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STEAM REFORMING OF DOE COMPLEX WASTE SIMULANTS

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ABSTRACT

Sandia National Laboratories has worked with Synthetica Technologies and Manufacturing and Technology Conversion International (MTCI) to demonstrate the applicability of their commercial steam reforming technologies for treating DOE low-level mixed wastes. Previously, Synthetica successfully demonstrated destruction of a Sandia formulated lab trash simulant. During November, 1994 Synthetica did not adequately process the aqueous halogenated organic liquid mixed waste simulant (MWTP-2110) formulated by the DOE Mixed Waste Integrated Program (MWIP). Testing at MTCI is ongoing and initial results appear to be favorable. Approximately 200 lbs each of the MWIP aqueous halogenated organic liquids (MWTP-2110), and absorbed aqueous and organic liquids (MWTP-3113/3114) simulants have been processed. At 1650 °F, destruction efficiencies of greater than 99% were obtained for tetrachloroethylene, toluene, and 1,2 dichlorobenzene. Product gases consisted primarily of H_2, CO_2, CO, and CH_4 and had higher heating values of up to 355 BTU/SCF. Conclusions concerning the suitability of the MTCI process for treating DOE mixed wastes will be drawn upon the completion of testing.

INTRODUCTION

Steam reforming is a process of reacting organic materials with high temperature steam to produce CO, CO_2, and H_2. Halocarbons also produce mineral acids (e.g., HCl). Traditionally steam reforming has been utilized as a process for producing molecular hydrogen from hydrocarbons.[1] More recently steam reforming has been developed as a non-oxidative alternative for waste destruction.[2] In the steam reforming environment, products of incomplete combustion (PICs) commonly seen in oxidizing environments such as polychlorinated dioxins and furans are not produced. Furthermore, by operating with an excess of steam, the formation of thermodynamically reformed products such as polynuclear aromatics may be greatly suppressed.

Sandia National Laboratories has worked with Synthetica Technologies and Manufacturing and Technology Conversion International (MTCI), two suppliers of steam reforming technology, to demonstrate and extend the applicability of steam reforming to DOE complex wastes. Synthetica markets a steam reforming apparatus that employs a two step process for waste destruction, gasification in a feed device at temperatures up to 1100 °F followed by destruction in an electrically heated high temperature reactor (2100 °F) known as a detoxifier. The MTCI single step process, is an intermediate temperature (1600 °F) fluidized bed that is heated by pulse combustion. The pulse combustor results in highly turbulent combustion mixing that significantly enhances heat transfer. The combustion gases do not mix with the feedstock or product gases.

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Therefore, both technologies destroy wastes in an oxygen free environment, and result in a hydrogen rich product gas.

Arrangements were made for each company to demonstrate their technology on mixed waste simulants formulated by the DOE Mixed Waste Integrated Program (MWIP).[3] The simulants that were tested include aqueous halogenated organic liquids (MWTP-2110), and absorbed aqueous and organic liquids (MWTP-3113/3114). The simulant compositions as employed in these tests are outlined in Table I. The formulations in Table I may differ slightly from other formulations as they were taken from a draft document. Testing was to be carried out in duplicate with 200 lbs of simulant being treated in each test. Metrics included characterization of the effluent gas and residual matter including the working fluid (condensed water).

Table I. Formulations of the Low-Level Mixed Waste Surrogates

Bulk Ingredients	**MWTP-2110** wt %[a]	**MWTP-3113/2110** wt%
Activated Carbon	5	5
Cation Exchange Resin	5	5
Water	10	19
Toluene	10	--
Tetrachloroethylene	10[b]	--
Mineral Oil	10	--
Ethylene Glycol	10	10
Perlite (SiO_2)	--	25
Vermiculite	19[c]	25
RCRA Metals		
CrO_3	0.1	0.1
$Ni(NO_3)_2*6H_2O$	0.1	0.1
$Pb(NO_3)_2$	0.1	0.1
$Cd(NO_3)_2*4H_2O$	0.1	0.1
RCRA Organics		
Naphthalene ($C_{10}H_8$)	5	5
1,2-Dichlorobenzene ($C_6H_4C_{12}$)	10[d]	5
Radionuclide Surrogate		
$CeCl_3$	0.3	0.3
CsCl	0.3	0.3

[a] The draft formulation of MWTP-2110 totaled 95%. Recipe was scaled to 100% for MTCI tests. For Synthetica tests activated carbon was increased to 10%.

