PNNL-24386

U.S. DEPARTMENT OF ENERGY

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

# Pilot-Scale Biorefinery: Sustainable Transport Fuels from Biomass via Integrated Pyrolysis and Catalytic Hydroconversion – Wastewater Cleanup by Catalytic Hydrothermal Gasification

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TR Hart

June 2015

Pacific Northwest
NATIONAL LABORATORY

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June 19, 2015

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Pacific Northwest National Laboratory
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# Executive Summary

DOE-EERE Bioenergy Technologies Office has set several goals to increase the use of bioenergy and bioproducts derived from renewable resources. One of these goals is to facilitate the implementation of the biorefinery. The biorefinery will include the production of liquid fuels, power and, in some cases, products. The integrated biorefinery should stand alone from an economic perspective, with fuels and power driving the economy of scale while the economics/profitability of the facility will be dependent on existing market conditions.

UOP LLC proposed to demonstrate a fast pyrolysis-based integrated biorefinery. Pacific Northwest National Laboratory (PNNL) has expertise in an important technology area of interest to UOP for use in their pyrolysis-based biorefinery. This Cooperative Research and Development Agreement (CRADA) project provides the supporting technology development and demonstration to allow incorporation of this technology into the biorefinery. PNNL developed catalytic hydrothermal gasification (CHG) for use with aqueous streams within the pyrolysis biorefinery. These aqueous streams included the aqueous phase separated from the fast pyrolysis bio-oil and the aqueous byproduct streams formed in the hydroprocessing of the bio-oil to finished products.

The purpose of this project was to demonstrate a technically and economically viable technology for converting renewable biomass feedstocks to sustainable and fungible transportation fuels. To demonstrate the technology, UOP constructed and operated a pilot-scale biorefinery that processed one dry ton per day of biomass using fast pyrolysis. Specific objectives of the project were to:

- Identify acceptable renewable feedstocks that are sustainable, currently available and/or whose availability can be increased in the future.
- Demonstrate that these feedstocks can be pyrolyzed to an oil suitable for further processing.
- Demonstrate that pyrolysis oil can be successfully upgraded to transportation fuels.
- Define the economics of the process.
- Perform a Life Cycle Analysis (LCA) of the process.

The anticipated outcomes of the project were a validated process technology, a range of validated feedstocks, product property and life cycle data, and technical and operating data upon which to base the design of a full-scale biorefinery. The anticipated long-term outcomes from successful commercialization of the technology were: (1) the replacement of a significant fraction of petroleum based fuels with advanced biofuels, leading to increased energy security and decreased carbon footprint; and, (2) establishment of a new biofuel industry segment, leading to the creation of U.S. engineering, manufacturing, construction, operations and agricultural jobs.

PNNL development of CHG progressed at two levels. Initial tests were made in the laboratory in both mini-scale and bench-scale continuous flow reactor systems. Following positive results, the next level of evaluation was in the scaled-up engineering development system, which was operated at PNNL.

The results of tests with bio-oil aqueous fraction suggested that the organic contaminants, even at high concentration, can be effectively converted to a fuel gas product by CHG. However, corrosion of the stainless steel reactor system by the acidic components appeared to be significant, based on the metal deposits on the catalyst, but no noticeable change was seen in the reactor itself. Sulfur stripping may also be necessary in order to maintain long-term catalyst activity. Carbon fouling of the catalyst was also suggested by the loss of porosity and surface area. Handling of the aqueous stream was also identified as an issue as the acidic components were corrosive to steel cans and could not be stored for any period of time in such without resulting in a significant iron contamination and even failure of the container.

# Acronyms and Abbreviations

| | |
|---|---|
| BET | Brunauer-Emmett-Teller |
| BJH | Barrett-Joyner-Halenda |
| BPR | back-pressure regulator |
| Btu | British thermal unit |
| CHG | catalytic hydrothermal gasification |
| COD | chemical oxygen demand |
| CRADA | cooperative research and development agreement |
| CRS | continuous-flow reactor system |
| CSTR | continuously stirred tank reactor |
| DOE | U.S. Department of Energy |
| EERE | Energy Efficiency and Renewable Energy Office |
| GC | gas chromatography |
| HHV | higher heating value [MJ/kg] |
| HPLC | high performance liquid chromatography |
| IBR | integrated biorefinery |
| IC | ion chromatography |
| ICP | inductively coupled plasma, atomic emission spectroscopy |
| ID | internal diameter |
| LC | liquid chromatography |
| LCA | life cycle analysis |
| LHSV | liquid hourly space velocity |
| MAWP | maximum allowable working pressure |
| MJ | mega-Joule |
| MSRS | mobile scaled-up reactor system |
| NA | not analyzed |
| ND | below detection limit |
| ppm | parts per million |
| P&ID | process and instrumentation diagram |
| SCF | standard cubic foot |
| SS | stainless steel |

# Contents

# Figures

# 1.0 Introduction

DOE-EERE Bioenergy Technologies Office has set forth several goals to increase the use of bioenergy and bioproducts derived from renewable resources. One of these goals is to facilitate the implementation of the biorefinery. The biorefinery will include the production of liquid fuels, power and, in some cases, products. The integrated biorefinery (IBR) should stand-alone from an economic perspective with fuels and power driving the economy of scale while the economics/profitability of the facility will be dependent on existing market conditions.

UOP LLC proposed to demonstrate a fast pyrolysis-based integrated biorefinery. PNNL has expertise in an important technology area of interest to UOP for use in their pyrolysis-based biorefinery. This CRADA project provided the supporting technology development and demonstration to allow incorporation of the technology into the biorefinery. PNNL developed catalytic hydrothermal gasification (CHG) for use with aqueous streams within the pyrolysis biorefinery. These aqueous streams included the aqueous phase separated from the fast pyrolysis bio-oil but, more importantly, the aqueous byproduct streams formed in the hydroprocessing of the bio-oil to finished products.

The purpose of this project was to demonstrate a technically and economically viable technology for converting renewable biomass feedstocks to sustainable and fungible transportation fuels. UOP was tasked with demonstrating the technology by constructing and operating a pilot-scale integrated biorefinery that could process one dry ton per day of biomass using fast pyrolysis. Subsequent upgrading to transportation fuels was not attempted at the IBR. Specific objectives of the project were to:

- Identify acceptable renewable feedstocks that are sustainable, currently available and/or whose availability can be increased in the future.
- Demonstrate that these feedstocks can be pyrolyzed to an oil suitable for further processing.
- Demonstrate that pyrolysis oil can be successfully upgraded to transportation fuels.
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The anticipated outcomes of the project were a validated process technology, a range of validated feedstocks, product property and life cycle data, and technical and operating data upon which to base the design of a full-scale biorefinery. The anticipated long-term outcomes from successful commercialization of the technology are: (1) the replacement of a significant fraction of petroleum based fuels with advanced biofuels, leading to increased energy security and decreased carbon footprint; and (2) establishment of a new biofuel industry segment, leading to the creation of U.S. engineering, manufacturing, construction, operations and agricultural jobs.

PNNL was tasked with developing CHG for use with aqueous streams within the pyrolysis biorefinery. These aqueous streams included the aqueous phase separated from the fast pyrolysis bio-oil and the aqueous byproduct streams formed in the hydroprocessing of the bio-oil to finished products. As other aqueous streams were identified as of interest within the biorefinery, these might also have been tested in CHG, but none were so identified. The development work progressed at two levels. Initial tests were made in the laboratory in mini-reactor scale and bench-scale continuous-flow reactor systems. Following positive results, the next level of evaluation was in the scaled-up engineering development system.

The Statement of Work for this CRADA project included two tasks for PNNL.

Task 1.

PNNL completed development tests of CHG for use with aqueous streams within the pyrolysis biorefinery. These aqueous streams included the aqueous phase separated from the fast pyrolysis bio-oil and the aqueous byproduct streams formed in the hydroprocessing of the bio-oil to finished products. The initial development work was done in the bench-scale continuous-flow reactor systems. Subsequent long-term tests were performed in the micro-scale reactor system.

Task 2.

Following initial tests in Task 1, in the laboratory, the next level of evaluation were in the scaled-up engineering development system. The demonstration tests were performed at Richland, Washington.

The Statement of Work included the following milestones for PNNL.

Milestones (months from start)

| | | |
|---|---|---|
| MS-1 | Demonstrate effectiveness of CHG to recover energy from aqueous waste streams and meet NPDES site discharge requirements | 42 |
| MS-2 | Verification of CHG treatment of wastewater streams produced during scaled-up bio-oil hydroprocessing tests | 59 |
| MS-3 | Completion of final report | 60 |

# 2.0 Methods and Equipment

CHG of organic contaminated wastewaters provides a highly efficient pathway to medium-Btu fuel gas. This gas product can be used directly in heat and power applications or has potential to be cleaned to pipeline quality gas or feedstock for hydrogen production. As compressed or liquefied natural gas, it has potential to displace imported petroleum used in transportation applications. Hydrothermal processing utilizes water-based solutions at moderate temperatures (350 °C) and sufficient pressure (3,000 psi) to maintain the water in the liquid phase as depicted in **Figure 1**. Previously, papers have been published addressing the processing environment,[i] catalyst systems for this environment,[ii,iii] continuous-flow reactor tests with fixed beds of catalyst in a tubular reactor,[iv] and process development tests with wet biomass feedstocks.[v]

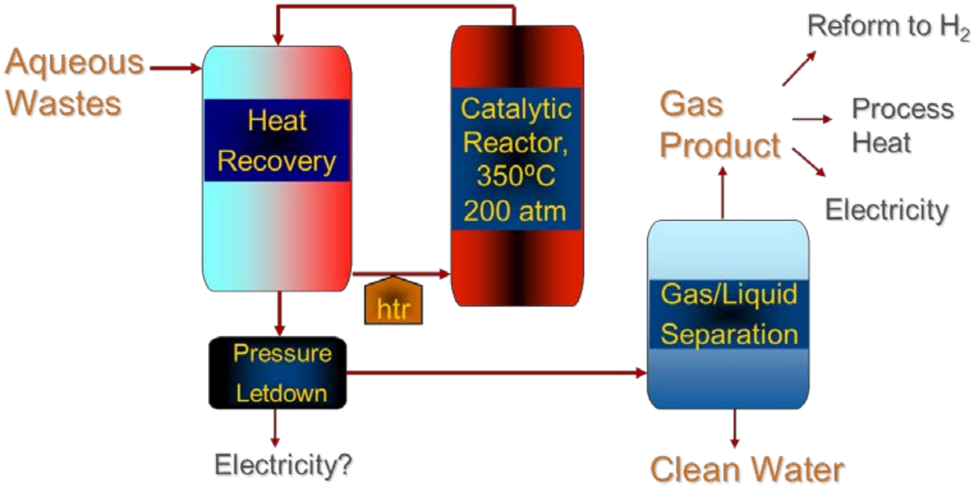

**Figure 1. Schematic of Catalytic Hydrothermal Gasification**

The use of hydrothermal processing (high-pressure, high-temperature liquid water) has received relatively limited study.[vi] One application of this processing environment has been demonstrated in the catalytic gasification of organics.[iv] In this application, heterogeneous metal catalysts accelerate the reaction of organics with water and produce methane and carbon dioxide as the product gases. It has been reported both as a means of recovering useful energy from organic-in-water streams and as a water treatment system for wet organic contaminants.

Developing catalysts for this processing environment has also been an important factor in making this processing technology viable.[ii,iii] More recently, we have demonstrated more stable catalyst formulations for wet gasification as described in patent claims.[vii,viii]

The equipment and procedures described below were used for the testing.

## 2.1 Lab-scale continuous-flow reactor system

The bench-scale Continuous-flow Reactor System (CRS) was designed for obtaining engineering data for the continuous-flow CHG process. The system consists of the high-pressure pump feeding system, product recovery system, data acquisition and control system, furnaces, and other equipment required to utilize the 1-liter tubular catalytic reactor. The feed line, operated at ambient temperature, was ½-inch 316 stainless steel (SS) tubing with 0.049 inch wall. All process lines at temperature of 200 ºC or above were ¼-inch 316 SS tubing with 0.065-inch wall. The system was based on a throughput of 1.5 liter of solution per hour and was typically operated over a test period of 6-10 h. The process flow diagram is shown in **Figure 2**. The solids separator and sulfur stripper were bypassed in these tests as the mineral content and sulfur content were considered too low to be of concern.

The pumping subsystem was designed to operate at feed pressures up to 3700 psig and flow rates between 0.2 and 4.0 L/h. This system consists of an Isco 500D pump. The valves and tubing on the high-pressure metering syringe pumps were configured to fill and empty the pumps based on controller commands. System piping included 0.5-inch (0.065-wall) 304 tubing SS on the outlet of the pump. Pump inlet piping was 0.5-inch (0.035 wall) 304 SS tubing. All valves and valve trim (except the pressure-control valve) were also made of SS. Using the Isco pump, the feeding rates were measured directly by the screw drive of the positive displacement syringe pump.

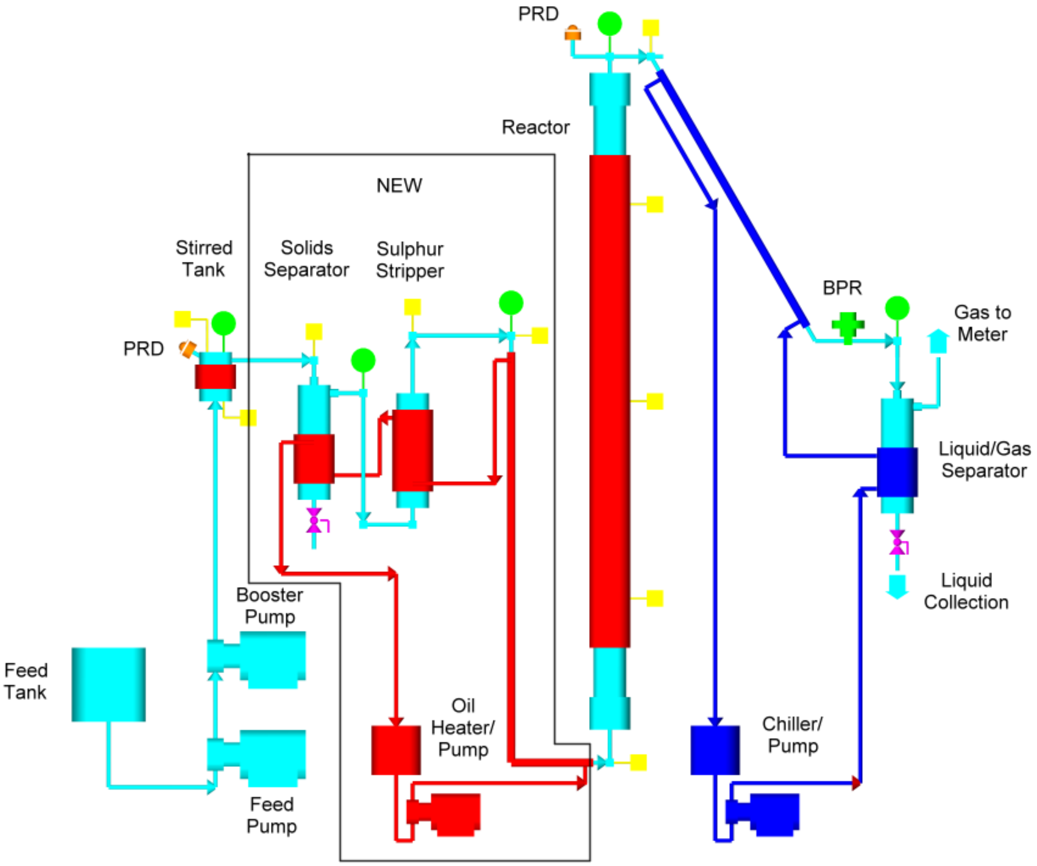

**Figure 2. Process Flow Schematic of the Bench-Scale Continuous-Flow Reactor System**

The gasification reactor was a 1-inch ID X 72-inch-long 304 SS tube. The vessel (MAWP 10,000 psi @ 72 ºF, or approximately7500 psi @ 400 ºC) had bolted-closure endcaps with metal o-rings on each end. The reactor furnace was a 6-kWe resistance heater split into three separately controllable zones. The pressure was controlled with a dome-loaded diaphragm back-pressure regulator (BPR).

After exiting the reactor, the product gases and water were cooled and vented through a BPR to an online phase separator. After separation the offgas was cooled by another chilled heat exchanger to further remove any entrained water, the liquid was accumulated in a weighed tank. The offgas was measured by a wet test meter and analyzed by a gas chromatograph. Pressure transducers on each vessel recorded pressures and noted pressure drops due to restriction and plugging. Each vessel and most transfer lines were also monitored for temperature. Three rupture discs protected the system.

The data acquisition and control system used in the CRS was a hybrid computer-based system employing discrete data acquisition devices and single-loop process controllers communicating to a central computer. The computer was used during experiments to monitor the process, calibrate instruments, and record data for later analysis. The data acquisition/control system regulated the furnaces and recorded the process parameters and offered off-normal warnings and auto-shut down. LabVIEW was used to coordinate these activities. Non-control sensors such as thermocouples and pressure transducers were monitored via the data acquisition unit.

Actual startup of the experiment usually required 2 to 4 h to bring operating conditions to the desired levels. Operating data were recorded, and data windows were defined based on steady-state (or near steady-state) operating conditions.

Gas samples could be withdrawn manually and analyzed every 30 to 60 min. The gaseous stream was mainly composed of $CO_2$, $CH_4$, $H_2$, and $C_2$+ hydrocarbons, as well as water vapor. Gas analysis was performed by gas chromatography (GC) as described earlier.[iii] The gas samples were withdrawn after cooling and depressurizing the product effluent to near ambient conditions. In the process, the gas product is effectively scrubbed by the liquid aqueous byproduct. As a result, the liquid byproduct contains some dissolved product gases. Particularly in the case of carbon dioxide, it is retained in the water by participating in acid/base chemistry with alkali cations derived from the feedstocks.

Once the gas samples from the experiments were analyzed, calculations were made to determine the conversion of the organic feedstock to gases. Carbon conversion to gas was then calculated on a mass basis for the carbon in the product gases as a percent of the carbon in the feedstock. The carbon balance is the key elemental balance for this process.

The liquid effluent was analyzed for chemical oxygen demand (COD) and pH. Percent COD reduction from the feed to product was a major process indicator, which was monitored to determine catalyst effectiveness. Anions, including chloride, were measured by ion chromatography (IC) using a Dionex DX 500 IC consisting of a GP40 Pump, EG40 Elluent Generator, ED40 Electrochemical Detector, with an AS3500 autosampler. An ASRS-Ultra 4 mm suppressor was used (at 100 mW) to minimize baseline drift. The chromatography was performed using an AG-11 guard column and an AS-11HC column running at 30 °C, with an hydroxide gradient from 0.5 mM to 41 mM and a flow rate of 1.2 ml/min. Certified standards were used to calibrate the IC.

