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Impacts of High-Temperature/High-Hydroxide on Thermolytic Production of Hydrogen from Glycolate and Other Tank Farm Organics - 21406

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ABSTRACT

Trace organic compounds in High-Level Radioactive Waste (HLW) tanks have the potential to produce flammable gases, predominately by radiolytic or thermolytic pathways. Savannah River National Laboratory (SRNL) has previously developed two model expressions for the rate of thermolytic production of hydrogen in HLW tanks at the Savannah River Site (SRS). A global model developed from thermolytic Hydrogen Generation Rate (HGR) measurements of HLW supernate tank samples as well as from non-radioactive simulant HGR testing with the most active hydrogen producing organic compounds found in SRS HLW tanks today. A model was also developed for glycolate, a new organic compound that is planned to be used in the alternate reductant flowsheet at the Defense Waste Processing Facility (DWPF). This model was developed using real waste tests from HLW tanks spiked with glycolate as well as non-radioactive simulant testing.

Further testing was undertaken to expand the region of applicability of these models to the higher temperatures and hydroxide concentrations found in HLW tank evaporator systems. For example, historical evaporator temperatures have been as high as approximately 164 °C and hydroxide concentrations have been as high as approximately 16 mol L^{-1}, which are much higher than the applicable ranges of the current models of up to approximately 134 °C and 12 mol L^{-1} hydroxide. Testing was performed using non-radioactive simulants, based on historical supernate measurements from evaporator tanks, with added glycolate or Xiameter™ AFE-1010, a polydimethylsiloxane antifoam that is a known hydrogen producer. All tests were done at the respective boiling points of the simulants to mimic evaporator conditions.

The testing has confirmed the applicability of both thermolytic hydrogen generation rate expressions (glycolate model and global model) at temperatures as high as 170 °C and hydroxide concentrations as high as 23 mol L^{-1}. Methane was also observed in testing with Xiameter at higher production rates than hydrogen. These rates were observed at temperatures higher than 100 °C and indicate that some organics found in HLW tanks may preferentially create methane.

INTRODUCTION

The millions of gallons of radioactive liquid waste produced at SRS from legacy nuclear material and fuel reprocessing operations are stored in 43 HLW tanks across the two tank farms onsite. The waste consists of three distinct layers; an insoluble sludge, salt cake, and supernatant. Organic compounds are also found within the waste in limited quantities. These organic species have been added throughout the site's history during various campaigns. For example, glycolate, a new organic compound is planned to be used in the alternate reductant flowsheet at the Defense Waste Processing Facility (DWPF) The SRS Liquid Waste Operator (LWO) Savannah River Remediation (SRR) contracted SRNL to evaluate the potential for these organic compounds to produce hydrogen by thermolysis.

To date, SRNL personnel have performed several series of tests on both radioactive and simulated caustic waste to measure the thermolytic production of hydrogen gas from organics, including glycolate.[1-4] These hydrogen generation rate (HGR) measurements performed by SRNL have led to the generation of model expressions for the thermolytic production of hydrogen from glycolate and non-glycolate organics in caustic waste.[4] The HGR expression for glycolate thermolysis is derived from simulant testing and confirmed with radioactive waste testing with added glycolate. The non-glycolate organic HGR expression is based on simulant tests with the most reactive organics in SRS HLW tanks that followed a similar thermolytic mechanism (hydroxide dependence and Arrhenius behavior), and a correction for the observed thermolytic reactivity of organics in radioactive waste. The models are shown below in Equations (1) and (2),

$$HGR_{GLY} = 5.32 \times 10^{4}[Na]^{1.520}[NO_3]^{0.282}[OH]^{1.441}\left[C_{Gly}\right]e^{\frac{-82,300}{RT}} \quad \text{(Eq. 1)}$$

$$HGR_{TOC} = 2.08 \times 10^{5}[OH]^{0.925}[C_{TOC}]e^{\frac{-82,900}{RT}} \quad \text{(Eq. 2)}$$

where,

HGR_{GLY} is the hydrogen production rate from the thermolysis of glycolate in mol s^{-1} m^{-3},

HGR_{TOC} is the hydrogen production rate from the thermolysis of other organics in mol s^{-1} m^{-3},

$[OH]$ is the concentration of hydroxide in mol L^{-1},

$[Na]$ is the concentration of sodium in mol L^{-1},

$[C_{GLY}]$ is the concentration of carbon from glycolate in mol L^{-1},

$[C_{TOC}]$ is the concentration of organic carbon not attributable to formate, oxalate, or glycolate in mol L^{-1},

$[NO_3]$ is the concentration of nitrate in mol L^{-1},

R is the ideal gas constant, 8.314 J mol^{-1} K^{-1}, and

T is the temperature in K.

