
Ammonia as nitrogen				5,100	5,700	5,750	5,400	5,450	5,200	5,430	mg/L			
ANIONS														
Chloride	5.09	<4.0	mg/L	—	<4.0	—	<4.0	—	<4.0	<4.0	mg/L			
Phosphate	47.1	<4.0	mg/L	—	<4.0	—	<4.0	—	<4.0	<4.0	mg/L			
Sulfate	283	<4.0	mg/L	—	<4.0	—	<4.0	—	<4.0	<4.0	mg/L			
COD	49,900	23,700	mg O ₂ /L	20	13	20	18	20	24	19	mg O ₂ /L			
DISSOLVED ORGANICS														
Glycolic acid	<0.03	<0.03	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
Glycerol	0.05	0.05	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
Formic Acid	<0.03	<0.03	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
Acetic Acid	0.37	0.04	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
Ethylene Glycol	<0.03	<0.03	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
Propylene Glycol	<0.03	<0.03	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
1,3-Propanediol	<0.03	<0.03	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
Acetaldehyde	<0.03	<0.03	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
Propanoic Acid	0.09	<0.03	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
Methanol	0.28	0.18	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
1,2-Butanediol	<0.03	<0.03	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
Ethanol	0.10	0.10	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
Butanoic Acid	<0.03	<0.03	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
2-Propanol	<0.03	<0.03	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
Acetone	0.16	0.14	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
1-Propanol	<0.03	<0.03	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
2-Butanol	<0.03	<0.03	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
2-Methyl-1-propanol	<0.03	<0.03	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
1-Butanol	<0.03	<0.03	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
2-Pentanone	<0.03	<0.03	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
Phenol	<0.03	<0.03	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
p-Cresol	0.08	0.07	wt%	—	<0.03	—	<0.03	—	<0.03	<0.03	wt%			
pH	8.01	9.15		9.12	9.14	9.16	9.18	9.13	9.06	9.13				
TOC	15,100	8,680	mg/L	—	1,110	—	1,130	—	1,170	1,130	mg/L			

Appendix C: CHG WERF-04 (Digested Solids Feedstock) Complete Data Set

Note: Cells in yellow indicate planned analyses per the QAPP (test plan)

Method/Analyte	CHG Gas							
	9/15/15 7:00	9/15/15 11:00	9/15/15 14:03	9/15/15 17:03	9/15/15 19:55	9/16/15 8:13	Average	Units
GAS ANALYSIS								
H2 - Hydrogen	1.66	1.92	< 0.01	1.84	1.79	1.78	1.80	vol%
O2 - Oxygen	0.28	0.25	< 0.01	0.16	0.17	< 0.01	0.21	vol%
N2 - Nitrogen	4.13	3.34	3.26	3.13	3.28	4.01	3.53	vol%
CH4 - Methane	92.99	93.2	95.4	93.9	93.5	93.1	93.7	vol%
CO2 - Carbon Dioxide	0.61	0.79	0.54	0.56	0.61	0.65	0.63	vol%
Ethylene	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	vol%
C2 - Ethane	< 0.01	< 0.01	< 0.01	< 0.01	0.09	< 0.01	0.09	vol%
Ammonia	NA	NA	NA	NA	NA	NA	NA	
SILOXANES		6/24/15 5:07	Sample Collected during WERF-01 CHG Run					
Hexamethyldisiloxane (L2)		< 0.0522						mg Si/m ³
Hexamethylcyclotrisiloxane (D3)		< 0.0782						mg Si/m ³
Octamethyltrisiloxane (L3)		< 0.0782						mg Si/m ³
Octamethylcyclotetrasiloxane (D4)		< 0.104						mg Si/m ³
Decamethyltetrasiloxane (L4)		< 0.104						mg Si/m ³
Decamethylcyclopentasiloxane (D5)		< 0.130						mg Si/m ³
Dodecamethylpentasiloxane (L5)		< 0.130						mg Si/m ³
Trimethylsilanol*		0.05						mg Si/m ³
Tetramethylsilane*		< 0.026						mg Si/m ³
		* - Analyzed as a tentatively identified compound (TIC). Result is estimated						