Elemental analysis of liquid and solid samples was performed by inductively coupled plasma - optical emission spectrometry (ICP). The ICP was a Perkin-Elmer 3000DV with an AS90 Autosampler, which has an instrument detection limit of about 1 ppb (for most elements) with a linear calibration up to 100 ppm (for most elements). Solid samples were prepared via microwave digestion in concentrated nitric and hydrochloric acids, then diluted to volume. The ICP was calibrated and verified with two independent certified standard sets. Spikes and dilutions were down for each batch of samples to check for and/or mitigate any matrix effects. The ICP process ran a constant pump rate of 1.5 ml/min for all samples and standards during analysis. A 3 ml/min rinse and initial sample flush was used to switch between each sample and standard. The plasma was run at 1450 W with argon flow. Trace metal grade (sub-ppb) acids and two independently NIST-certified calibration standard sets were used for calibration and method verification.

## 2.2 Mini-reactor system

Essentially the same methods were followed in the experiments using the mini-reactor system with the exception that the mini-reactor was designed for unattended, around-the-clock operation to validate long term processing.

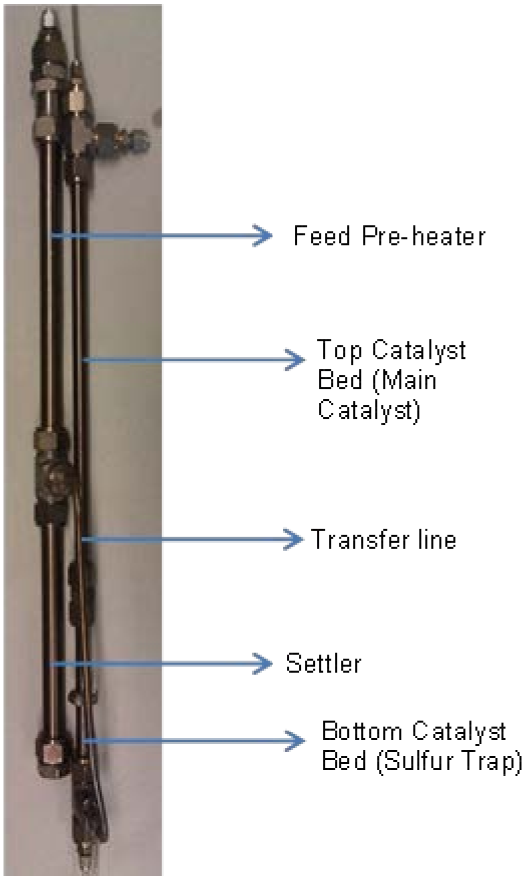

**Figure 3. Mini-reactor Assembly**

The mini-reactor process flow was similar to the earlier bench-scale tests. A separate solids settler portion of the reactor system was connected into the flow line downstream of the preheater. In this way, mineral precipitate could be settled and collected without plugging the catalyst bed and, subsequently, the reduced sulfur could be scrubbed from the stream by a bed of nickel particles, to reduce the poisoning of the catalyst bed. In the initial tests there was no sulfur scrubbing component used. After it was determined that there was a need for sulfur scrubbing was the nickel metal bed placed into the flow. The mineral precipitation capability was no needed in any of the tests due to the low mineral content of the feedstocks.

The main reactor has a length of ½" tube (0.049" wall) with a "t" fitting on the end, as shown in **Figure 3** — overall it is about 14.5 inches long with a 1/8” thermocouple down the center line. A calculation of the volume would be somewhat higher than the 22 cc of the Ru/C catalyst used in the experiment. The volume of catalyst was determined from the measured mass and calculated based on an apparent bulk density that was also measured (0.42 g/ml). Therefore, the catalyst added to the reactor must have not completely filled the annular space due to some hang-up around the thermocouple. The catalyst usage (liquid hourly space velocity) was based on the actual amount of catalyst added for the test. The Ru/C catalyst is a BASF formulation, which contains 7.8 wt % Ru on a proprietary graphitized carbon extrudate.

## 2.3 Scaled-up reactor system

The mobile scaled-up reactor system (MSRS) was designed based on the bench-scale unit.[iv] It was used previously for on-site demonstrations of CHG at industrial plants.[ix] For the tests reported here, it was updated with new electronic controls and data logging system, based on the Honeywell system used at the Hawaiian IBR site. In addition to the 500D ISCO pump, a high capacity version HPX was added to the mobile unit. With the two pumps, the capacity was increased to 20 L/h to utilize the four tubular reactors at full capacity of LHSV at up to 5 L of feedstock solution, $L^{-1}$ of catalyst $h^{-1}$. The P&ID of the mobile system is shown in **Figure 4**.

Another modification completed on the mobile unit was the addition of a recirculating cooler to eliminate the once-through cooling in the original system. For this application the solids separation was not needed so the settling tank and blow-down system was bypassed.

The MSRS is housed in a 20-ft x 8-ft trailer that is divided into two sections. The smaller of the two sections, located at the front of the trailer, serves to house the data acquisition and control equipment, the analytical equipment, all relevant documentation, and operator controls. The larger of the two sections located at the back of the trailer houses the reactor system.

The reactor system is completely self-contained within the back portion of the trailer. There is an operator access corridor located at the front of the system which provides access to the feed pumps, gas/liquid separator, and the back pressure regulators, as well as the switch panel to activate all of the system’s components. Access to the back portion of the trailer is limited to the access corridor, once the system is under pressure and fluid temperatures exceed 100 °C.

This system is designed to operate at relatively high temperatures and medium pressures at a MAWP of 426 °C and 3400 psig. The conversion reaction typically employs a catalyst to accelerate steam reforming and methane synthesis reactions to produce a useable, medium-BTU fuel gas.

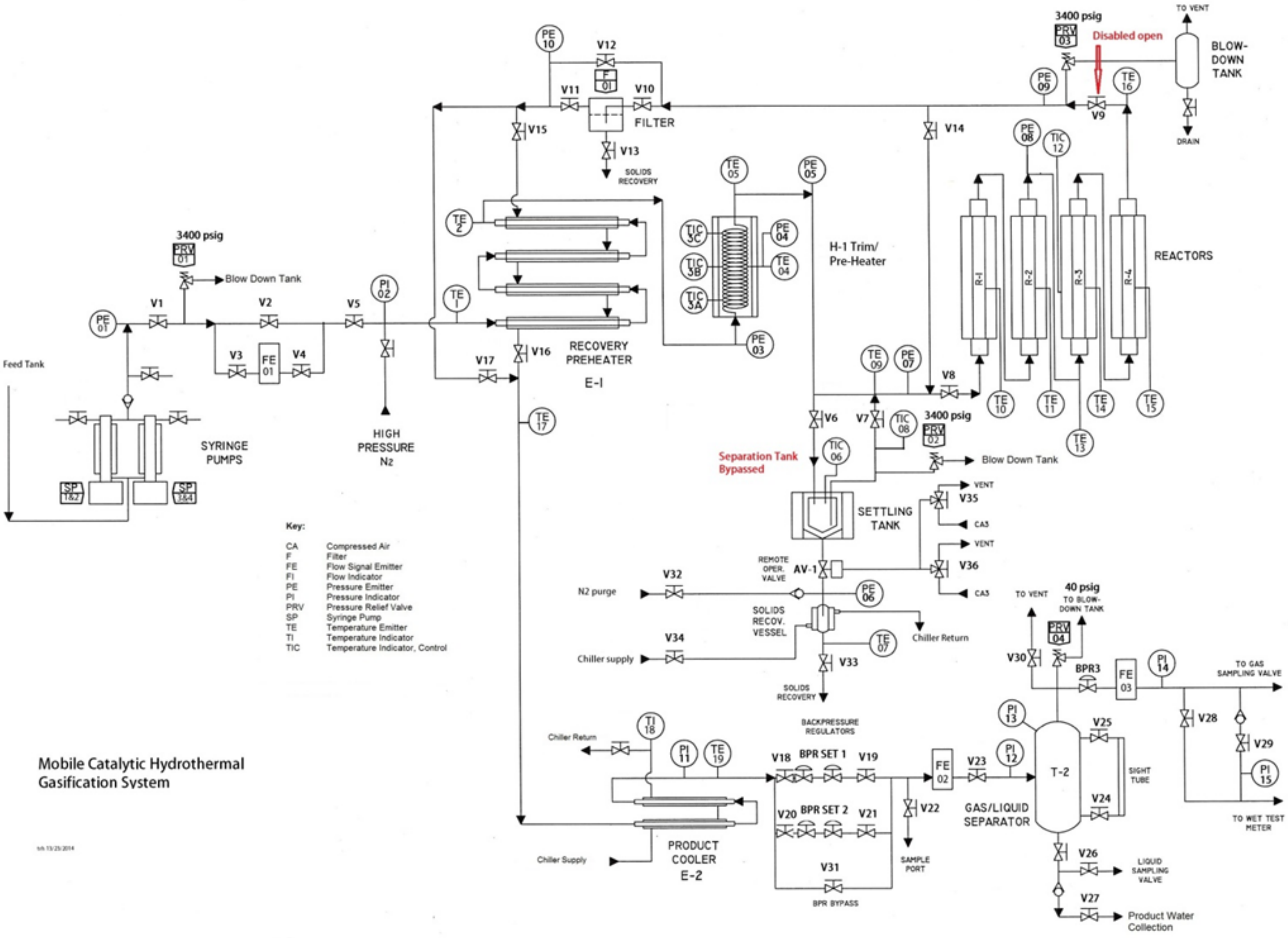

**Figure 4. Process and Instrumentation Diagram of the mobile CHG reactor system**

The objectives for testing are to determine the potentials for waste volume reductions, energy conversions, and catalyst performance for the organics-laden, aqueous feedstocks being produced by bio-oil processing.

The MSRS is comprised of heaters and pumps and tubing. The process pumps organics in water up to 3000 psig and 350 °C. The solution is passed through a filter to remove any inorganics, then across a catalyst bed to gasify the organics to mostly carbon dioxide and methane. The heat is recovered via tube-in-tube heat exchangers. The product is further cooled with a closed loop chiller to ambient temperature. The product is relatively clean process water and gas. The pressure is let down and the water/gas is separated and quantified. A gas chromatograph is used to determine the composition of the product gas. Pressure is maintained via two parallel, two-stage TESCOM back-pressure regulator combinations.

| | | |
|---|---|---|
| MAWP | 3400 psig | 426 °C |
| Nominal operation | 3000 psig | 350 °C |
| Liquid Flow rates | 4-20 L/h | |
| Gas production rates | 10 – 2000 L/h | Organic loading dependent |
| Gas composition | 58% $CH_4$, 40%$CO_2$, 2% $H_2$, trace other | |

Component ratings:

| | | |
|---|---|---|
| Tubing after cooling, ½” 0.049” | 3700 psig | Ambient to 100 °C |
| Tube in tube HX (Shell side) ¾” 0.109” tubing | 4582 psig | 426 °C |
| Tube in Tube HX (tube side) 3/8” 0.065” tubing | 5135 psig | 426 °C |
| M1 heater tubing 3/8” 0.065” | 5135 psig or (4940 psig $H_2$ max) | 426 °C or (538 °C heater max) |
| Reactors HIP (TOC11-40) | 5950 psig | 426 °C |
| Solids separator 1.8L (4680) | 4200 psig | 600 °C |
| BPR’s two stage letdown TESCOM’s | 6000 psig | 74 °C |
| Gas liquid separator After BPR’s (low pressure side) PRV set at 40 psig | 150 psig | ambient |

# 3.0 Bench-Scale Processing Tests

## 3.1 Lab-scale tests with fast pyrolysis product derivatives

The initial tests in this project focused on an aqueous fraction of bio-oil in anticipation that the bio-oil feedstock for hydrotreating could be improved by separation of the water and some of the light oxygenate components. These low molecular weight components were viewed as not useful for production of liquid hydrocarbon fuels and the hydrotreating of these materials would be a potential waste of hydrogen.

### 3.1.1 CT32-33 (11/5/2010)

The first sample of aqueous bio-oil received from UOP (CT32-33) was shipped in a steel 5-gallon can. Corrosion of the can was evident. ICP analysis of the sample showed 1970 ppm of Fe in the liquid. Liquid chromatography analysis identified the primary components as: 8.33% acetic acid, 2.71% hydroxyacetone, 1.36% methanol, 0.86% formic acid, and 0.32% ethanol

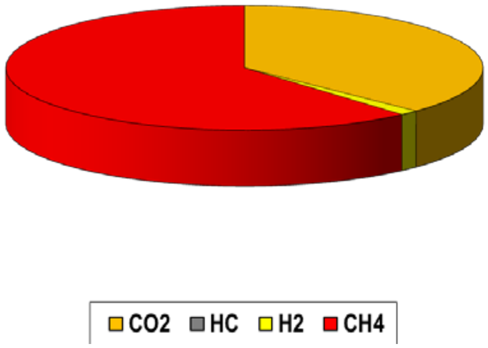

**Figure 5. Product gas composition from CHG of aqueous bio-oil.**

This sample was processed in the bench-scale CRS using the standard conditions of 350°C, 3000 psig, and a LHSV of 1.7 L feed - $L^{-1}$ of catalyst - $h^{-1}$. In the test the COD was reduced from the starting level of 165,300 ppm by 99.96%, producing a process effluent at 135 ppm COD. The gas product yield was 0.91 L / g organic of a medium-Btu gas with 627 Btu/SCF and the composition depicted in **Figure 5**. The test was performed with pH adjustment by addition of NaOH and $Na_2CO_3$, to increase the feed pH of 3.4 to >5, which led to salt precipitation in the catalyst bed, plugging the reactor and terminating the test. pH adjustment was not deemed necessary for this work and was not used again.

### 3.1.2 CT45-1 (3/30–31/2011)

The second sample of aqueous bio-oil (CT45) was received after shipment in a plastic bucket. Liquid chromatography analysis identified essentially the same primary components: 4.89% acetic acid, 1.64% hydroxyacetone, 0.55% methanol, 1.62% formic acid, and 0.55% ethanol, but also 1.58% 1,2,3-butanetriol and 1.09% 1-butanol as well as an astounding 10.33% succinic acid with 1.18% of a peak identified as (but unlikely) sorbitol.

The first test with this feedstock was performed in the mini-reactor system using the aqueous fraction diluted 50/50 with deionized water. This attempt to reduce the COD of the feedstock was unsuccessful as some of the organic components phase-separated upon addition of more water. The mixed phases were fed to the reactor but organic phase was susceptible to thermal reaction in the heat-up zone of the reactor forming a polymeric solid that plugged the reactor system and terminated the test.

The CT45-1 test was followed by three successful tests performed with aqueous bio-oil fractions. A single bed of Ru/C catalyst was used throughout these three tests. Time on stream amounted to 137.5 h total for the three tests. Up to 99.98% conversion of organic (measured by COD) was achieved. The feedstocks were all about ~15% organic content (COD 160,200-178,250 ppm). LHSV from 2-4 L feed - $L^{-1}$ of catalyst - $h^{-1}$ were evaluated. The test temperature was typically 350 °C, but 200 °C was also tested. The operating pressure was within the range of 190-200 atm. The typical gas composition of 55%/40% $CH_4/CO_2$ was produced with 1-2% $H_2$, 0-5% of higher hydrocarbon gases.

### 3.1.3 CS6-06 (4/26–29/2011)

For this test, the feedstock was produced at PNNL using a wiped-film distillation system. An aqueous fraction was recovered from the lower density bio-oil fraction of the bio-oil feedstock (CS6-06) produced at the National Renewable Energy Laboratory as part of CRADA #259[x] using corn stover feedstock. The lower density fraction phase separated from the bio-oil after condensation and cooling. The wiped-film distillation set point was 40ºC (pot temperature) with 70ºC film temperature and -1ºC in the primary trap followed by an isopropanol/dry ice cold finger. The system was operated at 5 torr (0.1 psi) pressure. As this was a continuous-flow still, a 300 ml/h feed rate was used after the first hour of devolatilizing. During the distillation, 32.5% was non-volatile, 60.4% of light distillate was recovered, 85% of which is water, and there was a loss of 7.1%. The analysis of the light distillate showed that it had a very similar composition to that determined for the CT32-33 product described above. LC analysis identified the primary components as: 7.10% acetic acid, 3.19% hydroxyacetone, 1.51% methanol, 0.38% formic acid, and 0.61% ethanol with 0.39% ethylene glycol and 0.24% succinic acid. Lesser amounts of other $C_3$ to $C_5$ alcohols and aldehydes were also noted. Chloride analysis detected 5 ppm Cl. ICP analysis showed 11 ppm of S and 1 ppm Na. The labor requirement was high for producing the CHG feedstock; 2/3 day distillation provided only 1/3 day of feed for the bench-scale reactor.

The aqueous fraction was tested for CHG in the mini reactor to allow a longer test. The test extended over 72 hours including a period of operation at lower temperature, 200 ºC. High conversion (99.93% of 177,600 ppm COD at 2.01LHSV[1]) was attained at the typical operating temperature of 350 ºC. At the lower temperature, the conversion was greatly reduced with the COD being reduced only 5% at LHSV of 4. By increasing the temperature back to 350 ºC, the conversion returned to a high level of 99.98% of a diluted feedstock (89,000 ppm COD) at the higher LHSV of 4.00.

### 3.1.4 CT45-2 and CT45-3 (5/23–24 & 6/7–8/2011)

The same catalyst bed was used in a subsequent test using the UOP CT45 feedstock. As shown in **Table 1** the activity of the catalyst remained high for over 110 hours, but some deactivation can be seen in the reduced conversion measured over the last 20 plus hours on stream.

During the period of high conversion, the gas composition was consistently 54-62% methane with 36 - 45% $CO_2$. The hydrogen and ethane concentrations each remained below 2%. As the activity level fell toward the end of the experiment, the gas composition shifted to less methane (48% $CO_2$ and 43% $CH_4$ at the end) and more hydrogen, ethane and higher hydrocarbons.

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[1] The unit for LHSV values mentioned in this report is *L feed - $L^{-1}$ of catalyst - $h^{-1}$*.

**Table 1. Results of CHG with aqueous bio-oil distillate**

| Test | Time on stream | Feed COD | LHSV | Product COD | Conversion % | g COD/hr |
|---|---|---|---|---|---|---|
| CT45-2 | 77-89.75 | 160,200 | 2.22 | 32 | 99.98 | 11.6 |
| | 92-98.67 | 160,200 | 2.50 | 37 | 99.98 | 13.0 |
| | 100-105.5 | 160,200 | 3.40 | 155 | 99.92 | 17.6 |
| CT45-3 | 107.5-111.5 | 178,250 | 1.97 | 56 | 99.98 | 11.4 |
| | 119.5-121.5 | 178,250 | 3.07 | 1,830 | 99.27 | 17.6 |
| | 133.3-138.2 | 178,250 | 2.01 | 8,913 | 96.47 | 11.2 |

The catalyst was analyzed after recovery from the reactor. As seen in **Table 2,** the analysis of the fresh catalyst showed, in addition to the Ru, some trace elements, such as K, Ca, Si, Na and some S with Mn and Al. The feedstock analysis suggested that only minor amounts of Na, Al, Si, and perhaps S would be introduced. However, after use the recovered catalyst contained a sizeable amount of Si and S, as well as Cu and Na. There was actually a lower level of K and Ca than found in the fresh catalyst. Most disturbingly, there was a large amount of Fe, Ni, Cr and even Mo—all elements found in the stainless steel composing the reactor wall. The presence of Cu is curious and unexplainable; it was found at such concentration on some of the catalyst extrudates (0.63wt% of total recovered catalyst) that they had a reddish tinge. The S is a key catalyst poison of concern when using Ru. The other elements could act as catalyst site fouling agents, causing deactivation as well, especially in combination with suspected carbon deposition. Nitrogen physisorption tests of the fresh and spent catalysts showed significant loss in pore volume and surface area (complete loss of the micropores) over the period of use, as presented in **Table 3**.