The model expressions given in Equations (1) and (2) were generated from testing within a specific range of salt concentrations and temperatures. The limits of applicability of these HGR rate expressions are given in TABLE I.

TABLE I. Previous Limits of Applicability for Total Organic Carbon (TOC) and Glycolate Thermolysis Model Expressions.

Parameter	**Glycolate Thermolysis**		**TOC Thermolysis**	
	Minimum	**Maximum**	**Minimum**	**Maximum**
Aluminum (M)	9.64E-04 M	2.49E+00 M	1.29E-03 M	1.98E+00 M
Nitrite (M)	2.21E-01 M	2.78E+00 M	2.21E-01 M	2.74E+00 M
Nitrate (M)	6.55E-02 M	6.34E+00 M	6.75E-02 M	5.58E+00 M
Hydroxide (M)	4.66E-02 M	1.22E+01 M	1.58E-01 M	1.25E+01 M
Sulfate (M)	4.94E-04 M	2.50E-01 M	4.94E-04 M	2.05E-01 M
Carbonate (M)	2.38E-03 M	6.54E-01 M	8.14E-03 M	7.23E-01 M
Sodium (M)	3.40E-01 M	2.56E+01 M	4.65E-01 M	2.47E+01 M
Temperature (°C)	60 °C	134 °C	70 °C	130 °C

Testing was undertaken to expand the parameter applicability range for hydroxide and temperature to include historical evaporator operating conditions in which hydroxide concentrations as high as 16.3 mol L^{-1} and temperatures as high 164 °C have been previously seen.

DESCRIPTION

Testing was undertaken using a 1.2 L polytetrafluroethylene (PTFE) vessel and lid. Fitted to the center of the lid was a Parr® high-torque magnetic drive connected to a PTFE agitator impeller and shaft that was used to mix the simulant inside the vessel. Surrounding the magnetic drive were eight ports with stainless-steel fittings used for the following: temperature control within the vessel by two Incoloy® 800 heating rods, monitoring liquid temperature within the vessel with an Inconel® 600 thermocouple, providing purge gas to continuously sweep the vapor space of the vessel, connecting the headspace of the vessel to a glass condenser, providing a route for reflux from the condenser back to the reaction vessel, and for adding the antifoams. Upstream from the reaction vessel, two MKS® mass flow controllers were used to supply CO_2-free compressed air or N_2 cylinder gas containing 0.5 vol % Kr and 20 vol % O_2. Downstream from the reaction vessel, a glass condenser was employed to remove condensable gases from the gas before proceeding to analysis. After passing through the condenser, the gas was sampled and quantified for hydrogen content by an Inficon Micro 3000 GC-TCD (gas chromatograph – thermal conductivity detector) or an Inficon Micro Fusion GC.

Reagent grade sodium nitrate, sodium nitrite, aluminum trinitrate nonahydrate, and a 50 wt % reagent grade sodium hydroxide solution were used as received. In the case where the targeted hydroxide concentration precludes the use of 50 wt % sodium hydroxide solution, reagent grade sodium hydroxide pellets were used as the hydroxide feedstock. For the test condition where the target nitrate-to-aluminum ratio would not permit the use of aluminum trinitrate, technical grade (>85%) sodium aluminate was used as the source of aluminum. OLI [5] was used to predict simulant densities; these densities were then used to calculate the desired amounts of salts and water needed to achieve the targeted molarities in test conditions. The reagents were added directly to the reaction vessel before sealing.

