INDUCTION-COUPLED PLASMA ENERGY RECYCLE AND CONVERSION (PERC™) OF MILITARY WASTE STREAMS

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ABSTRACT

Induction-coupled plasma (ICP) reactors operating at power levels in excess of 400 kW can be used to economically convert energetic military wastes - explosives, rocket fuels and chemical agents - into non-hazardous forms. A 15 kW ICP system has been developed and used to demonstrate the pyrolysis of hazardous military wastes. Use of induction-coupled plasmas as gas heaters offers the potential of safe and economic processing of these materials. Results from the 15 kW demonstration-scale system, processing slurries of "energetic" nitrocellulose/nitroglycerine propellants; ethylene diamine, a surrogate for the liquid rocket fuel unsymmetrical dimethyl hydrazine (UDMH); Malathion, a surrogate for the chemical agent "VX", will be presented. The design parameters and operational characteristics of the reactor system, chemical analyses of the conversion products and conversion/destruction efficiencies will also be reported.

1. INTRODUCTION

A 15 kW prototype plasma reactor was developed and used to pyrolyze "energetic" military wastes - propellants, liquid rocket fuels and chemical agents - using induction-coupled plasma (ICP) [1] technology. The process, known as PERC™ (Plasma Energy Recycle and Conversion) has demonstrated the feasibility of a plasma process for converting hazardous military wastes to potentially useful materials, such as "syngas," a mixture of CO and H_2, usable either as a fuel, or a precursor for chemical synthesis.

2. WASTE AND PLASMA PROCESSES

2.1 Military Waste Streams

Large stockpiles of hazardous military waste worldwide are now presenting environmental hazards, especially in the former Soviet Union. Materials such as nitrocellulose gun propellants, liquid and solid rocket fuels, high explosives and chemical agents are all strong candidates for destruction due to aging and deterioration. The commercial demil market is estimated to be ~$5 billion. Open burning, detonation and incineration are not commercially viable since no useful products are formed and the reaction products are environmentally unacceptable. Conversion to "syngas" eliminates pollution and could augment the power generation capabilities in countries like the Ukraine and Belarus which depend on aging nuclear reactors and high sulfur coal.

2.2 Plasma Technology for Waste Destruction

Thermal plasma processes have been used to destroy various waste streams in recent years as alternatives to incineration or chemical neutralization. Incineration has environmental disadvantages, including production of ash, requiring subsequent disposal, and the generation and release of NO_x and dioxin. Chemical neutralization is expensive and generates streams of material requiring disposal. Thermal plasmas can be operated over a wide range of conditions, such that processing can be carried out under reducing, oxidizing or neutral atmospheres, and enable heat input to be controlled independently of the waste stream, which cannot be readily achieved in combustion systems. The very high temperatures generated by thermal plasmas (>10,000 K) also offers the potential for rapid kinetics and improved destruction efficiencies over non-plasma processes.

Plasma/waste applications to date have included PCB destruction [2, 3], nuclear waste vitrification [4, 5], electric arc furnace dust reprocessing/smelting [6,7] and medical waste destruction [8]. Widespread commercial use of plasma technology for processing waste materials has, with the exception of smelting for the reclamation of metals, been limited by economic rather than technical considerations, specifically low efficiencies and high electrical power and process gas costs.

3. PERC TECHNOLOGY

3.1 Plasma Energy Recycle and Conversion (PERC™) System

The prototype PERC™ system, shown schematically in Fig. 1, comprised the following major components:

- High frequency (RF) plasma power supply
- Refractory lined primary reactor
- Insulated metal alloy tubular secondary reactor
- Instrumentation and sampling ports
- Induction-coupled plasma (ICP) torch
- Liquid/slurry feed injection system
- Off-gas treatment system

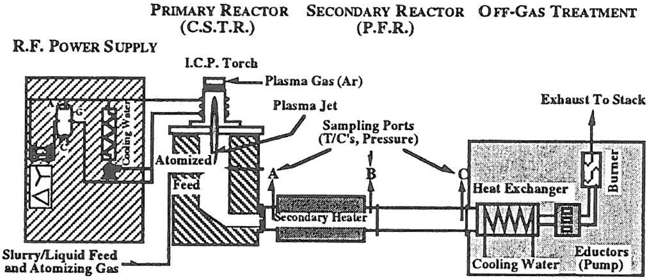

Figure 1. Schematic of PERC™ System.

3.1.1 Plasma Torch and Power Supply

An ICP plasma system was selected owing to the absence of refractory metal and/or copper electrodes. Induction-coupled plasma heaters offer several advantages over DC systems: continuous operation due to the absence of electrode erosion; no process stream contamination by electrode material; no moving parts; and the ability to operate with a wider range of plasma gases, including oxygen. The continuous operation capability of ICP torches is an important consideration for scale-up to production size.

The plasma power supply consisted of a high voltage DC rectifier/triode vacuum tube oscillator, linked to a "tank" circuit *via* a coaxial transmission line. The coil of the torch was connected across the output of the tank circuit to form a resonant circuit "tuned" to couple maximum power into the plasma. Power output was ~25 kW (plate power) with maximum power into the plasma limited to ~15 kW due to losses in the vacuum tube oscillator, tank circuit and torch cooling water. Typical PERC™ torch operating parameters are listed in Table 1.

Table 1. Typical PERC™ ICP Operating Parameters.