**Table 2. ICP analysis of the components in the CHG tests with aqueous bio-oil distillate**

| element | feed | fresh catalyst | used catalyst |
|---|---|---|---|
| Ru | <2 | 91465 | 65460 |
| K | <2 | 1571 | 275 |
| Ca | <2 | 523 | 47 |
| Si | 5 | 259 | 2796 |
| S | 1 | 143 | 1993 |
| Na | 9 | 96 | 150 |
| Al | 9 | 42 | <50 |
| Mn | <2 | 31 | <50 |
| Cu | <2 | <25 | 613 |
| Fe | <2 | <25 | 2754 |
| Ni | <2 | <25 | 2308 |
| Cr | <2 | <25 | 335 |
| Mo | <2 | <25 | 84 |

Surface area, porosity, and pore size analyses were determined using nitrogen adsorption/desorption collected with a QUANTACHROME AUTOSORB 6-B gas sorption system. The samples were degassed at 150 °C for 8-16 h under vacuum. The degassed samples were analyzed by nitrogen adsorption/desorption at a constant temperature 77.4K. The volume amount of $N_2$ gas that adsorbed/desorbed on/from the surface of sample vs. relative pressure was measured. The surface area was determined from the isotherm using the 5 points BET method. The BJH method was used for the porosity and pore size analyses.

**Table 3. Physisorption analysis of the catalysts in the CHG tests with aqueous bio-oil distillate**

| measurement | **fresh catalyst** | **used catalyst** |
|---|---|---|
| BET surface area, $m^2/g$ | 767 | 226 |
| t- method micro-pore surface area, $m^2/g$ | 166 | 0 |
| BJH pore volume, cc/g | 0.54 | 0.26 |

The results of these tests with bio-oil aqueous fraction suggest that the organic contaminants, even at high concentration, can be effectively converted to a fuel gas product by CHG. However, corrosion of the stainless steel reactor system by the acidic components appears to be significant, based on the metal deposits on the catalyst. Sulfur stripping may also be necessary in order to maintain long-term catalyst activity. Carbon fouling of the catalyst was also suggested by the loss of porosity and surface area.

## 3.2 Mini-reactor tests with UOP-derived hydrotreating byproduct feedstocks

Subsequent tests in the mini-reactor used as feedstock various aqueous products from the UOP bio-oil hydrotreating tests. Details of the production of the aqueous byproducts were not provided by UOP except for titles as used below. The biomass feedstock was not identified either. The first three products expressed a range of product compositions and concentrations, as seen in **Table 4**. Based on these results, it appears that a range of hydrotreating was undertaken such that the pyrolysis bio-oil product was more or less hydrogenated. Ammonium analysis showed a low level (4.5ppm) in the aqueous feed but a higher level (468ppm) in the fixed bed product.

Trace elements were quite low in the hydrotreating aqueous byproducts (shown in **Table 5**). Traces of biomass minerals are present. Sulfur content ranged over an order of magnitude from 2 to 20 ppm. Further analysis of the “mixed” feedstock showed a density of 0.9806 with a viscosity of 10.69 at 40 °C. Ion chromatography of the feedstocks for anion analysis (chloride, sulfate, etc.) was unsuccessful because of baseline displacement and interference apparently due to organic anions; however, sulfate was not detectable.

**Table 4. Chromatography Analysis of UOP-Provided Feedstocks**

| | **aqueous** | **fixed bed** | **Mixed** |
|---|---|---|---|
| COD | 166,467 ppm | 55,500 ppm | 87,048 ppm |
| $NH_4^+$ | 6.5 ppm | 468 ppm | 651 ppm |
| **HPLC** | | | |
| formic acid | 0.04% | 0.005% | 0.153% |
| acetic acid | 6.57% | 0.098% | 0.438% |
| propionic acid | 0.33% | 0.004% | ND |
| glycolic acid | 0.21% | NA | 1.111% |
| methanol | 0.45% | 0.012% | ND |
| ethanol | 0.03% | 0.383% | 0.051% |
| propanol | ND | 0.055% | ND |
| isopropanol | 0.06% | 0.127% | 0.011% |
| butanol | 0.25% | 0.015% | ND |
| pentanol | 0.16% | 0.072% | 0.382% |
| sorbitol | 0.07% | NA | 0.285% |
| xylose | ND | NA | 0.122% |
| glucose | ND | NA | 0.088% |
| methyl-acetate | 0.10 | ND | ND |
| | | | |
| **GCMS** | | | |
| phenol | present | ND | NA |
| o-cresol | present | present | NA |
| p-cresol | present | present | NA |

**Table 5. Trace elements by ICP-OES**

| element | **aqueous** | **fixed bed** | **mixed** |
|---|---:|---:|---:|
| sulfur | 2.2 | 5.8 | 19.3 |
| silicon | 81.9 | 52.7 | 14.9 |
| iron | 26.9 | <0.1 | <0.8 |
| sodium | 6.9 | 6.0 | 6.8 |
| aluminum | 5.9 | <0.1 | 1.3 |
| molybdenum | <0.1 | 5.6 | <0.8 |
| calcium | 1.1 | 0.9 | 1.5 |
| potassium | 3.9 | <0.5 | 3.8 |
| tungsten | 1.3 | <0.1 | <0.8 |
| nickel | 1.1 | <0.1 | <0.8 |
| phosphorus | <0.1 | 1.0 | 8.8 |
| zinc | 0.3 | <0.1 | <0.8 |
| magnesium | 0.1 | <0.1 | <0.8 |
| | | | |

### 3.2.1 UOP1 aqueous bio-oil upgrading (9/21–22/2011)

The first hydrotreater aqueous byproduct provided by UOP was a higher concentration organic in water liquid. This product was subsequently identified as produced in a continuously stirred tank reactor (CSTR) hydrotreater system. The feedstock was prepared by filtration of a trace amount of floating scum (0.4 g from 2200 g filtrate). There remained a floating layer of oil after the filtration. The float oil was not sent to the gasifier, but would be returned to the hydrotreated oil product stream in the actual process.

The mini-reactor system was used for the test at typical processing conditions of 350 ºC, 3000 psig with a 29-ml catalyst bed and was kept on stream for 31 h until all the liquid was processed.

In the test, the COD was reduced from 160,750 ppm by 99.9% producing a 265 ppm COD effluent at a LHSV rate of 2.2. The gas yield was 0.77 L/g organic (estimated from HPLC results) of a medium-Btu gas, 611 Btu/SCF. There was no difficulty in the operation of the test. Flow and product composition were consistent throughout. The chloride level in the effluent varied throughout the test from 66 ppm to 656 ppm and back to 21 ppm. No explanation for this variation is evident. Analysis by HPLC suggested that the remaining organic in the effluent was glucose and xylitol, but these identifications were not confirmed. Although the total sulfur in the feed was measured at 2.7 ppm, the last product out of the test measured at 9.5 ppm. Sulfate was so low that is was not quantifiable. Similarly, Ru was below the level of detection <0.8 ppm.

### 3.2.2 UOP2 fixed bed HT byproduct aqueous (10/13/2011)

The second test using the fixed bed HT aqueous as the feedstock followed after the first using the same catalyst bed. After three weeks in cold idle mode, the catalyst bed was reduced under hydrogen flow while heating through the temperature range from 50 to 350 °C over 5 h, before idling at temperature for 17 h (overnight). For the test, typical conditions were used – 350 ºC, 3000 psig with the 29-ml catalyst bed. The test extended for 14.2 h, during which the COD was reduced from 59,500 ppm by 99.6% to produce a 287 ppm COD effluent. At a LHSV of 4.3, 1.18 L/g organic of a medium-Btu gas (691 Btu/SCF) was produced. There was no difficulty in the operation of the test. Flow and product composition were consistent throughout. The chloride level in the feed was determined to be 138 ppm with no detectable sulfate. The effluent chloride level varied throughout the test from 249 ppm to 436 ppm. No explanation for this high level or variation is evident. The sulfate level remained <1 ppm throughout. Analysis by HPLC suggested that the remaining organic in the effluent was glucose and xylitol with some isopropanol, but these identifications were not confirmed. Although the total sulfur in the feed was measured at 5.8 ppm, the last product out of this test measured only 0.5 ppm. Sulfate was again so low that is was not quantifiable. Similarly, Ru was below the level of detection <0.8 ppm.

### 3.2.3 UOP3 mixed HT byproduct aqueous (12/14–15/2011 &1/3–4/2012)

The “mixed” hydrotreater aqueous byproduct provided by UOP was an intermediate concentration organic in water liquid. The feedstock was prepared by separating a floating oil (160.23 g from 5962 g aqueous feed). The float oil was not sent to the gasifier, but would be returned to the hydrotreated oil product stream in the actual process.

The third test using the mixed HT aqueous as the feedstock followed after the first two using the same catalyst bed. After 2 months in cold idle mode, the catalyst bed was reduced under hydrogen flow while heating through the temperature range from 50 to 350 °C over 2 h, before idling at temperature for 12 h (overnight). For the test, typical conditions were used 350 ºC, 3000 psig with the 29 ml of catalyst. The test extended for 13.8 h of steady conditions. During the steady state, the COD was reduced from 87,050 ppm by 99.9% to a 15 ppm COD effluent. Using a higher LHSV of 3.5, 0.58 L/g organic of a medium-Btu gas (557 Btu/SCF) was produced. Afterward (during the night) a process upset occurred and the system shutdown with an over-pressure alarm. The system was flushed with water for 5 days to clear blockage and clear feed contamination from the product collection system. The catalyst bed was then reduced under hydrogen flow at 280 °C for 4 h before returning to water flush mode at reaction conditions for 2 weeks. Upon reintroduction of the feed to the reactor system, the conversion was found to be less than 75%, so the test was terminated and the catalyst removed for analysis. Although the total sulfur in the feed was measured at 19.3 ppm, the three products tested from the steady state portion at the beginning and again at the end of this test measured <0.8 ppm. Sulfate was not discernable. The test effluent had non-detectable (<0.8ppm) Ru.

### 3.2.4 Catalyst bed analysis following aqueous product CHG

**Table 6** summarizes the elemental analysis of the feeds and the catalyst samples from these three tests. Although the sulfur content of the feedstocks is quite low, the catalyst is significantly sulfurized by the exposure. The apparent strong attraction of the Ru metal to the S, apparently to form the sulfide is evident considering the high concentration of the S at the front end (bottom) of the catalyst bed. Ni, Mo, and Cr are likely derived from construction material of the reactor system while the Fe could suggest a similar mechanism, but also could result from the aqueous bio-oil upgrading (CSTR) feedstock, which carried 26 ppm Fe, probably from corrosion during storage in steel cans. Al and P deposits apparently come from the feedstocks, while the Cu source is still unknown. The elements Na, K, Si, and Ca, which are trace components in the carbon support, appear to be stripped from the catalyst by the hydrothermal process. Although the catalyst bed samples display a reduced level of Ru, this result is believed to be due to carbon deposits in the pores of the catalyst, thus diluting the catalyst metal and potentially blocking catalyst sites. This conclusion is supported by the finding of no Ru leaving the system in the aqueous products.

**Table 6. Analytical results from ICP-OES**

| | **Ru %** | **P** | **S** | **Fe** | **Cu** | **K** | **Na** | **Si** | **Al** | **Ca** | **Ni** | **Mo** | **Cr** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Ppm | | | | | | | | | | | |
| Feeds | 0 | 0-9 | 3-19 | 27-0 | 0 | 0-4 | 6-9 | 82-15 | 6-1 | 1 | 0-0.6 | 0-6 | 0 |
| Fresh catalyst | 9.1 | <25 | 143 | NA | <25 | 1571 | 96 | 259 | 42 | 523 | <25 | <25 | <25 |
| Spent, bottom | 5.0 | 166 | 4500 | 348 | 710 | 82 | <40 | 178 | 175 | 117 | 2597 | 119 | 405 |
| Spent, middle | 6.3 | 449 | 3051 | 1205 | 180 | 82 | <40 | 168 | 268 | 227 | 1372 | 362 | 256 |
| Spent, top | 7.7 | 148 | 108 | 2137 | 112 | 83 | <40 | 147 | 163 | 45 | 1061 | 109 | 38 |

At the end of the “Mixed” feed test, deposits were recovered from several places in the feed system. The deposit in the preheater line was predominately Fe, Ni, and Cr with Al, P, S and Si as the other major components. These elements account for only 1% of the mass, suggesting that the bulk of the plug is carbonaceous polymer. Deposits further in the system contained some amounts of Ru, suggesting that catalyst fines may have made their way into the plugs. Higher levels of S, Ni and even Cu were also found in these deposits.

### 3.2.5 UOP4 HT (3/14–15/2012)

The results with the initial feedstocks containing only low levels of sulfur showed that system modification to accomplish sulfur scrubbing from the feed would be required to protect the CHG catalyst. The feedstock used in this test was from the same source as the previous test, “mixed” aqueous (Table 4 and 5). However, it phase separated after refrigerated storage for a month and a half. Also, the aqueous was filtered as visible solids were noted. The filtered solids amounted to only 0.0036 wt% of the aqueous. IC analysis of the feed (6 months after UOP3 test and 3 months after the UOP4 test) suggested it contained 40 ppm chloride, but 29 ppm sulfate. **This measurement of high sulfate in the stored aqueous byproduct suggests that the initial sulfide in the feed has oxidized to sulfate over time.** ICP analysis shows 25 ppm sulfur, therefore about 40% of the sulfur had been oxidized to sulfate. In the case of P, the ICP analysis showed 13 ppm. These ICP numbers are slightly higher compared to 19 and 9 ppm of S and P, respectively, measured earlier (see Table 5). Other elements found in this analysis were 28 ppm Na, 22 ppm Si, 3.5 ppm K, 1.9 ppm Al, and 1.8 ppm Ca. **Clearly there was not enough Ca to precipitate all the sulfate in the solids settler, allowing some sulfates to affect the catalyst activity over time.** GCMS analysis of the feed showed the typical pyrolysis products of acetic acid, hydroxyacetone, and levoglucosan, as well as a collection of phenol and alkyl-phenols.

For this test, a sulfur scrubbing bed of a nickel containing formulation (BASF G1-80 with 0.1%Cu) was placed in the system upstream of the Ru/C catalyst bed. Start-up of the system included a 28 h period of water flow during which a noticeable, amount of catalyst powder was flushed from the system. This powder represented an insignificant mass loss from the catalyst bed, but suggested that a water wash of the catalyst before filling the reactor could eliminate some downstream plugging problems.

The feed was introduced into the system and the catalyst initially exhibited high conversion at LHSV of 3, which within 12 h began to fail and within 17 h had dropped from nearly 100% conversion to less than 65%, with a similar drop in gas production rate. The feed COD was reduced from 76,500 ppm to around 10 ppm initially, and then to 26,350 ppm later. GCMS was used to identify some residual organic material, primarily phenol and alkyl-phenolics, but also some light carboxylic acids and cyclic ketones, as well as levoglucosan. In the gas product, GCMS was used to identify some residual organic material, primarily benzene and toluene with lesser amounts of alkyl-benzenes and small amounts of phenol and alkyl-phenolics, with some light alkanes.

IC analysis of the aqueous products from the CHG showed they contained the expected level of chloride, from 32 to 44 ppm. The sulfate had been reduced in the process to levels varying from 1 to 7 ppm. However, after filtering the aqueous products, ICP analysis showed <1 ppm S in the clear water sample. There was no evidence of catalyst metal leaching as the Ru measurement was below the detection level, <0.18 ppm. Analysis of the filtered solids showed that they were composed of catalyst dust (Ru) as well as sulfur scrubber particulates (Ni, Si, Mg), corrosion products from the reactor system (Fe, Cr, Mn), and Ca, Na, K, Al, and P from the feedstock. Some of this material may also be precipitated sulfate and phosphate compounds.

Analysis of the catalyst and scrubber beds after the test confirmed that a significant amount of sulfur was captured in the scrubber (about ¼) but over 10% ended up on the catalyst while another quarter passed through in the aqueous stream. The sulfur on the catalyst and in the aqueous apparently is the sulfate that was not captured by the Ni scrubber. Some of the balance of the sulfur precipitated at hydrothermal conditions but was not collected in the separator vessel, but was mobilized by the liquid water flow and passed on through the system to the condensate product collector.

The detailed analysis showed that the Ni in the scrubber was only slightly (<1%) reacted to nickel sulfide. It did not serve as an effective sulfur scrubber. However, the fact that a large portion of the S was in the form of sulfate, and therefore less reactive, is at least a partial explanation. The sulfur was evenly distributed through the Ni bed suggesting that it was reacting slowly. However, the Ru was a much more effective trap for the S, the S being over five times higher in concentration at the front of the bed (862 ppm) versus the back of the bed (157 ppm), with the middle portion of the bed having an intermediate level of S, while the fresh catalyst had <50 ppm. The high level of sulfiding of the Ru/C catalyst at the front end of the bed, about 5% of stoichiometric, compares to a level of 40% sulfidation reported in the literature as the maximum obtained in a hydrothermal environment. Therefore, the Ru catalyst had been sulfided to a large degree and certainly enough to have a large effect on its gasification and methanation activity. EDS analysis showed that the sulfur was highly associated with both the Ni and the Ru. There was also evidence of Ca and P (probably as calcium phosphate) coating the surface of the Ni scrubber. The Ru concentration in the spent catalyst had been reduced to 3/4th of the starting level, presumably by carbon deposition in the pores, as there was no evidence of Ru loss to the aqueous stream. In the case of the Ni scrubber, the pore volume was essentially unchanged but the surface area was reduced to 193 $m^2/g$ compared to a literature value of 272 $m^2/g$.

### 3.2.6 UOP 4B HT (8/7/2012)

A second attempt with this feedstock was made with a modified preheater/separator design to allow for better capture of precipitated minerals especially as Ca was added to the feedstock as $Ca(OH)_2$ at 0.3 g/L. The same sulfur scrubber material and Ru/C catalyst were used in the test at the same processing conditions: 350 °C, 3000 psig, and 3 LHSV. The system became plugged in less than 6 h of operation. Analysis of the recovered solids showed that the Ca/S ratio of 1.1 was more than sufficient to suggest calcium sulfate precipitation. With the inclusion of P in the calculation, assuming a 1.5 ratio of Ca/P, then the Ca/S ratio drops to 1, providing further confirmation of calcium phosphate and calcium sulfate precipitation. However, both Ca and S were also found in the sulfur scrubber bed while Ca, S and P were all found in the Ru/C bed, suggesting that the precipitator system was not fully functional in the mini-reactor system.

### 3.2.7 UOP 4C HT (9/6–7/2012)

A third attempt with this feedstock was made with the modified preheater/separator design to allow for better capture of precipitated minerals especially as Ca was added to the feedstock as $Ca(OH)_2$ at 0.3 g/L. The same S scrubber material and Ru/C catalyst were used in the test at the same processing conditions: 350 °C, 2950 psig, and 2.5 LHSV. The system remained unplugged during the total time on stream of 19.8 h of operation until the feedstock was consumed. The conversion remained high throughout with no evidence of catalyst deactivation. COD conversion was 99.99% producing a product gas of 70% methane, 28.5% carbon dioxide, and less than 1% hydrogen. The feedstock COD was 79,500 ppm COD and the effluent was about 13 ppm.