After the addition of all chemicals, the vessel was sealed and checked for leaks by mass balance of air flow through the process headspace. Once leak-free conditions had been confirmed, stirring was initiated and a purge flow of dried air was applied to the process to sweep residual CO_2 out of the vessel. The system controls were then set to apply heat via two electric heating rods such that the difference between the process (fluid) temperature and that of the heating rod interior could not exceed 40 °C. For the blank tests, the process fluid was brought to its boiling point. In all other tests, the process fluid was brought to within approximately 10 °C of its boiling point, at which point the organic additive was added and subsequently brought to boiling. In all tests, the purge gas was then switched to the typically lower-purge process gas stream (0.5 vol % Kr and 20 vol % O_2 in N_2). This point was designated as the start of the experiment.

The experiment continued while monitoring for hydrogen concentration via GC. To ensure hydrogen and methane concentrations stayed below their flammability limits, the purge rate was increased using both the air purge and the Kr tracer-containing gas stream as needed. The experiment duration was planned such that at a minimum, the vessel headspace could undergo approximately three vapor space volume turnovers (achieving 99.7% of pseudo steady-state, assuming continuously-stirred reactor dynamics; note that this time is volume and purge rate dependent). Once this time was reached and hydrogen measurements by GC stabilized or began to decrease, heating rod power was turned off and the experiment was stopped. The higher-purge air was then reapplied to the vessel to sweep out residual hydrogen. The simulant mixture was then removed from the vessel and subsampled as needed for product analyses. Density of the simulant was checked by weighing a known volume of the simulant using a calibrated autopipette and balance.

The high boiling point (HBP) test differed from above as follows: 1) the simulant was heated to its boiling point and excess water was removed until the desired boiling point (170 °C) was reached. At this point, a blank measurement was performed. Heating was then stopped, and the solution allowed to cool by approximately 10 °C before adding the organic species. It was then brought back to boiling and hydrogen concentration monitored by GC as above. 2) After the experiment was stopped and the vessel had cooled to approximately 160 °C, the simulant was sampled. The solution conformity was also confirmed by removing the lid and visually determining that solids were not present at the end of the experiment.

Either an Inficon Micro 3000 GC or an Inficon Micro Fusion GC was used to analyze offgas content for all experiments. The GCs were equipped with two analysis channels: one using a Molsieve 5A column for H_2, O_2, N_2, CH_4, and Kr analysis, and a second using a PoraPLOT Q column for N_2O and CO_2 analysis. Each column employed a thermal conductivity detector which measured against the background of pure argon (also used as a carrier gas). The GC calibration was verified before each experiment using a calibration gas with a composition of 50 ppm_v H_2, 100 ppm_v CH_4, 0.5 vol % Kr, 1 vol % N_2O, 1 vol % CO_2, and 20 vol % O_2 in N_2. The GCs were also used to qualitatively track the concentrations of He and H_2O.

When presented, HGR is reported in units of moles of hydrogen per second per cubic meter of simulant mixture (mol s^{-1} m^{-3}). The purge rates employed during this testing were supplied at standard conditions of 21.11 °C and 1 atm. The HGRs presented herein have been corrected to a standard temperature and pressure of 25 °C and 1 atm.

HGR Testing with Glycolate

The conditions used to evaluate HGRs from glycolate at elevated temperatures and hydroxide concentrations and the results of each test are given in TABLE II.

TABLE II. Conditions and Results of HGR Testing with Glycolate.

Run Name	Temp (°C)	[Al] (M)	[NO_2] (M)	[NO_3] (M)	[OH] (M)	[C_{Gly}] (M)	HGR (mol s^{-1} m^{-3})
HTH-1	138.3	9.90E-01	1.20E+00	7.90E-01	1.30E+01	4.20E-03	3.07E-05
HTH-2	107.4	4.30E-01	8.60E-01	3.40E+00	1.10E+00	4.30E-03	2.43E-08
HTH-3	105.4	9.50E-02	6.00E-01	7.80E-01	2.70E+00	4.20E-03	<1.29E-08
HTH-4	142.2	1.30E-02	4.30E+00	5.00E+00	1.10E+01	5.20E-03	2.32E-05
HTH-5	157.1	3.80E-01	1.90E+00	1.60E+00	1.90E+01	4.80E-03	5.04E-05
HTH-6	124.8	4.00E-01	1.70E+00	2.20E+00	9.00E+00	4.50E-03	9.04E-07
HBP	170.2	4.50E-01	2.20E+00	1.90E+00	2.30E+01	5.60E-03	1.08E-04

The highest temperature explored in this set of tests was recorded at 170.2 ± 2 °C in the HBP experiment. Similarly, the HBP experiment yielded the highest observed hydroxide concentration (23 M). These values fall far outside of the original bounds placed on the Glycolate Thermolytic HGR model.