APPENDIX D

FRESH CATALYST AND RANEY NICKEL METALS ANALYSIS DATA

METALS	CHG Sulfur Removal/Catalyst		
	R-Ni	Ru/C	Units
Ag - Silver	< 30	< 45	ppm (wt/wt)
Al - Aluminum	250,000	65.8	ppm (wt/wt)
As - Arsenic	< 30	< 45	ppm (wt/wt)
Au - Gold	< 30	< 45	ppm (wt/wt)
Ba - Barium	< 30	170	ppm (wt/wt)
Ca - Calcium	253	188	ppm (wt/wt)
Cd - Cadmium	< 30	< 45	ppm (wt/wt)
Co - Cobalt	259	< 45	ppm (wt/wt)
Cr - Chromium	< 30	< 45	ppm (wt/wt)
Cu - Copper	< 30	38.8	ppm (wt/wt)
Fe - Iron	789	101	ppm (wt/wt)
K - Potassium	80.6	2,990	ppm (wt/wt)
Mg - Magnesium	120	67.0	ppm (wt/wt)
Mn - Manganese	< 30	< 45	ppm (wt/wt)
Mo - Molybdenum	< 30	< 45	ppm (wt/wt)
Na - Sodium	3,460	186	ppm (wt/wt)
Ni - Nickel	490,000	< 45	ppm (wt/wt)
P - Phosphorus	< 30	< 45	ppm (wt/wt)
Pb - Lead	< 30	< 45	ppm (wt/wt)
Pd - Palladium	< 30	< 45	ppm (wt/wt)
Pt - Platinum	< 30	< 45	ppm (wt/wt)
Re - Rhenium	< 30	< 45	ppm (wt/wt)
Rh - Rhodium	< 30	< 45	ppm (wt/wt)
Ru - Ruthenium	< 30	72,500	ppm (wt/wt)
S - Sulfur	68.7	452	ppm (wt/wt)
Si - Silicon	100	79	ppm (wt/wt)
Sn - Tin	< 30	< 45	ppm (wt/wt)
Sr - Strontium	< 30	< 45	ppm (wt/wt)
Ti - Titanium	28.3	120	ppm (wt/wt)
V - Vanadium	< 30	< 45	ppm (wt/wt)
W - Tungsten	-	-	ppm (wt/wt)
Y - Yttrium	< 30	< 45	ppm (wt/wt)
Zn - Zinc	< 30	< 45	ppm (wt/wt)
Zr - Zirconium	< 30	< 45	ppm (wt/wt)

APPENDIX E

FEEDSTOCK PROXIMATE ANALYSIS DATA

Table E-1. Proximate Analysis of Sludge Feed Samples^a.

Sludge Feed	Solids (%) ^b	Ash (%) ^c	Nitrogen (%) ^d	Protein (%) ^e	FAME Lipids (%) ^f	Total Lipid Content (%) ^g	Carbohydrates (%) ^h	Mass Closure ⁱ
WERF-02	98.18	9.38	3.445	21.74	9.83	20.57	50.55	102
WERF-03	96.44	16.51	7.920	50.97	4.73	16.18	15.72	99.4
WERF-04	99.40	29.33	4.575	28.60	0.80	9.31	17.84	85.1

^a Sample analyses performed at California Polytechnic State University, San Luis Obispo, CA. All reported results are the average of two determinations, exceptions noted below

^b Samples were dried at 60°C for 23.75 hours. All reported data are corrected for percent solids, exceptions noted below

^c Samples subjected to 575°C for 17 hours

^d Samples analyzed for nitrogen using an Elementar Analysis System. Data reported from a single analysis for each sample, not corrected for percent solids

^e Protein concentration calculated by multiplying nitrogen concentration by 6.2 factor; on average proteins contain 16% nitrogen. Reported data is corrected for percent solids