After the test, a mineral plug was found in the feed line as it passed through the preheating zone. The mineral composition suggested calcium sulfate and phosphate but the ratios were not quite the perfect match as there was only enough calcium to account for ¾ of phosphate after subtracting the requirement for sulfate. Analysis of the recovered solids showed that the Ca/S ratio of 1.8 was not quite sufficient to suggest total calcium sulfate precipitation because with the inclusion of P in the calculation, the Ca/P was only 1.1. Still, both Ca and S were also found in the sulfur scrubber bed and in the Ru/C bed, suggesting that the precipitator system was not fully functional for sulfate capture while capturing all the P.

### 3.2.8 UOP5 HT (11/30–12/1/2012)

The results with the initial feedstocks containing only low levels of sulfur showed that system modification to accomplish sulfur scrubbing from the feed would be required to protect the CHG catalyst. The feedstock used in this test was a new shipment from UOP labeled, “Aqueous product from plant 27.” This feed labeled as IBR-UOP5 was received on July 25, 2012. It was a mixture of oil and aqueous phase products. A settling experiment was done overnight showing that most of the oil settled at the bottom of the container.

Separation of the oil phase from the aqueous phase was done by (1) centrifugation and (2) filtration. Centrifugation settled the oil much faster. Oil layered the surface of the centrifuge tubes. However, since the oil seemed to have similar viscosity as that of water, decanting the top layer became difficult once the oil was disturbed. The oil amount in the IBR-UOP5 sample seemed to be between 6-11 wt%.

Vacuum filtration through regular filter paper or glass fiber worked for previous UOP aqueous samples in removing the more viscous oil, but not for this one. Oil breakthroughs occurred. Gravity filtration with regular filters allowed better separation, but took a long time. Kaowool (fibrous insulation) was then used as a filter medium and seemed to work well in separating the bulk oil. The thickness and the large surface area of the kaowool allowed water to flow freely while trapping almost all of the oil. A few small droplets got through and breakthrough still occurred after over a liter of sample processed and so the kaowool did need to be replaced. The oil could be potentially recovered by washing the kaowool with the proper solvent.

Leaching of materials from the kaowool was determined by running ICP on the product recovered from filtering regular DI water. The result is shown in **Table 7** suggested that there were minor amounts of Na and Si, but a surprising amount of S.

**Table 7. Analytical results from ICP-OES analysis of UOP5 aqueous streams**

| | **Ca** | **S** | Si | K | Na | Fe | Mg | **Al** |
|---|---|---|---|---|---|---|---|---|
| Feed, as-received, settled | 5.2 | 24 | 12 | 10 | 9.4 | 1.5 | 1.5 | <0.9 |
| DI water through Kaowool filter | <0.8 | 14 | 2 | <1.5 | 3 | <0.8 | <0.8 | <0.8 |
| settled, filtered feed to reactor UOP5A | 46 | 26 | 11 | 11 | 8.0 | 2.0 | 1.2 | <0.8 |
| UOP5A early sample | <0.8 | <0.8 | 26 | 14 | 17 | <0.8 | <0.8 | <0.8 |
| UOP5A end sample | <0.8 | <0.8 | 22 | 11 | 7.9 | <0.8 | <0.8 | <0.8 |
| settled, filtered feed to reactor UOP5B | 49 | 21 | 10 | 10 | 10 | 2.6 | 1.4 | 0.8 |
| UOP5B early sample | <0.8 | <0.8 | 6.7 | 2.0 | 4.7 | <0.8 | <0.8 | <0.8 |
| UOP5B end sample | <0.8 | <0.8 | 6.1 | 2.4 | 4.9 | <0.8 | <0.8 | <0.8 |

LC analysis of the feed showed the typical pyrolysis product, acetic acid, with indications of ethanol, succinic acid, phenol, acetaldehyde, propylene glycol, and sorbitol with several unidentified components at higher concentration. The TOC of the filtered feedstock was measured as 1.54 % for 5A and 1.35 % for 5B.

IC analysis of the as-received, settled feed suggested it contained 28 ppm chloride, but 17 ppm sulfate. **This measurement of significant sulfate in the accumulated aqueous byproduct suggests that the initial sulfide in the feed may have been oxidized to sulfate over time.** ICP analysis showed 24 ppm sulfur, therefore about 35% of the sulfur was in the oxidized form of sulfate. In the case of P, the ICP analysis showed <0.9 ppm. Other elements found in this analysis were 9.4 ppm Na, 12 ppm Si, 10 ppm K, 1.5 ppm Fe, with 5.2 ppm Ca and 1.5 ppm Mg. **Again, there was not enough of the alkaline earths to effectively precipitate all the sulfate in the solids settler, which would impact on the catalyst activity over time.** Before feeding into the CHG system, about 0.084 g/L of $Ca(OH)_2$ was added into the filtered IBR-UOP5 with the objective of precipitating out $SO_4^{-2}$ before it could poison the catalyst.

For test UOP5, as in UOP4, a sulfur scrubbing bed of a nickel-containing formulation (BASF G1-80 with 0.1% Cu) was placed in the system upstream of the Ru/C catalyst bed. Start-up of the system for UOP5A included a 4 h reduction of the catalyst at 350 °C under hydrogen flow followed by cooldown over the weekend. A 10 h period of water flow for heat-up of the reactor system preceded actual feedstock introduction. After 14.6 of operation the system was determined to be at steady state. The test continued for an additional 23 h until the feed sample was exhausted. The catalyst exhibited high conversion at LHSV of 2.5 throughout, with COD conversion at four 9s (99.99%). The feed COD was reduced from 53,500 ppm to around 10. The gas product was consistently around 60% $CH_4$ and 40% $CO_2$ with only 0.4% $H_2$ and undetectable hydrocarbon gas products.

As shown in Table 7, ICP analysis showed <1 ppm of either S, Ca, Mg, or Fe in the aqueous product samples. Soluble elements included K, Na, and Si. There was no evidence of catalyst metal leaching as the Ru measurement was below the detection level, <0.8 ppm.

The test was restarted nine days later as UOP 5B using the same scrubber and catalyst beds with a second aliquot of the "Aqueous product from plant 27" which had been settled, filtered and doped with Ca, similar to UOP 5. The system was heated up over 3.3 h and then feed was introduced when the bed was at temperature. The catalyst continued to show high activity with COD conversion at LHSV of 3 at 99.98% over the relatively short 6.8 h test, which used up the balance of the feedstock. The feed COD was reduced from 44,000 ppm to around 20. The gas product was consistently around 70% $CH_4$ and 30% $CO_2$ with only 0.3% $H_2$ and undetectable hydrocarbon gas products.

As shown in Table 7, ICP analysis again showed <1 ppm of either S, Ca, Mg, or Fe in the aqueous product samples as was seen in UOP5A. Soluble elements included K, Na, and Si, although at lower levels than seen in UOP5A. There was no evidence of catalyst metal leaching as the Ru measurement was below the detection level, <0.8 ppm.

ICP analysis was performed on the solid residue collected from the settler of the UOP5A/B run. The residue was recovered by scraping off the inner surface of the ¾" tubing. The major components are Ca (33130 ppm), Fe (28940 ppm), S (28990 ppm), Ni (20580 ppm) and Ru (15460 ppm). The identified metals were about 13.5wt % of the sample analyzed, suggesting that most of it was coke/organic. Ca and S were not strictly stoichiometrically present for the formation of $CaSO_4$ (Ca/S = 0.91, when it should have been 1). The lesser components were Al (2548 ppm), P (1887 ppm), Cr (1650 ppm), Si (1347 ppm), Mg (593 ppm) Na (321 ppm), and Mo (244 ppm). The presence of Ni and Ru, Si and Al suggests that there were catalyst bits present in the settler. The extra sulfur may have been associated with the catalysts. Since the settler comes before the reactor, the presence of the catalyst particles was interesting. Two options could explain what happened: (1) catalyst particles were blown back during the *ex situ* leak check in the hood prior to the test, or (2) backflow in the instance that the feed pressure became less than the reactor pressure (in the presence of a stopped pump). The first explanation was avoided in subsequent tests by pressurizing in the same direction of flow as in the actual operation. Preliminary $H_2$ leak check was done in the hood for better access to the myriad of fittings of the modified micro unit. The counter flow of the test gas was done because of convenience and limitation based on the configuration of the reactor with respect to the hood. P was also present in the residue, suggesting that the Ca was able to capture some as $Ca_3(PO_4)_2$. However, this result would further lower the Ca/S ratio. One explanation would be precipitation of some of the sulfate by iron, perhaps through a reactor wall corrosion related mechanism.

Analysis was also performed by XRD on the S scrubber material and the gasification catalyst following the test. The composition detected for the spent material in the S scrubber bed did not include sulfide as would be expected if the scrubber were functioning to capture the 21-26 ppm S in the feedstock. The Ru catalyst bed included graphite and Ru metal phases with the Ru crystal size calculated at 21 nm, but again no sulfide was detected. Although the S was reduced to an undetectable level by passing through the reactor system, the fate could not be determined based on these analyses. $CaCO_3$ was detected in both the scrubber bed and the gasification catalyst. This suggests that there was excess calcium, which did not precipitate as sulfate or phosphate, and which precipitated when the carbon dioxide formation became sufficient.

### 3.2.9 UOP6 HT (2/21/2013 – 2/23/2013)

| | |
|---|---|
| Feed | Pilot plant aqueous phase water received from UOP (1/17/2013), vacuum filtered through GF-B, COD = 185,000 ppm, pH = 3.60 |
| Reactor configuration | sulfur scrubber bed followed by gasification catalyst bed |
| Total run time | 34.54 h |
| Reason for EOR | feed was all gone |
| Catalysts | Main: C3610 – 24.7 ml; 10.87 g<br>Sulfur scrubber: Raney Ni (Raney 5886 3x8 catalyst, Nickel Cat 19400-72) – 22.45 g (wet); ~ 8ml |
| Flowrates | 1st LHSV = 2/h (25 h)<br>2nd LHSV = 2.5/h (9.5 h) (from 14:32 2/22/13 to EOR) |
| Product COD ranges | Port: 0-20 ppm<br>Pot: 0-10 ppm |
| Gas products | $CO_2$ range (time): 24.4% – 38.8% (5th to 34.5th h)<br>$CH_4$ range (time): 65.5% - 76.5% (5th to 34.5th h)<br>$H_2$ range (time): 0.5% - 0.7% (5th to 34.5th h)<br>Ethane range (time): 0.1% to 0.5% (at least last 8 h) |

The feedstock sample was received from UOP on 1/18/13 labeled as aqueous phase pyrolysis oil. The sample out of the jar showed an oil phase settling at the bottom (**Figure 6a**) and a supernatant that became clearer after standing for a few days inside the refrigerator (**Figure 6b**). After vacuum filtering through a Whatman GF-B filter, the liquid that came out was quite clear. However, after a few days of standing on the lab bench, the filtrate turned greenish with some oil precipitating at the bottom (**Figure 6c**). COD of the as-received filtrate was 187,500 ppm while the COD of the filtered sample was 185,000 ppm. The difference may be due to filtering out of some organics or simply variation in measurement. As received, the pH was 3.6 and the TOC was 4.35 %.

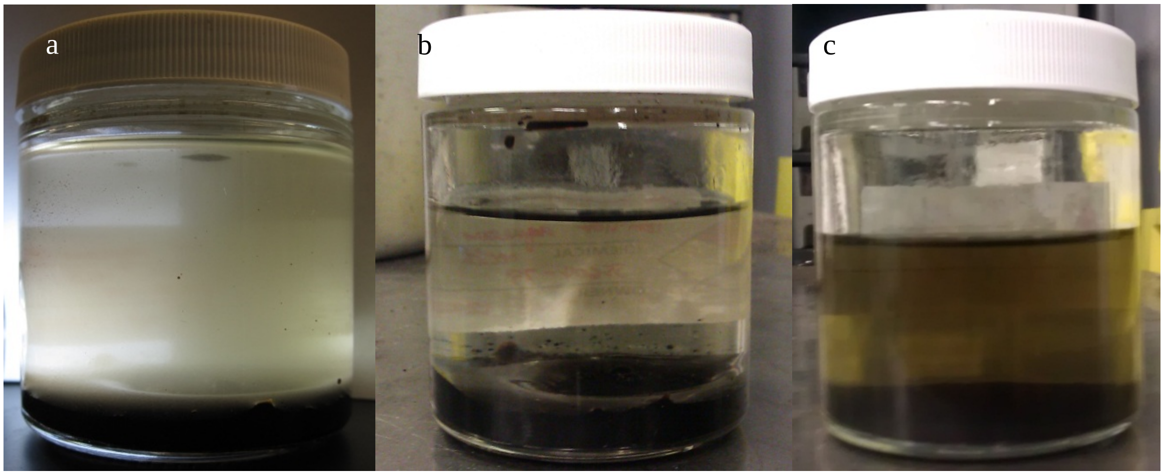

**Figure 6. Feed showing segregation of oil and aqueous phase. Supernatant became clearer after days of standing in the refrigerator**

ICP of the liquid showed the presence of the following elements: 18 ppm Na, 6.5 ppm K, 3.2 ppm Fe, 1.7 ppm Si, and 10 ppm S. Based on the small amount of S, no $Ca(OH)_2$ addition was done, as was done in UOP4 and 5 to precipitate out anions such $SO_4^{-2}$ and $PO_4^{-3}$.

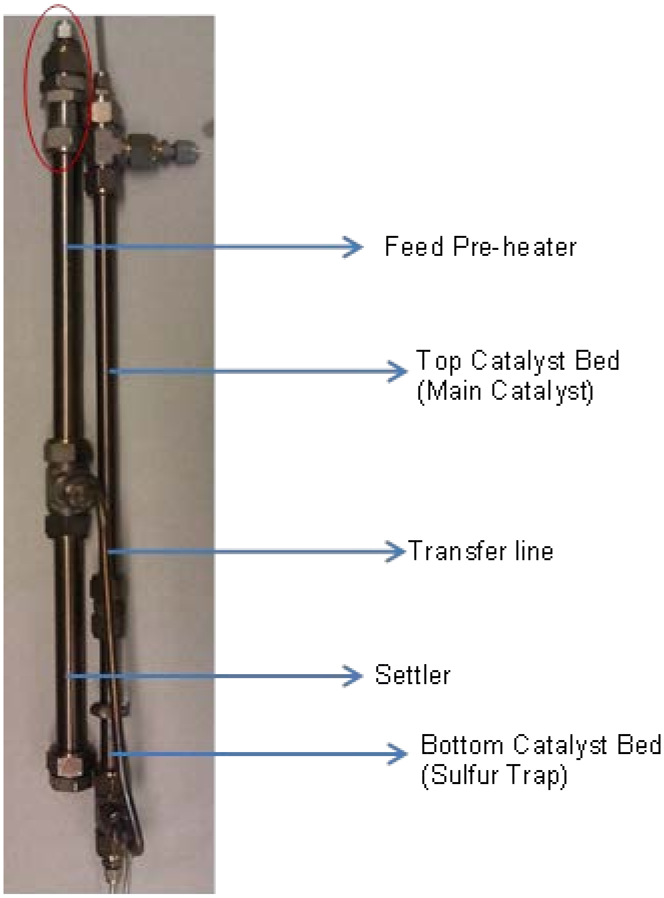

**Figure 7. Reactor assembly**

From the filtration procedure, the recovered oil was about 11.5 wt% of the filtered sample.

The reactor assembly used in this experiment is shown in **Figure 7.** This was same as the reactor used in IBR-UOP5b except for the replacement of the bulkhead union fitting (encircled portion in Figure 4) that allows for easier dismantling and leak-proofing of the ¾" fittings, as compared to a regular union.

During reduction, the top catalyst bed was reduced at 350 °C for 4 h. The bottom reactor though was only reduced at 320 °C due to overheating of the reactor wall temperature (>400 °C) at higher set bottom temperature. This problem was alleviated by improved insulation during the actual run, attributing the need for the heater to produce more heat to compensate for the heat loss to attain the target temperature. A slower and graded approach (~5 °C higher than current temperature reading) to keying in the set point to the bottom heating tape was also seen to be advantageous. During the actual gasification experiment, a highest of 40 °C differential between the bottom and the reactor wall thermocouple temperatures was seen.

Exotherms in both the top and bottom beds seemed to be present at the early stages of the experiment. Temperatures at the top thermocouple (about 4-5" into the bed) peaked at 2 h after start of feed at 362 °C, while the reactor wall temperature (outside the reactor but about 2" into the bottom reactor bed) peaked after 3 h at 391 °C. However, the top temperature evened out at around 350 °C after about 18 h on stream. At the same time, the reactor wall temperature was at 380°C. The bottom thermocouple readings were between 349.6 °C to 350.3 °C.

**Figure 8** summarizes the COD readings from the sample port ("port") and the liquid coming out of the spout going to the receiving vessel ("pot"). COD reduction was always 99.9% throughout the course of the run.