The HGRs reported in TABLE II were evaluated against the predictions made from the Glycolate Thermolytic HGR model (Eq.1).[4]

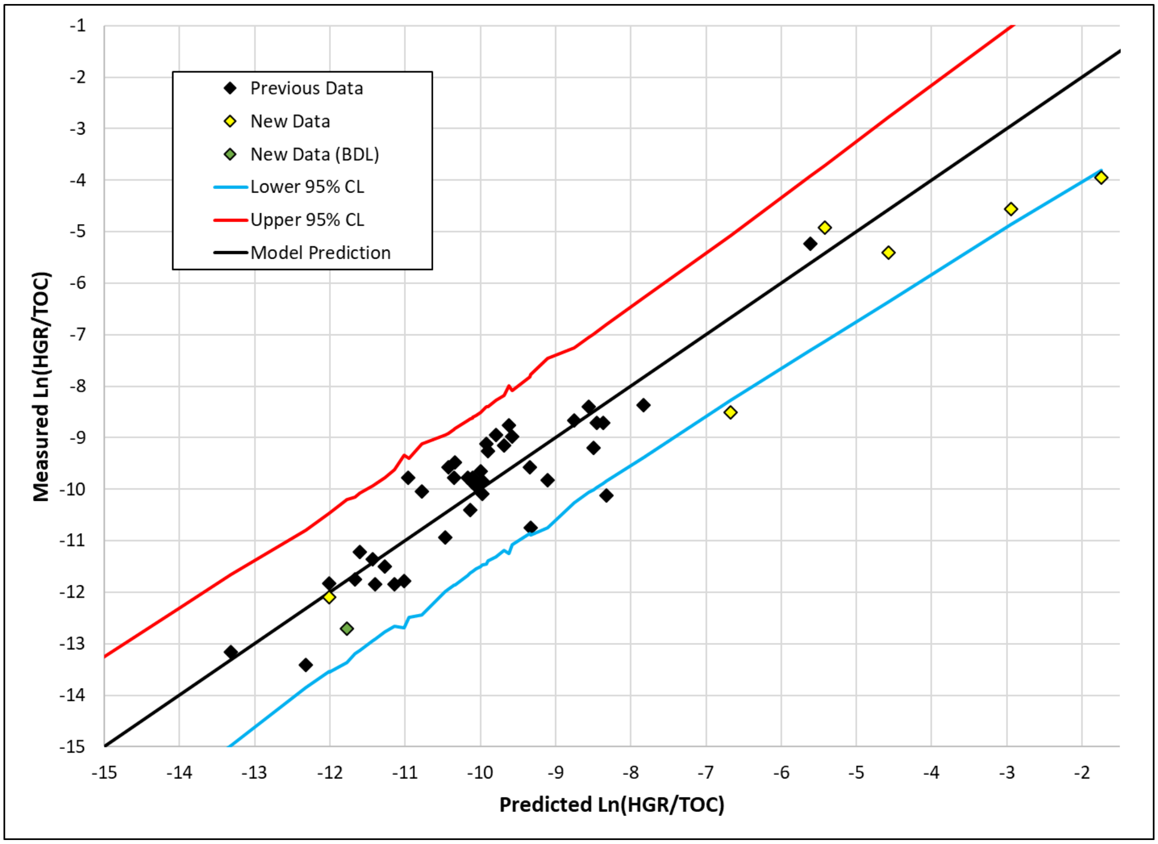

Figure 1. Model Evaluation of Glycolate HGR Data.

The results displayed in Figure 1 indicate that the Glycolate Thermolytic HGR model well describes the HGRs observed in high temperature/high hydroxide environments. Of the seven experiments performed, all seven fall below the upper 95% confidence limit (CL) for a prediction made with the model expression.