^f Fatty acid methyl ester (FAME) lipid content measured by gas chromatography

^g Total lipid content determined gravimetrically using accelerated solvent extraction (ASE)

^h Carbohydrate concentration determined using the MBTH (3-methyl-2-benzothiazolinone hydrazone) spectrophotometric method

ⁱ Combination of ash, protein, total lipid content and carbohydrate concentrations

REFERENCES

- Afif, E., P. Azadi, and R. Farnood, "Catalytic Hydrothermal Gasification of Activated Sludge," *Appl. Catal. B-Environ.*, **105**, 136-143 (2011).
- Badger, P., S. Badger, M. Puettmann, P. Steele, and J. Cooper, "Economic Analysis of Bio-oil," *BioResources*, **6**(1), 34-47 (2011).
- Baroutian, S., A. Smit, J. Andrews, B. Young, and D. Gapes, "Hydrothermal Degradation of Organic Matter in Municipal Sludge Using Non-Catalytic Wet Oxidation," *Chem. Eng. J.*, **260**, 846-854 (2015).
- Berglin, E.J., C.W. Enderlin, and A.J. Schmidt, "Review and Assessment of Commercial Vendors/Options for Feeding and Pumping Biomass Slurries for Hydrothermal Liquefaction," U.S. Department of Energy, Pacific Northwest National Laboratory report, PNNL-21981 (November, 2012).
- Cobble, J.W. and S.W. Lin, "Chemistry of Steam Cycle Solutions: Properties," in *The ASME Handbook on Water Technology for Thermal Power Systems*, P. Cohen (Ed.), American Society of Mechanical Engineers, New York, NY (1989).
- Channiwala, S.A. and P.P. Parikh, "A Unified Correlation for Estimating HHV of Solid, Liquid, and Gaseous Fuels," *Fuel*, **81**, 1051-1063 (2002).
- DOE Bioenergy Technologies Office, "Waste to Energy Workshop Summary," June 2015.
- DOE Bioenergy Technologies Office, "2013 Peer Review Report: Review Panel Summary Report and Project Results," February (2014).
- Elliott, D.C., "Review of Recent Reports on Process Technology for Thermochemical Conversion of Whole Algae to Liquid Fuels," *Algal Research*, **13**, 255-263 (2016).
- Elliott, D.C., "Hydrothermal Processing," In *Thermochemical Processing of Biomass: Conversion into Fuels, Chemicals, and Power*, R.C. Brown (Ed.), John Wiley & Sons, Chichester, UK, pp. 200-231 (2011).
- Elliott, D.C., "Description and Utilization of Product from Direct Liquefaction of Biomass," in *Proceedings of the Third-Symposium on Biotechnology in Energy Production and Conservation*, C.D. Scott (Ed.), Biotechnology and Bioengineering Symposium, Vol.11, John Wiley & Sons, New York, NY, pp. 187-198 (1981).
- Elliott, D.C. and J. Oyler, "Methods for Sulfate Removal in Liquid-Phase Catalytic Hydrothermal Gasification of Biomass," U.S. Patent # 8,608,981 (2013).

Elliott, D.C., P. Biller, A.B. Ross, A.J. Schmidt, and S.B. Jones, "Hydrothermal Liquefaction of Biomass: Developments from Batch to Continuous Process," *Bioresource Technol.*, **178**, 147-156 (2015).

Elliott, D.C., T.R. Hart, G.C. Neuenschwander, L.J. Rotness, G. Roesjadi, A.H. Zacher, and J. K. Magnuson, "Hydrothermal Processing of Macroalgal Feedstocks in Continuous-Flow Reactors," *ACS Sustainable Chem. Eng.*, **2**, 207-215 (2014).

Elliott, D.C., T.R. Hart, A.J. Schmidt, G.C. Neuenschwander, L.J. Rotness, M. V. Olarte, A.H. Zacher, K. O. Albrecht, R.T. Hallen, and J. E. Holladay, "Process Development for Hydrothermal Liquefaction of Algae Feedstocks in a Continuous-Flow Reactor," *Algal Research*, **2**, 445-454 (2013).