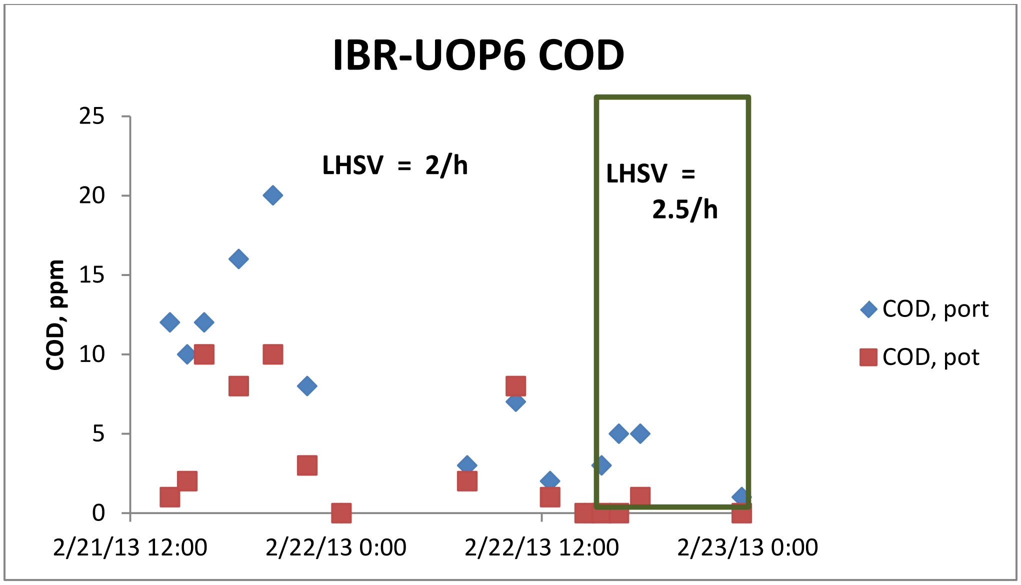

**Figure 8. COD values of the experiment**

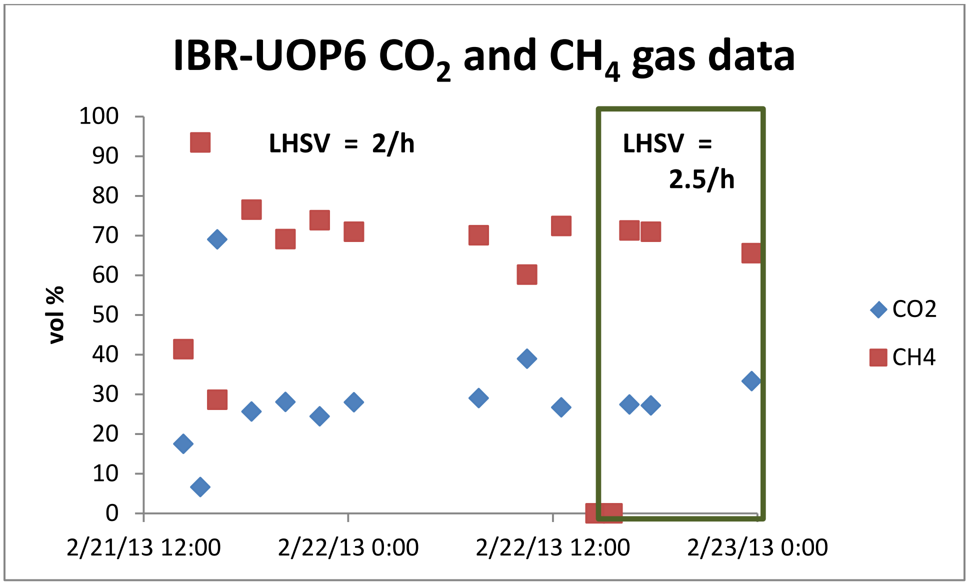

**Figure 9. $CO_2$ and $CH_4$ distribution during the run**

The major gas products were $CO_2$ and $CH_4$. Their concentrations are plotted as a function of time in **Figure 9.** Steady-state seemed to have been attained after about 5 h of time-on-stream with an average ratio of 30:70 of $CO_2$ and $CH_4$ respectively. During LHSV = 2, no ethane was found. After the switch to a higher flowrate of 2.5, ethane was seen to be 0.1 to 0.5% of the gas stream. However, the COD did not show much accompanying change.

### 3.2.10 UOP7 HT (3/13/13 – 3/15/13)

| | |
|---|---|
| Feed | Aqueous phase from pyrolysis oil hydrotreating (bench scale) from UOP (1/11/13), filtered through regular filter paper using positive pressure filter, COD = 48,600 ppm, pH = 7.13 as received |
| Reactor configuration | sulfur scrubber bed followed by gasification catalyst bed |
| Total run time | 33.5 h |
| Reason for EOR | Lack of feed, product quality went down (much higher COD) |
| Catalysts | Same as IBR-UOP6. (follow-on experiment with re-reduction in between)<br>Main: C3610 – 24.7 ml; 10.87 g<br>Sulfur scrubber: Raney Ni (Raney 5886 3x8 catalyst, Nickel Cat 19400-72) – 22.45 g (wet); ~ 8ml |
| Flowrates | 1st LHSV = 5 (22.8 h)<br>2nd LHSV = 1 (10.7 h) (13:20 3/14/13 to EOR) |
| Product COD ranges | Port: 14 – 0 ppm (first 20 h); up to 18050 ppm<br>Pot: 353 – 44 ppm (first 20 h); up to > 17600 ppm |
| Gas products | $CO_2$ range (time): 25.2-27.6% (9th to 20th h); 54.2–39.4% (20th h to EOR)<br>$CH_4$ range (time): 68.2%-70.5% (9th to 20th h); 43.7-55.6% (20th h to EOR)<br>Ethane range (time): 0.1% to 1.66% (5th h to EOR) |

The sample used for feedstock in this test was received from UOP on 1/11/13 labeled as "aqueous phase from pyrolysis oil." Communication with Steve Lupton at UOP clarified that this sample came from their bench scale plant. The sample out of the jar showed an oil phase that segregated and floated on top of an opaque orange liquid with a small amount of heavy oils settling at the bottom (see **Figure 10**). Most of the floating oil was filtered out through a positive pressure filter apparatus, though some small particles still went through with the filtrate. COD from the as-received filtrate was 45,833 ppm. As received, the pH was 7.13. Residual feed in the feed container at the end of the run was at 48,000 ppm while a small amount recovered from the pump was at 140,000 ppm. This very much higher concentration at the end of the run suggests the possibility of residual oils precipitating out from the filtrate while the feedstock was held in the pump.

**Figure 10. Feed showing segregation of oil and aqueous phase.**

ICP of the liquid showed the presence of only small amounts of trace elements: 29 ppm Si, 14 ppm Na, 7.3 ppm K, and 2.2 ppm Al. The critical element sulfur was found at 80 ppm. By IC analysis it was determined that 54 ppm of sulfate were present, representing 22% of the sulfur. Chloride was found at 39 ppm and the amounts of other trace anions were low: 2.4 ppm $PO_4$, 1.4 ppm $NO_3$, with peaks tentatively identified as Br at 2.4 ppm and F at 3.3 ppm.

Liquid chromatography of the feed was also done. The more polar components were resolved, identified and quantified. Major components were acetic acid (0.198 wt%), ethanol (0.176 wt%) and phenol (0.101%). Some unidentified high eluting components were seen and are expected to be alkyl or methoxyphenols. Minor components (i.e. less than 0.1 wt%) consist of glycolic acid, formic acid, ethylene glycol, propylene glycol, propanoic acid, methanol, ethanol, acetone, 1-propanol, 2-methyl-1-propanol and 1-butanol. TOC of this feedstock was 1.30 %.

The same reactor and catalysts bed as UOP6 was used for this experiment.

During reduction, the top catalyst bed was reduced at 350 °C for 4 h. The bottom reactor though was only reduced at 305 °C. The corresponding bottom reactor wall temperature at this bottom reactor temperature was 400 °C. During actual gasification run conditions, the top and bottom temperatures were consistently around 350 °C with the bottom reactor wall temperature at an average of 30 °C hotter. The pump stopped around 5 h into the run because of an erroneous high pressure reading due to a failing pressure transducer. The top reactor temperature read 352 °C about 25 min after the feed flow was restarted.

**Figure 11** summarizes the COD readings from the sample port ("port") and the liquid coming out of the spout going to the receiving vessel ("pot"). After 20 h into the run, the COD conversion went down from 99.9% to 76.9%, from which the COD of the product progressively went higher in the last 10 h of the experiment despite decreasing the flowrate to an equivalent LHSV of 1 from 5.

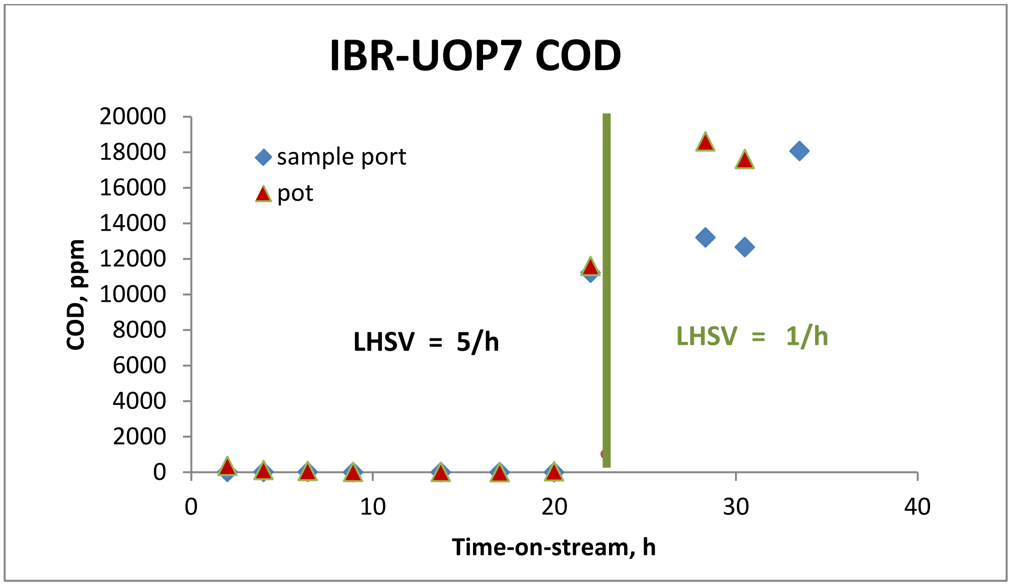

**Figure 11. COD values of the liquid products**

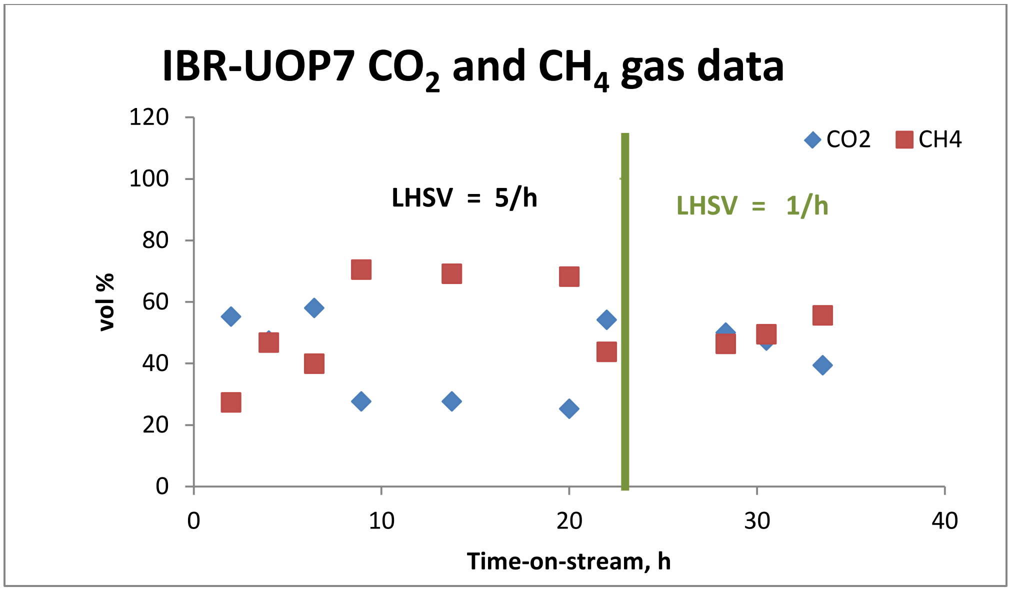

**Figure 12. $CO_2$ and $CH_4$ distribution during the run**

The major gas products were $CO_2$ and $CH_4$. As seen in **Figure 12**, steady-state seemed to have been attained after about 9 h of time-on-stream with an average ratio of 26:69 of $CO_2$ and $CH_4$, respectively. However, corresponding to the increase in the product COD, the ratio became closer to 50:50 $CO_2$:$CH_4$. As the LHSV was adjusted to attempt to recover the higher level of COD conversion, $CO_2$ seemed to trend back downward while the $CH_4$ amount inched higher. Due to lack of feed, this trend could not be fully validated through longer time-on-stream.

One possible explanation for this apparent loss of catalyst activity is the poisoning effect of S on the Ru/C catalyst. Though the Raney nickel acts as a sulfur trap, S breakthrough to the Ru catalyst still occurred. As shown in **Table 8,** S was distributed throughout the scrubber and catalyst beds.

XRD analysis of the spent scrubber bed and catalyst bed did not identify any sulfur phase in either bed. There was little noticeable change in either bed. There was an indication of aluminum hydroxide (boehmite) in the sulfur scrubber, which appears to be a hydrothermal product of the residual aluminum metal in the Raney nickel. Boehmite is the stable phase at hydrothermal conditions. There was a tentative identification of a very minor amount of aluminum nitride throughout the catalyst bed and a hint of calcium carbonate in the bottom (entry point) of the catalyst bed.

The likely cause of the sulfur poisoning of the catalyst bed despite the presence of a sulfur scrubbing bed was the sulfate content in the feedstock. IC analysis of the feed showed 54 ppm sulfate (effectively 23% of the total sulfur in the feedstock). In addition, small amounts of other anions were identified, 39 ppm chloride and 2 ppm phosphate. The sulfate form of sulfur is not effectively captured in the Raney nickel sulfur scrubbing bed. The reason for the presence of sulfate in the product of strongly reducing conditions was not clear.

**Table 8. Elemental analysis of used bed components, ppm**

| Elements | **Sulfur Scrubber** | | **Ru/C Catalyst** | | |
|---|---|---|---|---|---|
| | bottom | top | bottom | middle | top |
| Nickel | 460150 | 436650 | 5145 | 4422 | 2635 |
| Aluminum | 394900 | 404750 | 2089 | 1795 | 1139 |
| Ruthenium | ND | ND | 43100 | 51665 | 48560 |
| Sulfur | 4679 | 4126 | 4260 | 4837 | 3076 |
| Silicon | 3245 | 2925 | 262 | 406 | 296 |
| Iron | 1119 | 953 | 147 | 379 | 463 |
| Cobalt | 370 | 419 | 350 | 210 | 143 |
| Calcium | 60 | 49 | 113 | 134 | 105 |
| Potassium | ND | ND | 120 | 111 | 107 |
| Magnesium | 218 | 220 | ND | ND | ND |
| Sodium | ND | ND | 91 | 91 | 100 |
| Titanium | ND | ND | 93 | 107 | 97 |
| Manganese | 34 | 40 | ND | ND | ND |
| Molybdenum | ND | ND | 66 | ND | ND |

### 3.2.11 UOP8 HT (3/28/2013 – 3/30/2013)

| | |
|---|---|
| Feed | Pilot Plant 581 aqueous phase (1/11/13) from UOP, decanted, unfiltered, COD = 371,333 ppm as received, pH = 3.70 as received, 1400 ppm Fe |
| Reactor configuration | sulfur scrubber bed followed by gasification catalyst bed |
| Total run time | 39 h |
| Reason for EOR | Over-pressure, plug formation |
| Catalysts | Main: C3610 – 26.25 ml; 11.55 g<br>Sulfur scrubber: Raney Ni (5886 3x8 catalyst, 19400-72) 25.52 g (wet) ~ 8ml |
| Flowrates | LHSV = 2.5/h |
| Product COD ranges | Port: 0 – 35 ppm<br>Pot: 0 – 9 ppm |
| Gas products | $CO_2$:$CH_4$ 30:70 |

Sample was received from UOP on 1/11/13 labeled as Pilot Plant 581. Communication with Steve Lupton at UOP detailed that the pilot plant was equipped with an on-line hot separator that was very good at separating the oil phase from the aqueous phase. The catalyst used to produce this aqueous product was determined by UOP to be less active than expected. The liquid, though colored, seemed to be free of oil (**Figure 13**). It was not filtered before being processed. As received, the COD

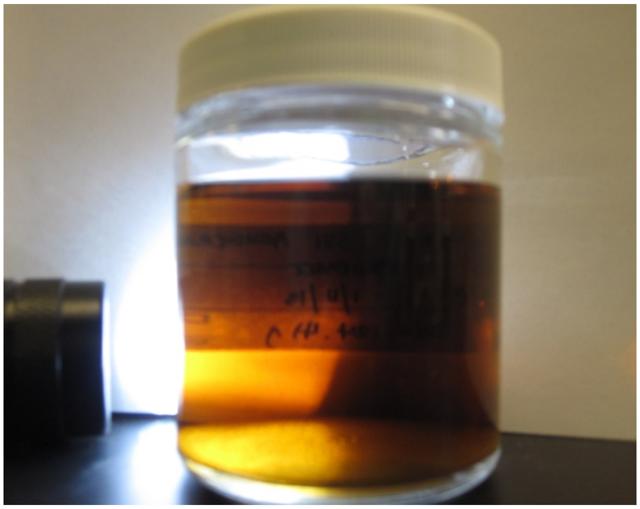

**Figure 13. IBR-UOP8 Feed.**
**No observable amount of oil found.**

was recorded at 371,333 ppm while the pH was at 3.70. Among the last three experimental feeds (i.e. IBR-UOP 6-8), this sample had the highest COD value. ICP of the liquid showed a high concentration of Fe (1408 ppm) aside from the usual biomass elements of K (3 ppm), Mn (6 ppm), and Na (9 ppm). Fe is presumed to be a contaminant from corrosion of the metallic container in which this liquid was collected.

Though S was not seen in the ICP (<0.8 ppm), a small amount of $SO_4^{-2}$ was reported at about 8 ppm (see **Table 9**). Considering the product quality degradation that occurred in the previous experiment (IBR-UOP7), a small amount of $Ca(OH)_2$ was added to the feed in an effort to capture the S as sulfate precipitate.

**Table 9. Anions identified in the feed through ion chromatography of the feed, as received**

| Anion | Concentration, ppm |
|---|---|
| $Cl^-$ | 95 |
| $NO_3^-$ | 18 |
| $SO_4^{2-}$ | 8 |
| $PO_4^{3-}$ | 0 |

Liquid chromatography of the feed was also done. The more polar components were resolved, identified and quantified. Major components were summarized in **Table 10**. Identified minor components (< 0.1 wt%) include propylene glycol, valeraldehyde and phenol. Unlike the aqueous feed produced from the “bench” process (IBR-UOP7), the majority of the organic in this aqueous phase were alcohols rather than the more recalcitrant phenolics. Based on this LC analysis a total organic carbon (TOC) can be calculated as 9.94 %, while the measured TOC for this aqueous product was 8.06 %.

The same reactor configuration was used as with IBR-UOP6 and IBR-UOP7. However, a fresh sulfur scrubber bed and catalyst bed were used. $Ca(OH)_2$ was added at 20.5 ppm.

**Table 10. Main compounds identified and quantified through liquid chromatography of the feed (as received)**

| Compound | Amount, wt% |
|---|---|
| Acetic Acid | 2.3 |
| Propanoic Acid | 0.4 |
| Methanol | 0.9 |
| 1,2-butanediol | 0.2 |
| Ethanol | 11.0 |
| acetone | 0.8 |
| methyl acetate | 0.4 |
| 1-propanol | 1.4 |
| Ethyl Acetate | 0.9 |
| 2-Butanol | 0.4 |
| 2-methyl-1-propanol | 0.3 |
| 1-butanol | 0.3 |

During reduction, the catalyst bed was reduced at 350 °C for 4 h. The bottom portion of the reactor containing the sulfur scrubber was only reduced at 315 °C. The corresponding bottom reactor wall temperature at this bottom reactor temperature was less than 400°C. During actual gasification run conditions, the top reactor temperatures were higher, reaching as high as 387 °C and the temperature was less stable.

**Figure 14** summarizes the COD readings from the sample port ("port") and the liquid coming out of the spout going to the receiving vessel ("pot"). After 33.5 hours at LHSV of 2.5, COD conversion was still at 99.9%. However, an overpressure occurred and caused the end of the run. A plug was probably formed between the settling tank and the lower reactor bed. The solids recovered from the settler tank were 68% iron with minimal amount of other elements, which suggests an iron oxide or hydroxide precipitate. Spent catalysts were analyzed by ICP and XRD. Sulfur poisoning was found throughout the beds at low level. The fact that it was not concentrated at the front of the nickel bed suggests that sulfate was the form as it entered the bed and was reduced and reacted to metal sulfide as it passed through the beds. Iron deposits were also found throughout the beds. Calcium manganese and sodium were also found concentrated at the front end of the catalyst bed.