Six of the seven points fall below the model prediction line, suggesting further that the model expression provides a measure of conservatism when predicting HGRs from glycolate at high temperatures and hydroxide concentrations. A single data point is reported as a “BDL”, or “below detection limit” measurement. In this case, the hydrogen produced from glycolate could not be adequately differentiated from that of the glycolate-free experiment due to purge rates and GC limitations. The true value of this data point is expected to fall lower than that shown by the empty diamond in Figure 1, and is therefore not expected to be problematic.

These results suggest that the Glycolate Thermolytic HGR expression may be used to predict glycolate in conditions with temperatures as high as 170 °C and hydroxide concentrations as high as 23 M. These new bounds are expected to completely include evaporator operations.

HGR Testing with XiameterTM AFE-1010

From previous testing XiameterTM AFE-1010 was found to be one of the most reactive organic species towards hydrogen production.[4] Antifoam components like XiameterTM AFE-1010 have not been directly added to the SRS HLW tanks in >15 years.[4] After years of exposure to caustic environments and radiation fields, one can expect that the most reactive organic species have degraded in HLW tank waste and have depreciated in reactivity (compared to that expected from the addition of “fresh” organic material). In earlier studies, it was determined that the kinetic behavior of the most reactive organics in the HLW tanks follows a single profile characterized by 1) positive hydroxide dependence, and 2) Arrhenius-type temperature dependence. In earlier testing, it was shown that the same hydroxide- and temperature-dependent behavior was observed with XiameterTM AFE-1010, Reillex® HPQ, and IONAC A-641 ion exchange resin degradation products. It is therefore expected that hydroxide and temperature changes would impact these reactive organics in a similar way. It follows, then, that only one of these species needed further evaluation in the expanded hydroxide and temperature regimes investigated in this study. XiameterTM AFE-1010 was chosen for 1) material availability, and 2) similarity to organics expected in SRS HLW tanks.

The conditions and results of testing used to investigate HGRs from XiameterTM AFE-1010 are given in TABLE III.

TABLE III. Conditions and Results of HGR Testing with XiameterTM AFE-1010.

Run Name	Temp (°C)	[Al] (M)	$[NO_2]$ (M)	$[NO_3]$ (M)	[OH] (M)	[TOC] (M)	HGR (mol s^{-1} m^{-3})
HTH-1	138.8	9.47E-01	1.13E+00	7.50E-01	1.20E+01	4.25E-04	< 5.97E-05
HTH-2	107.5	4.30E-01	8.60E-01	3.44E+00	1.07E+00	4.51E-04	8.09E-08
HTH-3	105.2	9.37E-02	5.87E-01	7.73E-01	2.63E+00	4.21E-04	4.33E-08
HTH-4	142.7	1.26E-02	4.26E+00	4.97E+00	1.04E+01	5.10E-04	1.14E-06
HTH-5	156.6	3.51E-01	1.73E+00	1.46E+00	1.79E+01	4.51E-04	6.40E-07
HTH-6	125	4.14E-01	1.74E+00	2.33E+00	9.39E+00	4.76E-04	5.64E-07
HBP	170.5	4.43E-01	2.18E+00	1.85E+00	2.26E+01	5.89E-04	2.11E-06

The highest temperature and hydroxide concentration recorded in this set of tests is similar to those seen in testing with glycolate (170.2 °C and 23 M).

The results of testing with XiameterTM AFE-1010 are evaluated against the kinetic model derived from freshly-added organics (performed in previous studies [4]) and displayed graphically in Figure 2. The previous data taken from testing with Xiameter™ AFE-1010, as well as digestion products from IONAC A-641 and Reillex® HPQ ion exchange resins, are indicated with black diamonds. New data taken with Xiameter™ AFE-1010 (tests described in TABLE III) are indicated with yellow diamonds, and empty diamonds when hydrogen could not be detected.