[b] Reduced to 0.5% for Synthetica test. Difference made up with methanol.

[c] Reduced by approximately 40% for Synthetica test.

[d] Reduced to 0.5% for Synthetica test. Difference made up with toluene.

SYNTHETICA TESTS

In previous tests conducted using Synthetica's drum feed evaporator and detoxifier on a Sandia devised simulant, mass reductions of about 20:1 and volume reductions of greater than 150:1 were demonstrated.[4] Also, a simple mass balance verified the steam reforming chemistry (consumption of water and waste). The simulant chosen for these tests represented a week's worth of lab-trash generated in the SNL hot cell and consisted primarily of shredded solid carbonaceous material such as lab coats, paper towels, and plastic with about 5% by weight organic liquids. Despite a noticeable in-leakage of air, the exhaust gas was found to be well enough characterized and to contain low enough levels of pollutants that permits could be sought from local regulatory agencies. Therefore the conclusion of the tests was that steam reforming could be a practical alternative for SNL to pursue for treating its own mixed and low-level radioactive waste. Similar results were anticipated for other wastes.

The MWIP aqueous halogenated organic liquids simulant (MWTP-2110) proved to be more challenging to the Synthetica system. The amount of tetrachloroethylene and dichlorobenzene in the waste simulant was reduced as indicated in Table I in order to accommodate limitations for chlorocarbons in the detoxifier. Also, the amount of the inert vermiculite was scaled down by about 40% so that the entire volume of waste simulant could fit into a single drum. The resulting formulation with its high levels of volatile organics could not be successfully processed with the equipment currently available at Synthetica. During the attempted processing of this waste simulant, several problems were encountered.

A significant leakage of air into the system occurred as the reactor temperatures increased during startup. This problem was initially diagnosed as a ruptured burst disk. Replacement of the disk and subsequent startup of the system and commencement of the test ensued. Approximately two hours and thirty minutes into the test run, an abnormally high pressure drop across the absorber bed was observed. At the same time symptoms of a plugged condenser were observed by test personnel. As a result of these problems, the test director terminated the run to protect the equipment. Investigations conducted after the system had cooled revealed the absorber bed was plugged with soot, while the condenser was completely plugged by large crystals of what was believed to be naphthalene, and a second black tar-like substance.

Investigation by Synthetica personnel into possible causes for the plugged absorber bed revealed a cracked reactor bed which allowed leakage of air into the system. Other possible explanations for the plugged bed include inadequate steam and design limitations of the current system for processing waste containing large amounts of volatile organics. Toluene and naphthalene comprised 19.5 and 5 percent of the MWTP-2110 waste simulant respectively.

Two weeks after the attempted test run, Synthetica and Sandia mutually agreed to terminate further test efforts. Sandia's decision was made based on several factors including system repair time, contractual period of performance, and optimism on successful completion of other mixed-waste tests given the simulant recipes and current equipment.

Synthetica has designed new system components that when fabricated, should improve their ability to process wastes such as those proposed in these tests.

MTCI TESTS

Testing of mixed waste simulants is currently underway at MTCI. Currently, one test has been performed with each of the two feedstocks shown in Table I. Duplicate tests have yet to be performed. During the tests, the composition of the effluent gas (CO, CO_2, H_2, O_2, N_2, CH_4, C_2H_4, C_2H_6, C_3H_6, and H_2S) was measured by gas chromotography on a five minute interval. Several samples were also collected by an independent laboratory for GC/MS analysis to provide confirmation of the results. The flue gas from the pulse combustors was also periodically analyzed by a combustion analyzer. At least four solids samples were withdrawn from the reactor during each test to help evaluate mass and volume reduction and the fate of the RCRA metals and radionuclide surrogates in the simulants. At the conclusion of each test, the entire volume of bed material was removed to assist in this analysis. Samples of condensate were also taken. Temperatures were recorded at 1 minute intervals, flow rates were recorded at 20 minute intervals, and the condensate collected was measured at 10 minute intervals. During the duplicate tests, gas sampling will be performed to allow for the measurement of dioxins and furans via EPA procedure 23.