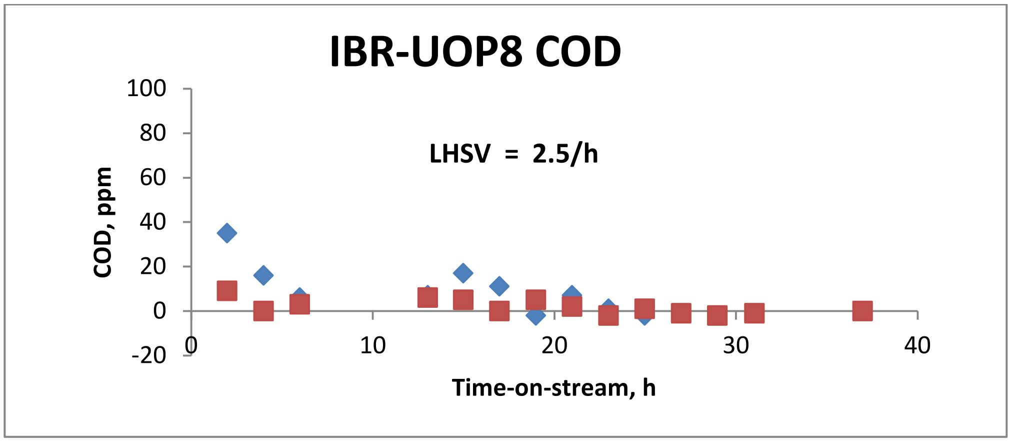

**Figure 14. COD values of the product water**

The major gas products were $CO_2$ and $CH_4$ (**Figure 15**). Steady-state seemed to have been attained within 4 hours of time-on-stream with an average ratio of 30:70 of $CO_2$ and $CH_4$ respectively.

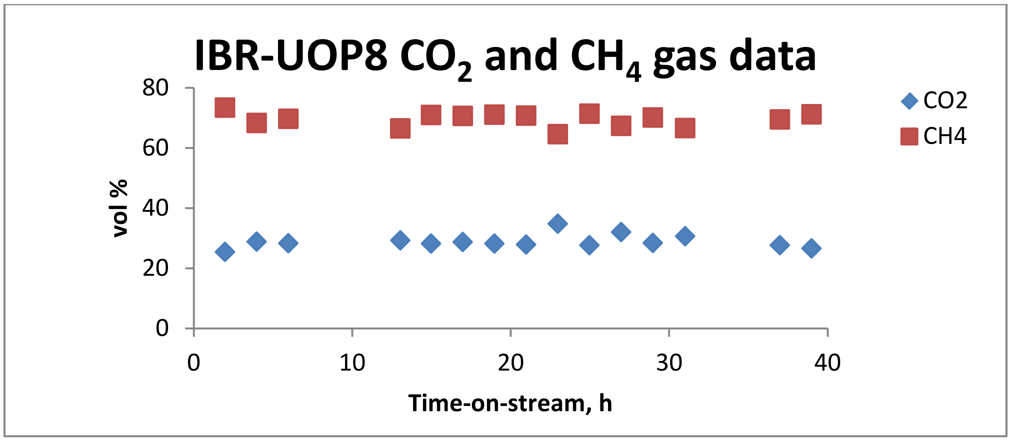

**Figure 15. $CO_2$ and $CH_4$ distribution of the gas product**

### 3.2.12 UOP9 HT (12/17/2013 – 12/19/2013)

| | |
|---|---|
| Feed | HT Upgrading aqueous phase (9/17/13) from UOP, decanted, unfiltered, COD = 76,000 ppm as received, pH = 5.04 as received, 1750 ppm $NH_4$ |
| Reactor configuration | sulfur scrubber bed followed by gasification catalyst bed |
| Total run time | 46.5 h |
| Reason for EOR | out of feed |
| Catalysts | Main: C3610 – 11.72 g→27.9 mL<br>Sulfur scrubber: Raney Ni (Raney 5886 3x8 catalyst, Nickel Cat 19400-72) – 17.4 g (wet) |
| Flowrates | LHSV = 2/h |
| Product COD ranges | Port: 97 – 24 ppm |
| Gas products | $CO_2$:$CH_4$ 32:67 |

The feedstock sample was received from UOP on 9/19/13, labeled as Upgrader water. The liquid had a small amount of precipitated oil on the bottom of the transfer vessel (**Figure 16**). It was not filtered before being processed. As received, the COD was recorded at 76,000 ppm while the pH was at 5.04. ICP of the liquid showed the usual biomass elements of Si (33 ppm), Na (10 ppm), K (7 ppm), and Fe (2 ppm).

S was also present in the ICP (11 ppm) and $SO_4^{-2}$ was reported at 56 ppm (see **Table 11**) equivalent to 19 ppm S. The other anion contaminants were present in low concentration.

**Table 11. Anions identified in the feed through ion chromatography of the feed, as received**

| Anion | Concentration, ppm |
|---|---|
| $SO_4^{2-}$ | 56 |
| $Cl^-$ | 44 |
| $NO_3^-$ | 12 |
| $PO_4^{3-}$ | 3 |
| $Br^-$ | 2 |

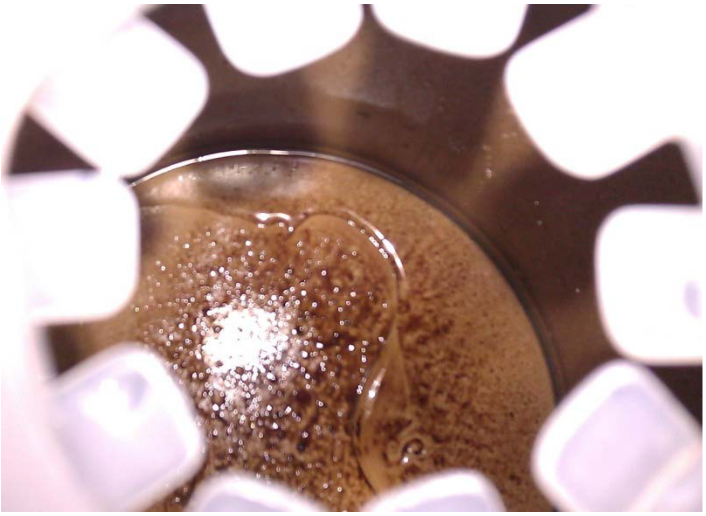

**Figure 16. Oil scum on container wall for IBR-UOP9 feed.**

Gas chromatography of the feed was also done. Major components were summarized in **Table 12**. The majority of the organic in this aqueous phase were the more recalcitrant phenolics with alcohols also present in significant amounts. The amounts shown in **Table 11** are only semi-quantitative relative amounts as a proportion of the volatile components.

The same reactor configuration was used as with IBR-UOP6, 7, and 8; however, a fresh S scrubber bed and catalyst bed were used.

**Table 12. Main compounds identified through gas chromatography-mass spectrometry of the feed (as received)**

| Compound | Amount, wt% |
|---|---|
| Ethanol | 22.2 |
| 1-propanol | 3.7 |
| 2-Butanol | 1.0 |
| Phenol | 1.1 |
| methyl phenol | 48.3 |
| dimethyl phenol | 7.5 |
| ethyl phenol | 3.5 |
| $C_3$-phenol | 0.4 |

**Figure 17** summarizes the COD readings from the sample port and the gas flow rate over the 46 hours of test. The COD in the effluent dropped continuously through the test suggesting some initial contamination in the sample line. After 46.5 hours at LHSV of 2, COD conversion was still at >99.9%. The gas product flow increased quickly over the first 10 hours to the steady flow throughout the most of the test. It remained high throughout with no indication of catalyst deactivation.

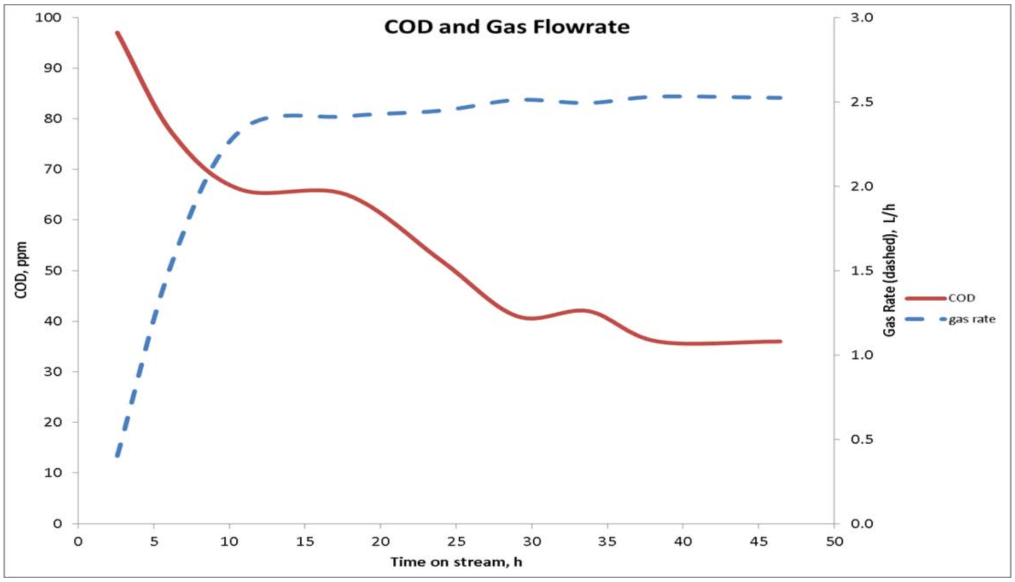

**Figure 17. COD values of the product water and gas flow rate in UOP9 HT**

The major gas products, as is typically seen, were $CO_2$ and $CH_4$ (**Figure 18**). Steady-state seemed to have been attained within 6 h time-on-stream with an average ratio of 32:67 of $CO_2$ and $CH_4$ respectively. GC-MS analysis of the product water showed no evidence of organic contaminants and the graph was essentially the same as that from a deionized water blank.

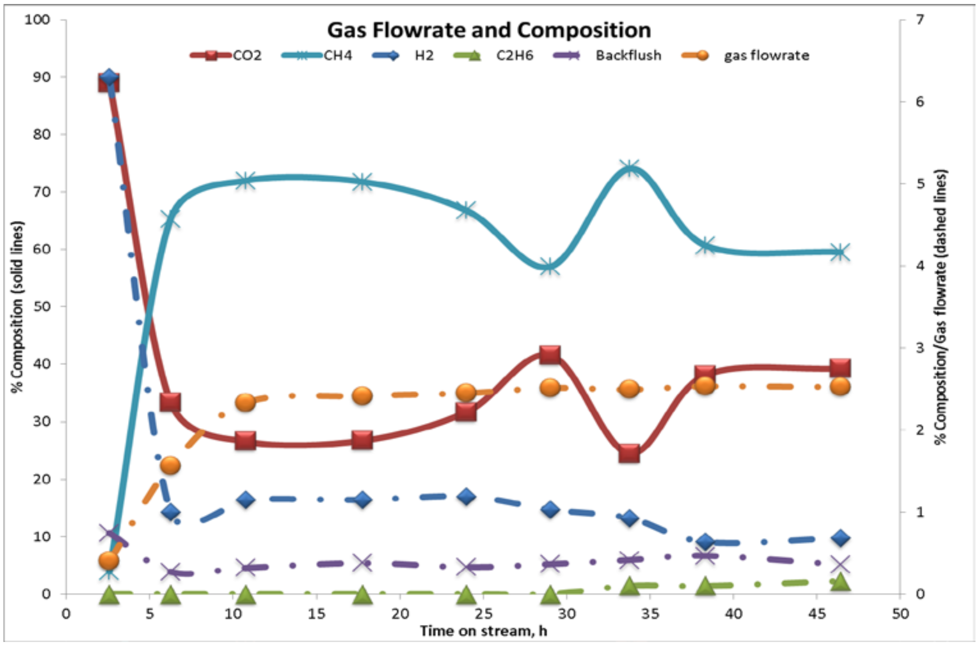

Figure 18. Gas composition and flow rate in UOP9 HT

## 3.3 Mini-reactor tests with model compound mixtures

In order to perform long-term catalyst activity tests in the mini-reactor, a chemical model of the hydrotreating aqueous product was produced in quantity from model compounds, because the aqueous feedstock was not available from UOP in sufficient quantity. The model compounds were purchased from Sigma-Aldrich at 99% purity or as high a purity as was available. The specific components were selected based on the list of components found by UOP in their byproduct waters from hydrotreating bio-oil in their first 35 runs at Des Plaines. The composition of three separate batches made for the tests is shown in **Table 13**. Although sulfide was expected in the aqueous byproduct, it was not measured by UOP and was not included in the simulant. Alkali metals and alkaline earths were believed by UOP to be below 10 ppm and were not added to the simulant.

### 3.3.1 L1 (8/27/2013 – 9/6/2013)

| | |
|---|---|
| Feed | model compounds in DI water simulant |
| Reactor configuration | no sulfur scrubber bed before gasification catalyst bed |
| Total run time | 148 h (time on stream) |
| Reason for EOR | out of feed |
| Catalyst | C3610 – 21.14 g→50.3 mL (126g/300cc density measurement) |
| Flowrates | LHSV = 2/h → 4/h → 5/h |
| Product COD ranges | Port: 227 ppm – 16 ppm → 78 ppm – 6 ppm → 20 ppm – 7 ppm |
| Gas products | $CO_2$:$CH_4$ 30:68 → 31:67 → 30:67 |

**Table 13. Composition of three batches of simulated bio-oil hydrotreating water product**

| | Weight, g | | |
|---|---|---|---|
| **organics** | **Batch 8/27/13** | **Batch 9/3/13** | **Batch 9/5/13** |
| Acetone | 26.1 | 26.3 | 26.2 |
| Ethanol | 887.0 | 887.5 | 887.0 |
| p-cresol | 132.3 | 132.3 | 132.3 |
| methanol | 115.0 | 115.0 | 115.0 |
| 1-propanol | 113.0 | 113.0 | 113.1 |
| isopropanol | 29.0 | 29.0 | 29.0 |
| 1-butanol | 26.0 | 26.2 | 26.0 |
| 2-butanol | 22.0 | 26.3 | 22.1 |
| acetic acid | 243.0 | 243.1 | 243.1 |
| ethyl acetate | 28.0 | 28.1 | 28.1 |
| phenol | 4.1 | 4.2 | 4.2 |
| **SUM** | 1625.5 | 1631.0 | 1626.1 |
| **water** | 10000.0 | 9397.5 | 10000.0 |
| **Factor (wt.O/wt.Feed)** | 0.14 | 0.15 | 0.14 |
| COD, ppm measured | 319,500 | 410,000 | 313,500 |
| C | 52.7% | 52.8% | 52.7% |
| H | 11.5% | 11.5% | 11.5% |
| O | 35.8% | 35.7% | 35.8% |

The first simulant run proceeded over two weeks including a shutdown over the long holiday weekend. In **Figure 19** the data for COD in the effluent and the gas product flow rate are plotted over the time of the experiment. The large blank area in the middle is the weekend break wherein the reactor was shutdown to idle at room temperature with no feedstock flow. After the weekend the reactor was heated back up to temperature with feedstock flow increased to a higher LHSV of 4 and then a final operating period at an LHSV of 5. The initial high COD in the effluent is attributed to contamination in the sample

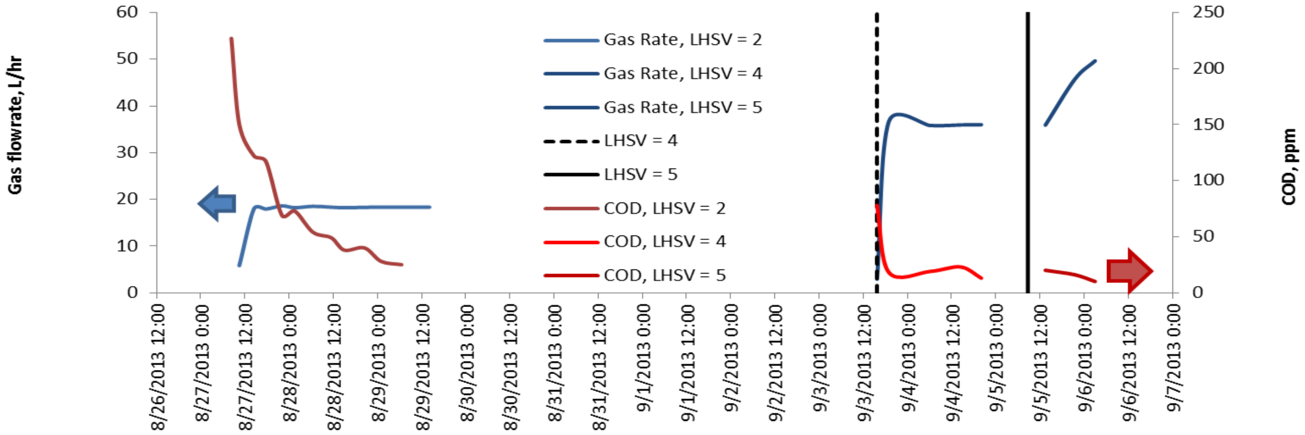

**Figure 19. COD values of the product water and gas flow rate in model compound test L1**

port from insufficient clean out. The COD of the effluent appears to stabilize at a very low level with COD conversion at >99%.

There is a direct linear relationship between increasing gas flow rate and increasing LHSV as shown in **Figure 20.**

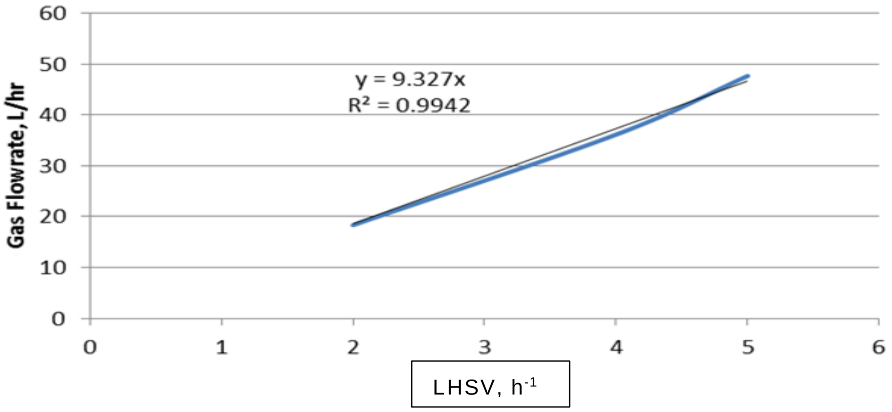

**Figure 20. Relationship of gas flow rate and LHSV in model compound test L1**

Based on the data in Figure 19, conversion data can be calculated. Carbon conversion to gas, COD conversion and overall material balance are plotted in **Figure 21**. The data calculations are based on windows of operation extending from about 3 to 5 hours. The consistency of the data is demonstrated in the graph.