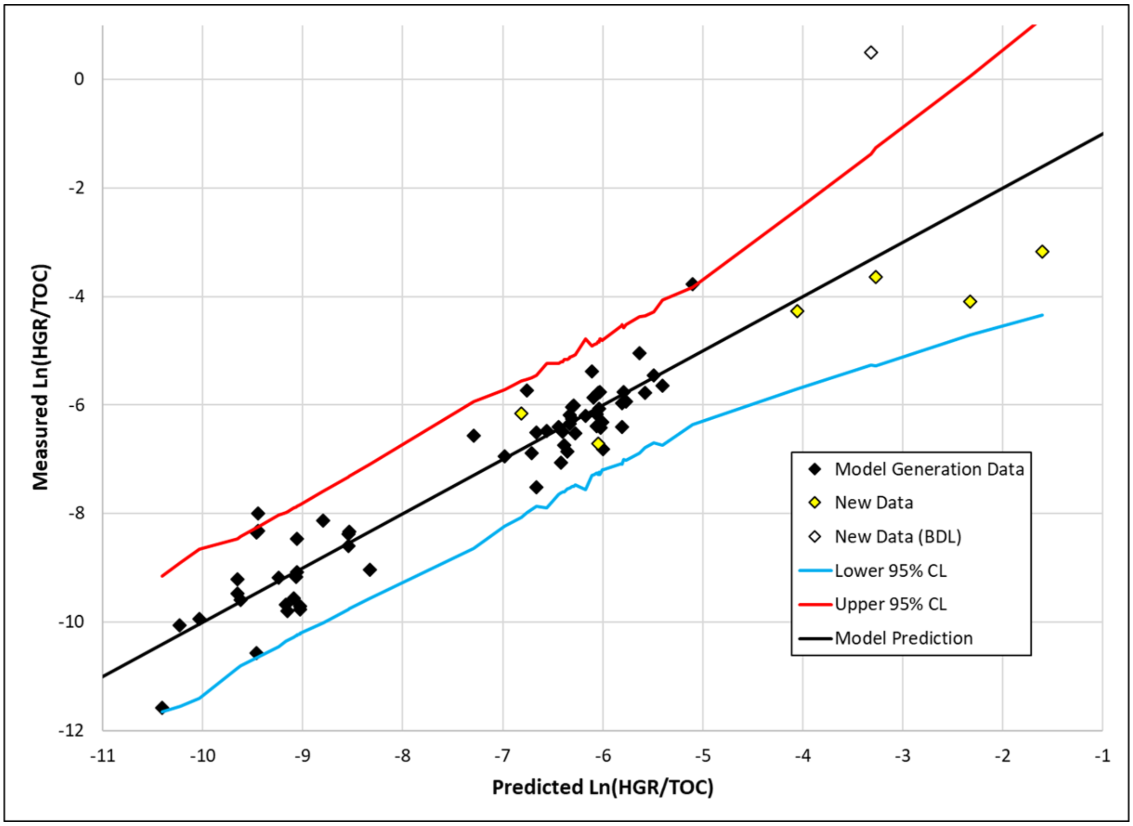

Figure 2. Model Evaluation of Xiameter™ AFE-1010 HGR Data.

As is shown in Figure 2, the new data points taken with Xiameter™ AFE-1010 at elevated temperature and hydroxide agree nicely with the kinetic model predicted and described in previous testing. Of the seven experiments performed, all measurable HGRs fall within the 95% confidence limit for a single prediction, and five of those six measurable HGRs fall below the kinetic model prediction. It should be noted that the single point plotted above the upper 95% confidence limit in Figure 2 has been determined as a "BDL" measurement. This test exhibited a relatively large detection limit due to 1) a greatly increased presence of hydrogen in the Xiameter-free and Xiameter-added tests (likely from the high TOC impurities in sodium aluminate (only available as Technical Grade, 85%), the source of aluminum in this test), and 2) an elevated purge rate required to control the flammability of methane being simultaneously produced from the thermolysis of Xiameter™ AFE-1010. Given that this point is reported as a "BDL" measurement, it does not provide evidence of failure to fit within the kinetic model derived in earlier testing.

The results suggest that the kinetic behavior expressed in the Global TOC Thermolytic HGR expression (Eq. 2) may be extrapolated to temperatures as high as 170 °C and hydroxide concentrations as high as 23 mol L^{-1}. This supports the use of the Global TOC Thermolytic HGR expression to predict non-glycolate thermolysis in the evaporator system.

Methane Generation Observations from Xiameter™ AFE-1010 Testing

Significant evolution of methane was observed during HGR testing with Xiameter™ AFE-1010. No such observation was made with glycolate or in the absence of added organics, suggesting that this phenomenon is unique to testing with chemicals similar to those found in Xiameter™ AFE-1010. While the GCs used during these experiments were calibrated for methane measurement, the experimental setup used for testing was optimized for hydrogen measurement at the cost of suboptimal methane measurements. Therefore, the observations and measurements presented here should be viewed as preliminary; testing with an optimized apparatus would be expected to yield values with a higher degree of precision.