FLC, "Reaching New Peaks with Technology Transfer – FLC National Awards," Federal Laboratory Consortium for Technology Transfer National Meeting brochure, April 29, 2015, <https://www.federallabs.org/index.php?tray=publication&tid=0&cid=1FL1312>.

Govind, R., "Ammonia Removal from Wastewater," white paper available at http://www.academia.edu/4907207/AMMONIA_REMOVAL_FROM_WASTEWATER

Havrin, R.G., "The Comparison and Selection of Separations Equipment for the Municipal Industry (Centrifuges versus Belt Filters)," Centrisys Corp. white paper available at <http://centrisys.com/sites/all/themes/theme549/downloads/Centrifuges-vs-Belt-Filters.pdf>.

Hazlebeck, D.A., "Hydrothermal processing with phosphate additive," U.S. Patent # 6,238,568 (2001).

He, C., C. Chen, A. Giannis, Y. Yang, and J. Wang, "Hydrothermal Gasification of Sewage Sludge and Model Compounds for Renewable Hydrogen Production: A Review," *Renew. Sust. Energ. Rev.*, **39**, 1127-1142 (2014).

Hong, G.T., W.R. Killilea, and T.B. Thomason, "Method for Solids Separation in a Wet Oxidation Type Process," U.S. Patent # 4,822,497 (1989).

Huang, H., X. Yuan, H. Zhu, H. Li, Y. Liu, X. Wang, and G. Zeng, "Comparative Studies of Thermochemical Liquefaction Characteristics of Microalgae, Lignocellulosic Biomass, and Sewage Sludge," *Energy*, **56**, 52-60 (2013).

Itoh, S., A. Suzuki, T. Nakamura, and S. Yokoyama, "Production of Heavy Oil from Sewage Sludge by Direct Thermochemical Liquefaction," *Desalination*, **98**, 127-133 (1994).

Marrone, P.A. and G.T. Hong, "Corrosion Control Methods in Supercritical Water Oxidation and Gasification Processes," *J. Supercrit. Fluids*, **51**(2), 83-103 (2009).

Marrone, P.A., M. Hodes, K.A. Smith, J.W. Tester, "Salt precipitation and scale control in supercritical water oxidation – Part B: Commercial/full-scale applications," *J. Supercrit. Fluids*, **29**(3), 289-312 (2004).