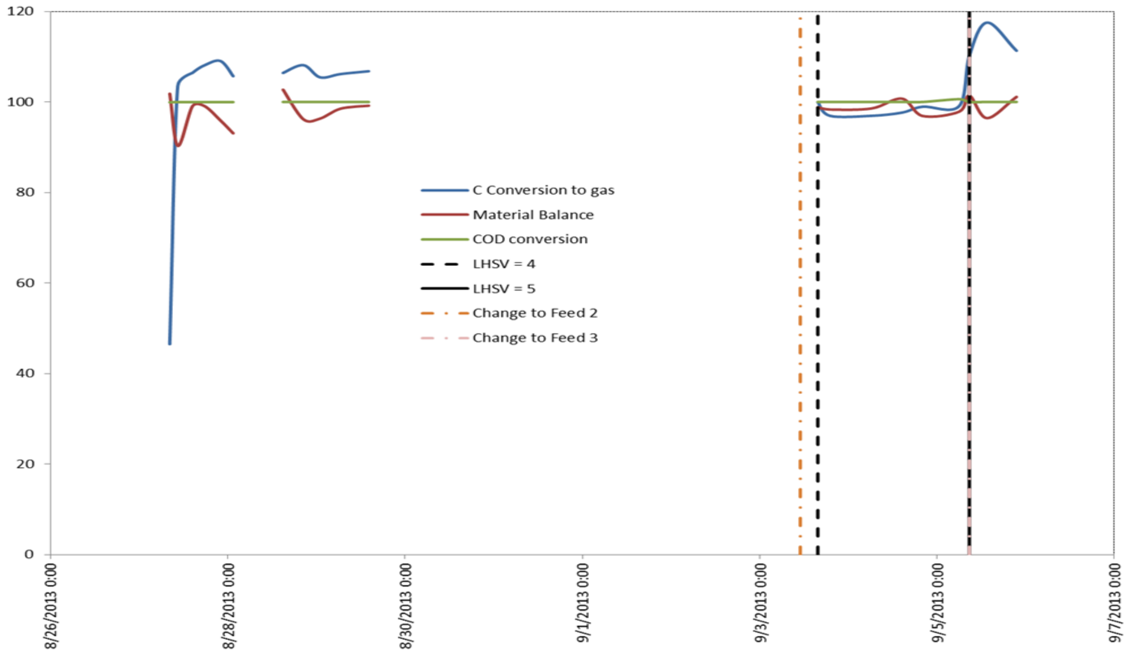

**Figure 21. Carbon conversion to gas, COD conversion and mass balance in model compound test L1**

Gas composition was also quite consistent throughout the test, as seen in **Figure 22**.

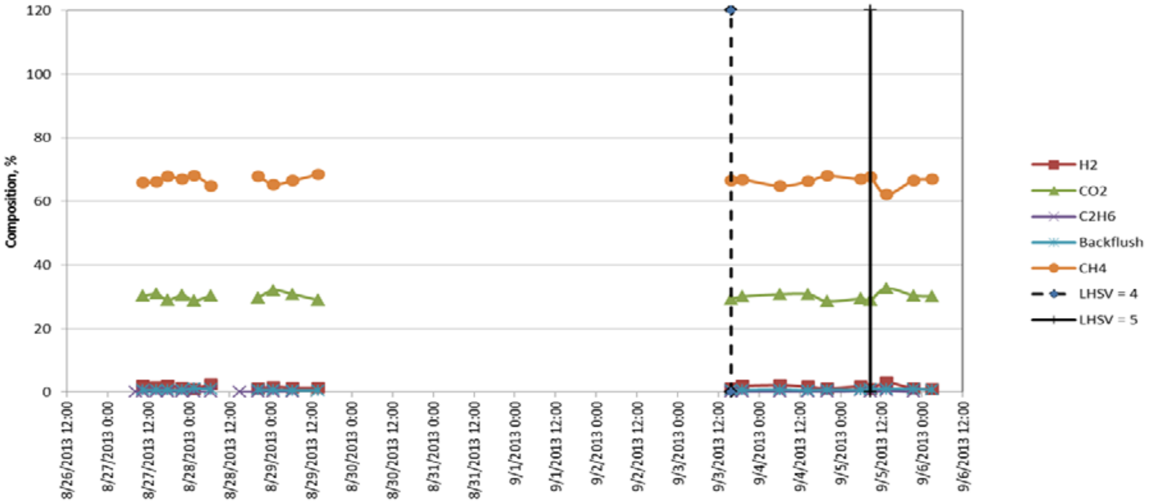

**Figure 22. Gas product composition in model compound test L1**

Analysis of the liquid product by GCMS can be compared to the feedstock, as shown in **Figure 23**. While the model compounds used in the test are readily observable, there is no detectable organic material in the aqueous product from the test following the catalytic processing.

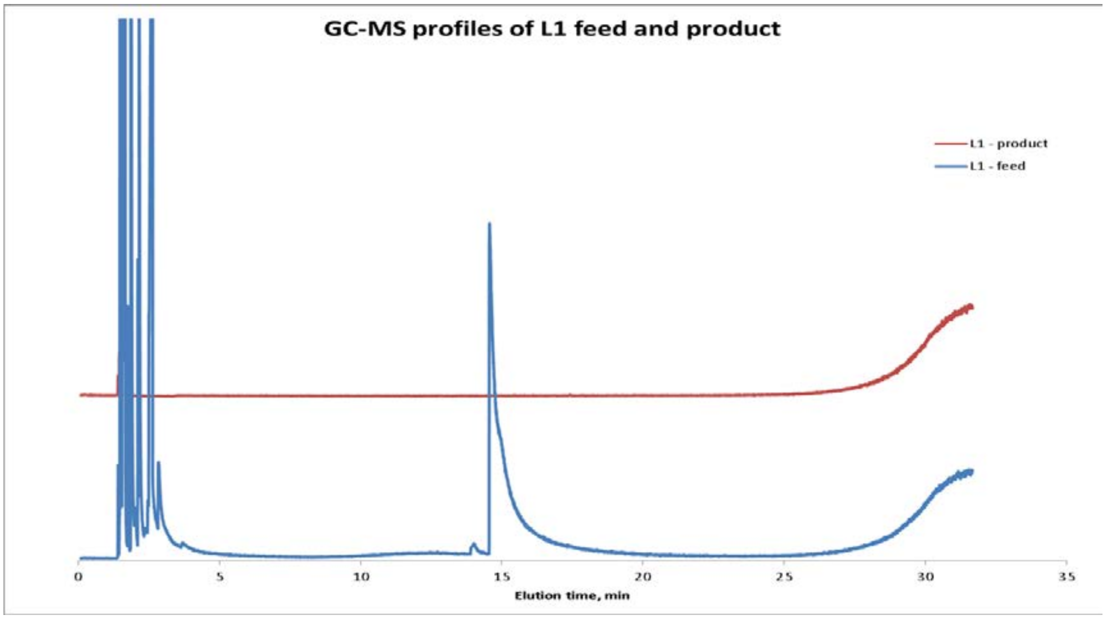

**Figure 23. Comparison of model compound feed and aqueous product**

These results verify that the major organic components in the byproduct aqueous stream from hydrotreating bio-oil can be effectively converted to gas product by CHG at LHSV of up to 5 even with a high concentration of organic loading of 14 to 15 wt%. These tests were performed without potential interference from trace components such as alkali or sulfide.

### 3.3.2 L2 (1/6/2014 – 1/15/2014)

| | |
|---|---|
| Feed | model compounds in DI water simulant with glucose and furfural added |
| Reactor configuration | no sulfur scrubber bed before gasification catalyst bed |
| Total run time | 160 h (time on stream) |
| Reason for EOR | out of feed |
| Catalyst | same catalyst bed from test L1 |
| Flowrates | LHSV = 2/h |
| Product COD ranges | Port: 51 ppm – 7 ppm |
| Gas products | $CO_2$:$CH_4$ 31:68 |

The second simulant run proceeded over two weeks including a shutdown over the weekend. The test included four operating periods: 1) the model mixture was processed to confirm that the catalyst bed was still active, 2) glucose was added to the model mixture, 3) furfural was added to the model mixture, and 4) both glucose and furfural were added to the model mixture. The actual components added to make up the feedstocks are detailed in **Table 14.** The overall composition remains fairly consistent in all cases.

**Table 14. Composition of feed streams used in test L2**

| | **Batch 1/6/14** | **Batch 1/8/14** | **Batch 1/9/14** | **Batch 1/13/14** |
|---|---|---|---|---|
| | **IBR-UOP-L1 last feed** | **Additional glucose** | **Additional furfural** | **Model compound mix + glucose + furfural** |
| acetone | 26.16 | 7.85 | 10.44 | 15.25 |
| ethanol | 887.02 | 266.11 | 354.51 | 161.95 |
| p-cresol | 132.29 | 39.69 | 52.96 | 77.27 |
| methanol | 115.04 | 34.51 | 46.09 | 67.07 |
| 1-propanol | 113.08 | 33.92 | 45.39 | 65.91 |
| isopropanol | 29.03 | 8.71 | 11.67 | 16.95 |
| 1-butanol | 26.05 | 7.82 | 10.47 | 15.14 |
| 2-butanol | 22.13 | 6.64 | 9.26 | 13.03 |
| acetic acid | 243.11 | 72.93 | 97.24 | 141.64 |
| ethyl acetate | 28.06 | 8.42 | 11.26 | 16.38 |
| phenol | 4.19 | 1.26 | 1.61 | 2.34 |
| water | 8373.84 | 2512.15 | 3318.51 | 3512.30 |
| glucose | | 30 | | 47.25 |
| furfural | | | 34.59 | 49.53 |
| Sum of feed | 10000.00 | 3030.00 | 4004.00 | 4202.00 |
| Sum of organic | 1626.16 | 517.85 | 685.49 | 689.70 |
| Factor (wt. org/wt. feed) | 0.16 | 0.17 | 0.17 | 0.16 |
| C | 52.7% | 52.0% | 53.2% | 53.2% |
| H | 11.5% | 11.2% | 11.1% | 9.9% |
| O | 35.8% | 36.8% | 35.6% | 37.5% |

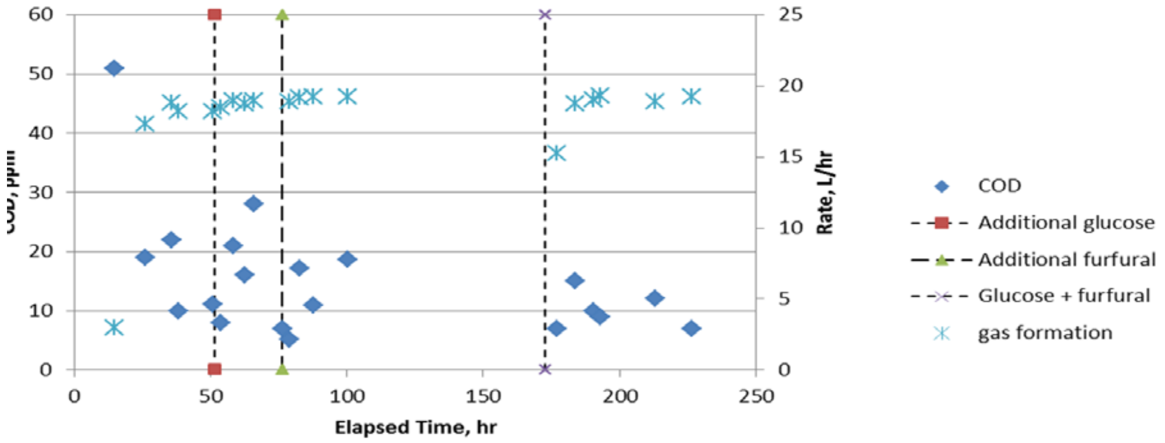

Figure 24. COD values of the product water and gas flow rate in model compound test L2

In **Figure 24,** the data for COD in the effluent and the gas product flow rate are plotted over the time of the experiment. The large blank area in the middle is the weekend break wherein the reactor was shutdown to idle at room temperature with no feedstock flow. After the weekend the reactor was heated back up to temperature with feedstock flow. The initial high COD in the effluent is attributed to contamination in the sample port from insufficient clean out. The COD of the effluent appears to stabilize at a very low level with COD conversion at >99%.

Based on the data in Figure 24, conversion data can be calculated. Carbon conversion to gas, COD conversion and overall material balance are plotted in **Figure 25.** The data calculations are based on windows of operation extending for varying lengths of time. The consistency of the data is demonstrated in the graph.

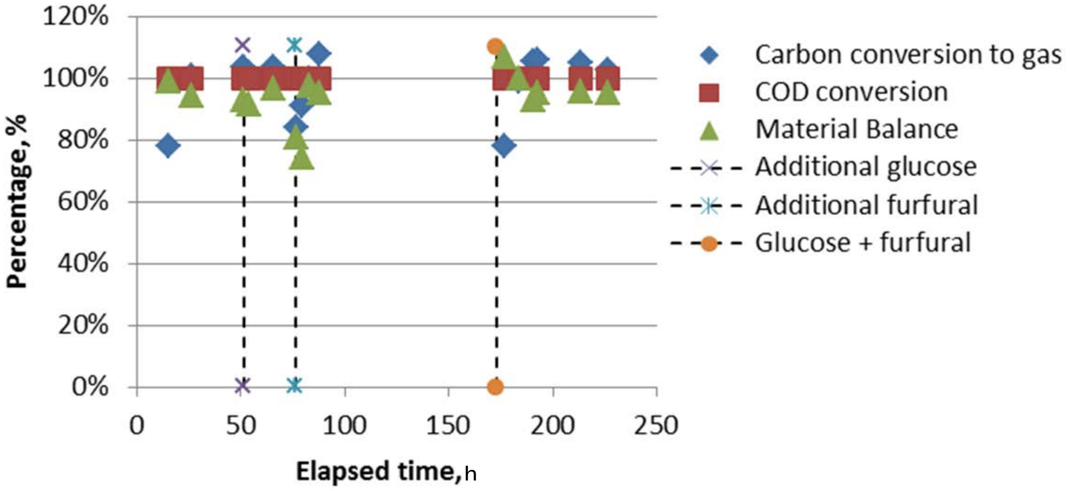

Figure 25. Carbon conversion to gas, COD conversion and mass balance in model compound test L2

Gas composition was also quite consistent throughout the test, as seen in **Figure 26** with little variation with the minor changes in feed composition.

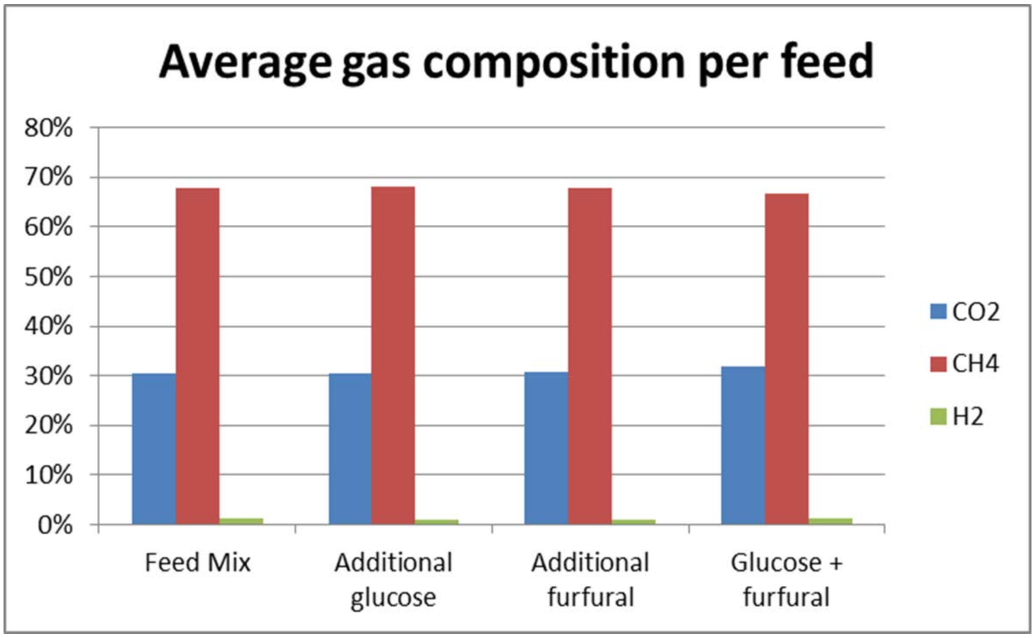

**Figure 26. Gas product composition in model compound test L2**

Similar to test L1, analysis of the liquid product by GCMS showed there was no detectable organic material in the aqueous product from the test following the catalytic processing. Additional analysis by LC showed effectively the same thing, no observable peaks.

These results verify that the major organic components in the byproduct aqueous stream from hydrotreating bio-oil can be effectively converted to gas product by catalytic hydrothermal gasification even with a high concentration of organic loading of 16 wt%. Further, the reaction is not interfered by the inclusion of either glucose or furfural or both. These two components represent the highly reactive bio-oil components, which are acknowledged to be the prime candidates for catalyst fouling in the hydrotreating process. This test showed that if even a significant portion of these components somehow bypass the hydrotreater reaction zone and were found in the aqueous byproduct, they would not cause problems in the subsequent catalytic gasification for fuel value recovery. However, these tests were performed without potential interference from trace components such as alkali or sulfide.

## 3.4 Mini-reactor tests with PNNL hydrotreater aqueous products

In order to prepare for scaled-up operations to demonstrate the CHG technology on bio-oil hydrotreating aqueous byproduct, the aqueous products from some of the bio-oil hydrotreating tests at PNNL were used as feedstock. The scaled-up operation was planned to follow these tests when the scaled-up hydrotreater at PNNL became operational and sufficient quantities of aqueous byproduct were available. In addition, a new formulation of the ruthenium on carbon catalyst produced by BASF had become available for use in our technology and validation of the new formulation was also needed.

### 3.4.1 HT-AQ-CHG-1 (8/20/2014 – 8/29/2014)

An initial test was made with a combined aqueous product from a number of hydrotreating tests. This material had been in storage for anywhere from weeks to months after the various hydrotreating tests. Although the specific details for its production were not determined, it was assumed that this would be useful test of a product representative of the range of products as produced by UOP, as described above. The test was made with a new formulation of the Ru on carbon extrudate catalyst from BASF.

| | |
|---|---|
| Feed | mixed aqueous byproducts from PNNL bench-scale bio-oil hydrotreating |
| Reactor configuration | sulfur scrubber bed before gasification catalyst bed |
| Total run time | 185 h (time on stream) |
| Reason for EOR | deactivated catalyst |
| Catalyst | 15.22 g Raney Ni, 504020656 Ru/C 11.93 g→23.39 mL (0.51g/cc density measurement) |
| Flowrates | LHSV = 2/h → 1/h |
| Product COD ranges | 52 ppm – 6000 ppm |
| Gas products | $CO_2$:$CH_4$:$H_2$:$C_2$ 31:61:5:0 → 8:19:59:4 |

The test was on stream for 6 days before catalyst deactivation became evident. The effluent COD was never as low as with the model compound tests using the C3610 catalyst. Also, the hydrogen level in the product gas remained higher than is typically seen previously. The COD in the effluent continued to increase in subsequent days even after the feed rate was reduced to 1 LHSV. Simultaneously, the gas composition exhibited the recognized transition from that of a highly active catalyst (strong gas flow with high methane to carbon dioxide ratio with minimal hydrogen and higher hydrocarbon gases) to that of a deactivated catalyst (minimal gas flow with high hydrogen, increased higher hydrocarbon gases and greatly reduced methane and carbon dioxide). Calculations based on gas composition and gas flow show that the methane and carbon dioxide track together and fall to 1/10th of the initial production while the hydrogen production about doubles.