TABLE IV lists the conditions and observed methane generation rates (MGRs) from the tests performed with Xiameter™ AFE-1010. The respective HGRs and the observed CH_4:H_2 ratio is reported as well for convenient review.

TABLE IV. Methane Generation Results from Testing with Xiameter™ AFE-1010.

Run Name	Temp (°C)	[OH] (M)	[TOC] (M)	HGR (mol s^{-1} m^{-3})	MGR (mol s^{-1} m^{-3})	CH_4:H_2
HTH-1	138.8	1.20E+01	4.25E-04	< 5.97E-05	1.70E-05	>0.3:1
HTH-2	107.5	1.07E+00	4.51E-04	8.09E-08	1.04E-07	1:1
HTH-3	105.2	2.63E+00	4.21E-04	4.33E-08	7.93E-08	2:1
HTH-4	142.7	1.04E+01	5.10E-04	1.14E-06	8.86E-05	78:1
HTH-5	156.6	1.79E+01	4.51E-04	6.40E-07	2.31E-05	36:1
HTH-6	125	9.39E+00	4.76E-04	5.64E-07	3.29E-06	6:1
HBP	170.5	2.26E+01	5.89E-04	2.11E-06	9.08E-05	43:1

Almost universally, the MGRs observed during testing with Xiameter™ AFE-1010 met or exceeded the HGRs observed, with the single exception (HTH-1) yielding an undetermined ratio of >0.3:1 for CH_4:H_2. This suggests that methane is more easily formed from Xiameter™ AFE-1010 than hydrogen at the conditions employed during this testing (i.e., temperatures greater than 100 °C).

A preliminary model for methane formation may be derived from the data given in TABLE IV. This model is displayed graphically in Figure 3.