In the first test that was performed at MTCI, 195 lbs of the 3113/3114 simulant was processed at 1500-1550 °F. During the second test, 198 lbs of the 2110 simulant was processed at 1600-1650 °F. During each of these tests, silica sand was used as the bed material. Due to the large number of samples collected for analysis many of the results from the two tests are currently unavailable. However the results that are available appear to be favorable.

Table II. Destruction Efficiencies in MTCI Reformer

Component	Temperature (°F)	Feed %	Destruction Efficiency
Tetrachloroethylene	1650	10	>99.999
Toluene	1650	10	99.211
1,2 Dichlorobenzene	1650	10	99.731
1,2 Dichlorobenzene	1550	5	98.046[a]
			98.915
Naphthalene	1550	5	99.844

[a] Samples were analyzed at two different laboratories

Table II summarizes the destruction efficiencies obtained for many of the key organic components present in the tests. At 1550 °F, the destruction efficiency of 1,2 dichlorobenzene exceeded 98% while that of naphthalene exceeded 99%. These compounds are recognized as being very thermally stable and therefore represent something of a worst case for the system. Elevating the temperature to 1650 °F in the second test resulted in raising the destruction efficiency of 1,2

dichlorobenzene to greater than 99%. MTCI is currently considering the addition of a second stage, higher temperature reactor to their system in order to achieve even greater destruction efficiencies.

The composition of the reformer effluent gas for each test is summarized in Table III. A complete mass balance has not yet been performed. However, the primary gaseous products were H_2, CO_2, CO, and CH_4. The large quantity of CO_2 is indicative of water/gas shift chemistry rather than oxidative combustion. The H_2S shown in Table III probably originates from the ion exchange resin in the simulants. The HCl formed from the chlorocarbons was collected in the scrubber downstream of the reformer. Also included in Table III are heating values for the product gas. The heating value of the gas can be utilized in the MTCI system by feeding the gas to the pulse combustion system.

Table III. Typical MTCI Reformer Product Gas Analysis

	MWTP-2110	MWTP-3113/3114
Avg. Reformer Temperature (°F)	1646	1575
Component (% V/V)		
H_2	53.25	52.49
CH_4	7.88	6.63
CO	21.75	20.44
CO_2	14.87	19.24
C_2H_6	1.78	0.45
C_2H_4	0.14	0.00
H_2S	0.33	0.74
Higher Heating Value (BTU/SCF)	355	310

CONCLUSIONS

The equipment available at Synthetica at the time of these tests was inadequate to process the aqueous halogenated organic liquid mixed waste simulant (MWTP-2110). Based on this outcome and other considerations further testing was not attempted. Synthetica is in the process of designing new system components that when fabricated, should improve their ability to process wastes such as those proposed in these tests.

Testing at MTCI has not been completed. However, initial results for the MWIP aqueous halogenated organic liquids (MWTP-2110) and absorbed aqueous and organic liquids (MWTP-3113/3114) simulants appear to be favorable. At 1650 °F, destruction efficiencies of greater than 99% were obtained for tetrachloroethylene, toluene, and 1,2 dichlorobenzene. Product gases consisted primarily of H_2, CO_2, CO, and CH_4 and had higher heating values of up to 355 BTU/SCF. A more complete evaluation of the suitability of the MTCI process for treating DOE mixed wastes will be possible when the remaining tests are complete and the data is analyzed. Complete mass balances including the fate of the metals and radionuclide surrogates will be available.

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