Appendix D: Fresh Catalyst and Raney Nickel Complete Metals Data Set

- Marshall, W.L. "Water and Its Solutions," *Chemistry*, **48**(2), 6-12 (1975).
- Martynova, O.I. "Solubility of Inorganic Compounds in Subcritical and Supercritical Water," in *High Temperature, High Pressure Electrochemistry in Aqueous Solutions*, D. Jones and R.W. Staehle (Eds.), National Association of Corrosion Engineers, Houston, TX, pp. 131-138 (1976).
- Molton, P.M., A.G. Fassbender, and M.D. Brown, "STORS: The Sludge-to-Oil Reactor System," U.S. EPA Project Summary: EPA/600/S2-86/034, June (1986).
- NAABB (National Alliance for Advanced Biofuels and Bioproducts) Final Report, U.S. DOE, <http://www.energy.gov/eere/bioenergy/downloads/national-alliance-advanced-biofuels-and-bioproducts-synopsis-naabb-final> (2014).
- Qian, L., S. Wang, D. Xu, Y. Guo, X. Tang, and L. Wang, "Treatment of Municipal Sewage Sludge in Supercritical Water: A Review," *Water Res.*, **89**, 118-131 (2016).
- R&D Magazine, 2015 R&D 100 Award Winners, <http://rd100awards.com/2015-rd-100-award-winners> (2015).
- Ravich, M.L. and F.E. Borovaya, "Phase Equilibria in the Sodium Sulphate-Water System at High Temperatures and Pressures," *Russ. J. Inorg. Chem.*, **9**(4), 520-534 (1964).
- Shanableh, A. and E.F. Glynna, "Supercritical Water Oxidation – Wastewaters and Sludges," *Wat. Sci. Tech.*, **23**, 389-398 (1991).
- Suzuki, A., T. Nakamura, S. Yokoyama, T. Ogi, and K. Koguchi, "Conversion of Sewage Sludge to Heavy Oil by Direct Thermochemical Liquefaction," *J. Chem. Eng. Jpn.*, **21**(3), 288-293 (1988).
- Tanger, J.C. and K.S. Pitzer, "Calculation of the Ionization Constant of H₂O to 2,273K and 500 MPa," *AICHE J.*, **35**(10), 1631-1638 (1989).
- Tester, J.W., H.R. Holgate, F.J. Armellini, P.A. Webley, W.R. Killilea, G.T. Hong, and H.E. Barner, "Supercritical water oxidation technology: Process development and fundamental research," in *Emerging Technologies in Hazardous Waste Management III*, W.D. Tedder, F.G. Pohland (Eds.), Vol. 518, ACS Symposium Series, American Chemical Society, Washington D.C., pp. 35-76 (1993).
- Uematsu, M. and E.U. Franck, "Static Dielectric Constant of Water and Steam," *J. Phys. Chem. Ref. Data*, **9**(4), 1291-1306 (1980).
- Vandenburgh, S., Gas Treatment System Design Approach Memorandum by CDM Smith sent to P. Kistenmacher of Silicon Valley Clean Water, Redwood City, CA, July 18, 2012.

Vardon, D.R., B.K. Sharma, J. Scott, G. Yu, Z. Wang, L. Schideman, Y. Zhang, and T.J. Strathmann, "Chemical Properties of Biocrude Oil from the Hydrothermal Liquefaction of *Spirulina* Algae, Swine Manure, and Digested Anaerobic Sludge," *Bioresource Technol.*, **102**, 8295-8303 (2011).

WEF, "Design of Municipal Wastewater Treatment Plants: WEF Manual of Practice No. 8, ASCE Manuals and Reports on Engineering Practice No. 76," Fifth Ed., McGraw-Hill, New York (2010).

Xu, C. and J. Lancaster, "Treatment of Secondary Sludge for Energy Recovery," in *Energy Recovery*, E. DuBois and A. Mercier (Eds.), Nova Science Publishers, New York, NY, pp. 187-212 (2011).

Xu, D., S. Wang, X. Tang, Y. Gong, Y. Guo, Y. Wang, and J. Zhang, "Design of the First Pilot Scale Plant of China for Supercritical Water Oxidation of Sewage Sludge," *Chem. Eng. Res. Des.*, **90**, 288-297 (2012).

Yan-qing, S, Zhen, S., and Jing-lai, Z., "Transformation Regularity of Nitrogen in Aqueous Product Derived from Hydrothermal Liquefaction of Sewage Sludge in Subcritical Water," *Environm. Sci.*, **36**(6), 2210-2215 (2015).

Zhao, P., Y. Shen, S. Ge, and K. Yoshikawa, "Energy Recycling from Sewage Sludge by Producing Solid Biofuel with Hydrothermal Carbonization," *Energ. Convers. Manage.*, **78**, 815-821 (2014).



Water Environment & Reuse Foundation
1199 North Fairfax Street, 9th Floor ■ Alexandria, VA 22314-1177
Phone: 571-384-2100 ■ Fax: 703-299-0742 ■ Email: werf@werf.org
www.werf.org
WE&RF Stock No. LIFT6T14

Co-published by

IWA Publishing
Alliance House, 12 Caxton Street
London SW1H 0QS
United Kingdom
Phone: +44 (0)20 7654 5500
Fax: +44 (0)20 7654 5555
Email: publications@iwap.co.uk
Web: www.iwapublishing.com
IWAP ISBN: 978-1-78040-840-8



June 2016