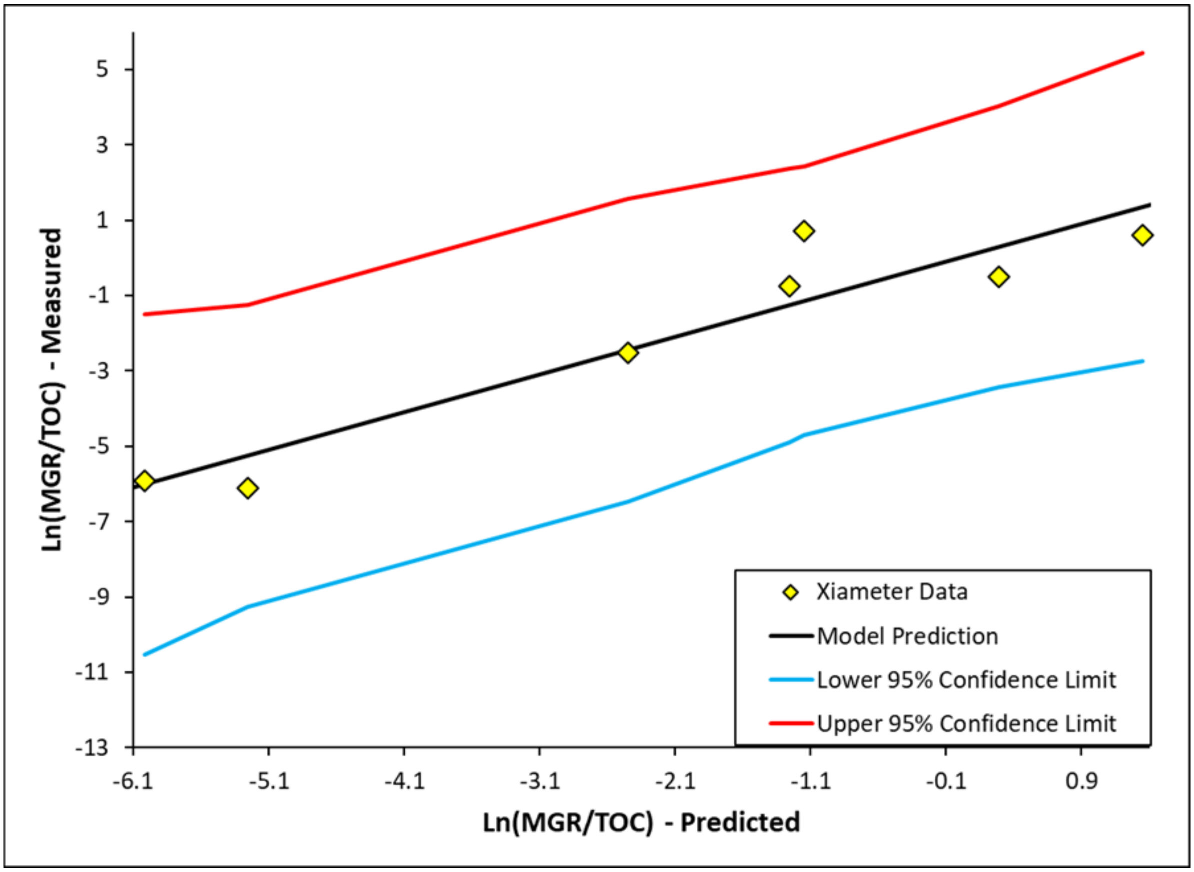

Figure 3. Preliminary Model Fit for Methane Generation from Xiameter^{TM} AFE-1010 Testing.

The model shown in Figure 3 is derived using JMP 14 to fit the data in TABLE IV. The derived model is given in Equation 3.

$$MGR_{Xia} = 1.35 \times 10^{10}[OH]^{1.046}[C_{Xia}]e^{\frac{-93,100}{RT}} \qquad \text{(Eq. 3)}$$

where,

MGR_{Xia} is the methane production rate from the thermolysis of Xiameter in mol s^{-1} m^{-3},

$[OH]$ is the concentration of hydroxide in mol L^{-1},

$[C_{XIA}]$ is the concentration of carbon from Xiameter in mol L^{-1},

R is the ideal gas constant, 8.314 J mol^{-1} K^{-1}, and

T is the temperature in K.

The model derived using JMP suggests a positive influence of hydroxide concentration on methane generation. This dependency is similar to the hydroxide influence observed on hydrogen generation.

It is known that polydimethylsiloxane (PDMS) is the antifoaming agent in Xiameter™ AFE-1010. Furthermore, oligomers of PDMS (such as octamethylcyclotetrasiloxane, or OMCTS) are known to exist in trace amounts in Xiameter™ AFE-1010. Methylsiloxanes (such as PDMS and OMCTS) have been known to produce methane at elevated temperatures in the presence of hydroxide and water.[6] Given these observations, a simple hydroxide-catalyzed hydrolytic mechanism may be proposed for the formation of methane from methylsiloxanes (such as those found in Xiameter™ AFE-1010). This mechanism is displayed in Figure 4.

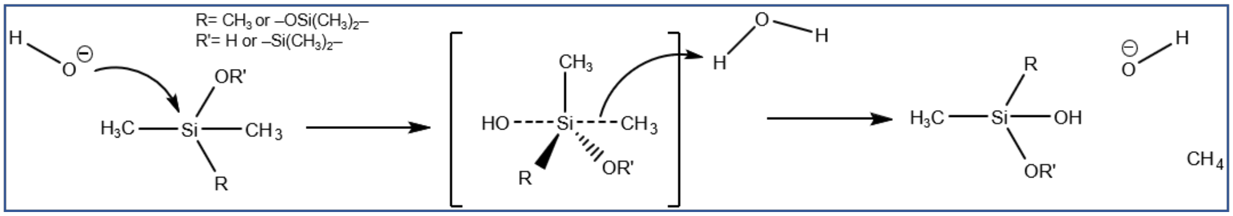

Figure 4. Proposed Mechanism of Methane Formation from Methylsiloxanes.

CONCLUSION

The range for both the Glycolate Thermolytic HGR expression and the Global TOC Thermolytic HGR expression, used to predict thermolytic HGRs, have been expanded to include temperatures as high as 170 °C and hydroxide concentrations as high as 23M. Methane was observed from tests with Xiameter at production rates higher than those observed for hydrogen. A preliminary model suggests that increasing hydroxide and increasing temperature causes an increase in MGR from Xiameter.

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