Analysis of the aqueous streams by ICP showed a significant amount of S in the feedstock, 43 ppm while the other elements were below detection (<1 ppm) except 23 ppm Si, 11 ppm Na, and 3 ppm K. IC analysis suggested that most of the S was present as sulfate (93 ppm $SO_4$ = 31 ppm S). The product effluent showed an initial content of 3 ppm sulfur but none subsequently, suggesting that the sulfur scrubber (or catalyst bed) was acting as an effective sulfur capture point. The IC analysis essentially confirmed these readings. Si was nearly constant throughout. Na and K were much elevated at the beginning of the test, 115 ppm and 75 ppm respectively, and fell back over time, suggesting some leaching of these elements from the carbon support. There was a slightly noticeable Ni content (1-3 ppm) in the effluent sporadically through the test. Ru was below the level of detection throughout the test.

Analysis of the scrubber bed and catalyst bed following the shutdown of the test suggested that the deactivation of the catalyst was a direct result of S poisoning. Although the Ni bed analyses ranged from 3038 to 16370 ppm S, the Ru catalyst analysis was consistently 11640 to 11260 ppm S. Such a high loading of S on the Ru catalyst, equivalent to a 30% transition to $RuS_2$, in a hydrothermal environment is expected to effectively deactivate the gasification activity. It further suggests that the sulfur scrubber bed was not effective in the current configuration. However, since most of the S was found as sulfate in the feedstock it is not surprising that the Ni did not effectively capture the sulfur as it has been recognized that the Ru can reduce and capture sulfate much more effectively while the Ni is effective with reduced sulfur forms.

Subsequent to the CHG test, more detailed analysis of the HT byproduct aqueous phases produced at PNNL was undertaken. Four product samples were tracked for S by ICP and $SO_4$ by IC as shown in **Table 15**. The results suggest that the initially collected products contain high levels of sulfur, which falls dramatically over a week. The conclusion was that $H_2S$ dissolved in the water was volatilized over time. At the same time, the products as produced contained no detectable sulfate. It was found that sulfate had formed over 3 weeks, apparently by oxidation of the remaining dissolved sulfur compounds.

**Table 15. HT Aqueous sample analyses**

|  | 58-5 | 58-5 | 58-9 | 58-9 | 59-5 | 59-5 | 59-9 | 59-9 |
|---|---|---|---|---|---|---|---|---|
|  | S, ppm | $SO_4$, ppm | S, ppm | $SO_4$, ppm | S, ppm | $SO_4$, ppm | S, ppm | $SO_4$, ppm |
| as produced | 763 | ND | NA | ND | 566 | ND | NA | ND |
| 1 days | NA | ND | NA | ND | NA | ND | NA | ND |
| 5 days | NA | NA | 21 | NA | 49 | NA | 42 | NA |
| 3 weeks | 46 | 0.5 | 22 | 0.3 | 62 | 4.8 | 46 | 29 |

ND = below level of detection NA = not analyzed

### 3.4.2 HT-AQ-CHG-2 (10/3-5/2014, 11/12-14/2014, and 11/22-23/2014)

A second test was undertaken with the PNNL aqueous byproduct from bench-scale tests of bio-oil hydrotreating. The feedstock was better controlled and was taken from the hydrotreater to the gasification rig after only a short interlude and with care to limit oxidation. The test was performed in three parts as dictated by the availability of the aqueous stream from the HT tests.

| | |
|---|---|
| Feed | aqueous byproduct from PNNL bio-oil hydrotreating HT221, HT224, HT225 |
| Reactor configuration | sulfur scrubber bed before gasification catalyst bed |
| Total run time | 98.9 h (time on stream) |
| Reason for EOR | deactivated catalyst |
| Catalyst | 9.84 g Raney Ni, 504020656 Ru/C 11.81 g→22.71 mL (0.52g/cc density measurement) |
| Flowrates | LHSV = 2/h |
| Product COD ranges | 14-44 ppm, 100-2100 ppm, 120-10000 ppm |
| Gas products | $CO_2$:$CH_4$:$H_2$:$C_2$ 29:52:5:0 → 36:55:4:1 → 42:44:6:2 |

The composition details of the three feedstocks are provided in **Table 16**. The other metals not listed were below the level of detection, <0.8 ppm or <1 ppm. The products actually represent very different hydrotreater operations. HT221 was catalyzed by sulfided catalysts while HT224 and HT225 were catalyzed by precious metal catalysts, which are expected to act as sulfur stripping beds. This effect is most obvious in HT225 while less so for HT224. Further tests were restricted to the use of aqueous from hydrotreating with sulfided catalysts only, in order to test the capability of the system for operation with the more typical catalyst system.

**Table 16. Bench-scale HT aqueous byproducts used in CHG minireactor tests**

| Feedstock | HT 221 | HT 224 | HT 225 |
|---|---|---|---|
| S | 59 ppm | 34 ppm | <5 ppm |
| Na | 10 ppm | 43 ppm | 30 ppm |
| K | <2 ppm | 249 ppm | 162 ppm |
| Ca | <0.8 ppm | 544 ppm | 372 ppm |
| Fe | <0.8 ppm | 348 ppm | 205 ppm |
| Mg | <0.8 ppm | 283 ppm | 177 ppm |
| Mn | <0.8 ppm | 26 ppm | 16 ppm |
| Si | 14 ppm | 1 ppm | 1 ppm |
| COD | 16,100 ppm | 266,200 ppm | 259,000 ppm |
| N-$NH_4^+$ | 29 ppm | NA | NA |
| pH | NA | 3.61 | 4.02 |
| $SO_4^=$ | NA | 8 ppm | 0.34 ppm |
| $Cl^-$ | NA | 35 ppm | |

The tests were operated over the time period described above and the test was terminated during the 3rd portion of the experiment because of blockages of flow. Examination of the BPR discovered black dust suggesting catalyst disintegration. Examination of the catalyst bed after the experiment discovered that it was solidified with a white precipitate such that the catalyst bed pellets required drilling to allow their removal from the tubular reactor. Based on the feedstock analyses in Table 16 showing significant levels of Fe, Ca, and Mg, it is not surprising that the analysis of the sulfur scrubber bed and the catalyst bed also showed major deposits of these elements, as presented in **Table 17**. The sulfur scrubber bed showed evidence of functioning as designed, but a significant amount of sulfur made it way to the Ru gasification catalyst and probably contributed to the deactivation of the catalyst.

**Table 17. Recovered solids analysis following the three periods of the CHG 2 test**

| elements | CHG2 Raney Ni S scrubber bed | CHG2 Ru/C catalyst bed |
|---|---|---|
| **Ni** | **426550** | 1218 |
| **Al** | **274200** | 542 |
| **S** | **8158** | **1673** |
| Na | 46 | 74 |
| K | 92 | 199 |
| Ca | 161 | 57730 |
| Fe | 1940 | 22645 |
| Mg | 422 | 22645 |
| Mn | <35 | 2056 |
| Si | 137 | 158 |
| **Ru** | <35 | **51805** |
| Ba | <35 | 64 |
| Sr | <35 | 175 |
| Ag | 38 | 97 |
| Co | 288 | <35 |
| Cr | <35 | 39 |
| Pt | <35 | 356 |
| Zr | <35 | 53 |

### 3.4.3 HT-AQ-CHG-3 (2/3-4 and 7-8/2015)

| | |
|---|---|
| Feed | aqueous byproduct from PNNL bio-oil hydrotreating HT230 |
| Reactor configuration | sulfur scrubber bed before gasification catalyst bed |
| Total run time | 78.9 h (time on stream) minus 8 hours of low pressure operation |
| Reason for EOR | deactivated catalyst |
| Catalyst | 8.12 g Raney Ni, 504020656 Ru/C 11.07 g→21.29 mL (0.52g/cc density measurement) |
| Flowrates | LHSV = 2/h |
| Product COD ranges | 105-443 ppm → 4100-6300 ppm |

The mini-reactor for CHG was restarted, after replacing the sulfur scrubber bed and the gasification catalyst bed following CHG2, when feedstock became available from the bench-scale hydrotreater operating with a sulfided catalyst. The test operated over two days until the BPR failed and the reactor pressure dropped to 10 atmospheres over night while the feed continued to flow. The feed flow was stopped, the BPR was repaired and the test restarted. The catalyst activity had already given indication of deactivation, based on slightly increased COD in the effluent. The effluent COD level suggests a COD conversion of 99% falling to 97%. The normal corroborative data from the gas composition was unavailable due to operator error with the gas chromatograph. After restart, the catalyst activity, based on COD conversion, was much reduced and the test was terminated shortly thereafter. The

COD conversion was only 65% at the restart and it fell to 47% within 12 h of operation. No attempt was made to regenerate the catalyst.

Sulfate analysis was performed on the feedstock and the aqueous product by ion chromatography (IC). The feedstock contained 34 ppm sulfate while the products ranged from 1 to 3 ppm sulfate, suggesting that there was significant sulfur retention in the reactor. The sulfate analysis was confounded by an underlying broad peak that was not identified. The predominant peak in the IC analysis of the feedstock was tentatively identified as thiosulfate, which was not detected in the CHG products; therefore we conclude that it was reacted at the hydrothermal conditions. Chloride levels were also significant, about 25 ppm in the feedstock and 30 ppm in the CHG aqueous product.

# 4.0 Scaled-up reactor tests with simulated hydrotreater byproduct water

As the hydrotreater planned for the Hawaiian IBR was never built and the scaled-up hydrotreater at PNNL was never operational in the time period of this project, a simulant test was made with the mobile scaled-up unit. The test was performed as a means to demonstrate the refurbished system and validate its operability for future needed processing. It is envisioned that HTL aqueous byproduct processing or hydrotreater aqueous processing by CHG might be a useful option and would be wanted when the scaled-up processing units for HT and HTL at PNNL are brought on-line later in FY2015 or FY2016.

In order to perform a test in the scaled-up reactor, a chemical model of the hydrotreating aqueous product was produced in quantity from model compounds, similar to that tested earlier. The model compounds were acquired at 99% purity or as high a purity as was available. The specific components were selected based on the list of components found by UOP in their byproduct waters from hydrotreating bio-oil in their first 35 runs at Des Plaines. The composition of the batch made for the test is shown in **Table 18**. Although sulfide was expected in the aqueous byproduct, it was not measured by UOP and was not included in the simulant. Alkali metals and alkaline earths were believed by UOP to be below 10 ppm and were not added to the simulant.

**Table 18. Composition of the batch of simulated bio-oil hydrotreating water product**

| organics | Weight, kg |
|---|---|
| ethanol | 12.00 (95%) + 3.75 (100%) |
| methanol | 1.92 |
| 1-propanol | 1.76 |
| 2-propanol | 1.12 |
| 1-butanol | 0.45 |
| 2-butanol | 0.33 |
| acetic acid | 3.21 |
| ethyl acetate | 0.16 |
| phenol | 2.46 |
| **SUM** | 27.16 |
| **water** | 295 |
| **Factor (wt. organic/wt. feed)** | 0.082 |
| COD, ppm measured | 171,500 |
| C | 53.1% |
| H | 11.6% |
| O | 35.2% |

A single test was made in the scaled-up reactor on May 12, 2015.

| | |
|---|---|
| Feed | aqueous byproduct simulant |
| Reactor configuration | no sulfur scrubber bed before gasification catalyst bed |
| Total run time | 16 h (time on stream) including 7 hours of heat-up and cool-down with DI water flow |
| Reason for EOR | poor pressure control resulted in inconsistent operation |
| Catalyst | 504020656 Ru/C 2371g → 4.4 L (0.54g/cc density measurement) |
| Flowrates | LHSV = 2/h |
| Product COD ranges | 50 ppm initially, but essentially 0 ppm through most of the test |

This short demonstration test validated the operating systems in the mobile scaled-up reactor system with the exception of the 2-stage BPR pressure let-down operation. During the heat-up portion of the test using only DI water as the feedstock, there was steady pressure control. However, within 20 minutes of introduction of the organic laden feedstock followed by the initiation of gas production, the BPR system began to react erratically. Within the first hour of feedstock introduction, the initial water samples showed evidence of catalyst particulate carryover, despite extensive washing of the catalyst bed previously. After 2 h with feedstock on line the water samples had cleared of particulate and remained so for the balance of the test. Yet the pressure instability continued throughout the test and even increased in severity toward the end of the test. After shutdown of the simulant feed and return to DI water flush the pressure instability subsided. These results suggest a difficulty for proper pressure letdown over the Tescom BPRs with the mixed phase product containing both liquid water and fuel gas.

During the 5 h window of relatively steady-state operation, gasification of the organics in the feedstock was essentially complete with no measureable COD in the effluent. The product gas composition was essentially 67% methane, 31 % carbon dioxide and 2% hydrogen. While feeding the 171,500 ppm COD feedstock at a LHSV of 1.94 L/L/h, a gas product of 97 L of gas per L of feedstock was produced. There was no evidence of catalyst deactivation over the period of this short run as the gas composition remained constant as did the COD conversion.

# 5.0 Conclusions and Recommendations

PNNL was tasked with developing catalytic hydrothermal gasification (CHG) for use with aqueous streams within the pyrolysis biorefinery. These aqueous streams included the aqueous phase separated from the fast pyrolysis bio-oil and the aqueous byproduct streams formed in the hydroprocessing of the bio-oil to finished products. As other aqueous streams were identified of interest within the biorefinery, these might also have been tested in CHG, but none were identified. The development work progressed at two levels. Initial tests were made in the laboratory in mini-reactor scale and bench-scale continuous-flow reactor systems. Following positive results, the next level of evaluation was in the scaled-up engineering development system.

The results of tests with bio-oil aqueous fraction suggested that the organic contaminants, even at high concentration, can be effectively converted to a fuel gas product by CHG. However, corrosion of the stainless steel reactor system by the acidic components appeared to be significant, based on the metal deposits on the catalyst, but no noticeable change was seen in the reactor itself. Sulfur stripping may also be necessary in order to maintain long-term catalyst activity. Carbon fouling of the catalyst was also suggested by the loss of porosity and surface area. Handling of the aqueous stream was also identified as an issue as the acidic components were corrosive to steel cans and could not be stored for any period of time in such without resulting in a significant iron contamination and even failure of the container.

Tests were performed in the mini-reactor with various aqueous products from the UOP bio-oil hydrotreating tests used as feedstock. The products expressed a range of component composition and concentration. Based on these results it appeared that a range of hydrotreating of bio-oil was undertaken such that the product was more or less hydrogenated and the resulting aqueous byproduct had more or less soluble oxygenated components. COD of up to 178,250 ppm was effectively processed at 2 LHSV in fixed-bed, continuous-flow catalytic reactors achieving >99% conversion in both the bench-scale system and the mini-reactor. The typical product containing methane and carbon dioxide was produced.

Trace elements were quite low in the hydrotreating aqueous byproducts. Traces of biomass minerals were present. Sulfur content ranged over an order of magnitude from 2 to 20 ppm. Ion chromatography of the feedstocks suggested that sulfate was not detectable.

The results with these feedstocks containing only low levels of sulfur showed that system modification to accomplish sulfur scrubbing from the feed would be required to protect the CHG catalyst. After refrigerated storage for a month and a half, analysis by IC suggested the aqueous byproduct contained 29 ppm sulfate. This measurement of high sulfate in the stored aqueous byproduct suggested that the initial sulfide in the feed was oxidized to sulfate over time. ICP analysis showed 25 ppm sulfur, therefore about 40% of the sulfur had been oxidized to sulfate. Other elements found in this analysis were 28 ppm Na, 22 ppm Si, 3.5 ppm K, 1.9 ppm Al, and 1.8 ppm Ca. Clearly there was not enough Ca to precipitate all the sulfate in the solids settler, which would allow the soluble sulfate to impact on the catalyst activity over time.

Detailed analysis of the HT byproduct aqueous phases produced at PNNL was undertaken for S by ICP and $SO_4$ by IC. The results suggested that the initially collected products contained high levels of sulfur, which fell dramatically over a week. The conclusion was that $H_2S$ dissolved in the water was volatilized over time. At the same time, the products as produced contained no detectable sulfate. It was found that sulfate had formed over three weeks, apparently by oxidation of the remaining dissolved sulfur compounds.

Analysis of the catalyst and scrubber beds after one test confirmed that a significant amount of sulfur was captured in the scrubber (about ¼) but over 10% ended up on the catalyst while another quarter passed through in the aqueous stream. The sulfur on the catalyst and in the aqueous apparently was the sulfate that was not captured by the Ni scrubber. Some of the balance of the sulfur precipitated at hydrothermal conditions but was not collected in the separator vessel, but was mobilized by the liquid water flow and passed on through the system to the condensate product collector.

The detailed analysis showed that the Ni in the scrubber was only slightly (<1%) reacted to nickel sulfide. It did not serve as an effective sulfur scrubber. However, the fact that a large portion of the S was in the form of sulfate, and therefore less reactive, is at least a partial explanation. The sulfur was evenly distributed through the Ni bed suggesting that it was reacting slowly. Therefore, the Ru catalyst had been sulfided to a large degree and certainly enough to have a large effect on its gasification and methanation activity. EDS analysis showed that the sulfur was highly associated with both the Ni and the Ru. There was also evidence of Ca and P (probably as calcium phosphate) coating the surface of the Ni scrubber. The Ru concentration in the spent catalyst had been reduced to 3/4th of the starting level, presumably by carbon deposition in the pores, as there was no evidence of Ru loss to the aqueous stream.

Extended runs were also performed with model compound mixtures simulating the hydrotreater aqueous byproduct at the high concentration end of the range (313,500 to 410,000 ppm COD). These experiments which did not include sulfide compounds or alkali impurities operated at high conversion >99%, even at LHSV of up to 5. Gas composition was also quite consistent throughout the test with little variation with the minor changes in feed composition. There was a direct linear relationship between increasing gas flow rate and increasing LHSV. Analysis of the liquid product by GCMS showed there was no detectable organic material in the aqueous product from the test following the catalytic processing. Additional analysis by LC showed effectively the same thing, no observable peaks.

These model compound results verified that the major organic components in the byproduct aqueous stream from hydrotreating bio-oil could be effectively converted to gas product by catalytic hydrothermal gasification even with a high concentration of organic loading of 16 wt%. Further, the reaction was not interfered by the inclusion of either glucose or furfural or both. These two components represent the highly reactive bio-oil components, which are acknowledged to be the prime candidates for catalyst fouling in the hydrotreating process. This test showed that if even a significant portion of these components somehow bypass the hydrotreater reaction zone and were found in the aqueous byproduct, they would not cause problems in the subsequent catalytic gasification for fuel value recovery. However, these tests were performed without potential interference from trace components such as alkali or sulfide.

The mobile scaled-up reactor system at PNNL was refurbished and put into operating condition by the addition of a modern data acquisition and control system. The unit was operated with simulated aqueous byproduct to demonstrate its functionality. The only question arising from the test was the failure of the pressure control system, which will require further improvements to allow long-term operation in this application.

# 6.0 References

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