Torch	Tafa Model 66
Coil	76 mm (3") Ø, 4 Turns
Plate Power	~25 kW
Plate Voltage	9 kV
Plate Current	2.5 A
Frequency	2.5 - 5 MHz (tunable)
Plasma Forming Gas	Ar
Plasma Gas Flow	18-140 slm (40-300 scfh)
Cooling Water	~60 slm @ 0.275 MPa (13 GPM @ 40 psi)

3.1.2 Primary and Secondary Reactors

The reactor system (Fig. 1) consisted of two vessels in series. Hot argon from the ICP torch supplied heat to a primary reactor vessel where pyrolysis of injected organic waste materials was initiated. Reactants were then directed through an orifice into the secondary reactor where pyrolysis was completed.

The primary reactor, designed as a continuous stirred tank reactor (CSTR) provided both turbulent mixing between plasma heated gas and injected feed and sufficient residence time (~6 s) to initiate chemical reactions. The tubular metal secondary reactor, designed as a plug-flow reactor (PFR), provided additional residence time (~10 s) for completion of pyrolysis. Additional heat input was provided to the secondary reactor by a 6 kW, resistance heated, tube furnace operated at up to 1100 °C.

Table 2. Reactor Design Summary.

Parameter	Primary Reactor	Secondary Reactor
Design	CSTR	PFR
Heat Source	15 kW, ICP	6 kW, Resistance Furnace
Insulation	Refractory (int)	50 mm Fiber Blanket (ext)
Length	460 mm (internal)	2 x 2 m sections
Diameter	180 mm (internal)	76 mm
Operating Pressure	-50 mm water column	-50 mm water column
Temperature	650-1100 °C	~1000 °C
Residence Time	~6 s	~10 s

3.1.3 Off-Gas System

Gaseous reaction products were quenched by a water-cooled heat exchanger at the exit of the secondary reactor. The primary reactor was maintained at sub-atmospheric pressure (-50 mm H_2O column), using air-driven eductors. Gas flow from the reactor was thus diluted and further cooled by additional air supplied by the eductors. The resulting process gas stream was then directed into a thermal oxidizer to ensure that no flammable or explosive gases were discharged to the atmosphere.

3.1.4 Feed System

Liquid and slurry feeds were atomized into the primary reactor ~300 mm downstream from the plasma region using Ar as the atomizing gas. Feeds with suspended solids, such as energetics (double-base propellant), were homogenized using an air-driven microfluidizer prior to injection.

3.2 Experimental Methodology

The plasma was ignited and the reactor brought up to operating temperature (700-800 °C) over a 2-3 hr preheating period. Once the desired primary reactor temperature was attained the plasma gas flow rate was reduced to 50 slm (105 scfh) and the system allowed to reach thermal equilibrium. A "baseline" gas sample was taken when the system reached equilibrium conditions running on either pure argon, or feeding water, to enable in-leaks of air to be quantified. Feed was then introduced at flow rates of 10.8 and 18.2 ml/min and atomized using 24 and 70 slm (50 and 150 scfh) of Ar respectively to vary the reactor gas residence time. Temperatures and chemical species concentration were monitored to ensure that both thermal and chemical equilibrium were attained before sampling commenced typically ~15 minutes after equilibrium was reached.

Experiments were carried out to investigate the feasibility of the PERC™ process for converting three materials - energetics, liquid rocket fuel and chemical agents - into CO and H_2. An emulsion of kerosene, water and nitrocellulose/nitroglycerine double-base propellant (23.6%/70.7%/2.88%/2.00% respectively) plus a surfactant (sorbitan monolaurate) was fed into the primary reactor and gas samples collected under steady state conditions (650-700 °C). Ethylene-diamine (E-D) was used as a surrogate for the liquid rocket fuel UDMH owing to safety considerations. The molecular structure (Eqn (2)) and bond energies of E-D are similar to those of UDMH. The feed, formulated to achieve complete conversion of all the C and H in the feed to CO and H_2 gas, was a 62% ethylene diamine/38% water mixture. The pesticide Malathion was used as a surrogate for the chemical agent "VX" and for this material experiments were carried out to determine destruction efficiency (DRE). A stoichiometric solution of Malathion and water was fed into the reactor at 10.8 ml/min.

3.3 Instrumentation, Sampling and Analysis

Thermocouple sensors and gas sampling ports at key points in the secondary reactor (Fig. 1) were used to monitor and record the temperature profile along the reactor and withdraw gas samples for analysis. The temperature inside the primary reactor was also monitored using a computerized data acquisition system. In most experiments samples of reaction products were withdrawn for analysis off-line, however, in some cases samples from the exit of the primary reactor were analyzed on-line using a residual gas analyzer (RGA), gas chromatograph (GC) and FTIR to identify the various species present.

Product gas samples were quenched to ~60 °C, withdrawn into 4 l sample bags at Ports A, B and C (Fig. 1) and analyzed by RGA, NO_x meter, Gas Chromatograph and FTIR techniques.

4. RESULTS AND DISCUSSION

4.1 Energetics

Analysis of gas samples from Port A (Table 3) showed that feed was converted primarily to CO and H_2 together with some CO_2 and CH_4 and trace amounts of C_2H_4 and C_2H_2. The presence of CO_2 and NO_x was due to small air leaks into the reactor. NO_x levels were ~200 ppm running on pure Ar, and 300-400 ppm when feeding energetics. This increase was believed to be due to breakdown of the feed material, providing a source of N_2 which reacted with O_2 from air leaks to form NO_x.

4.2 UDMH/Ethylene-Diamine

Analysis of gas samples from Port A (Table 4) indicated that feed material was converted primarily to CO, H_2 and free N_2. No liquid water was collected during pyrolysis, indicating that all reactant water was consumed by reaction.

Low levels of NO_x (4-9 ppm) during pyrolysis of the ethylene diamine/water feed are believed to be due to the presence of H_2 in the reactor, which reduced NO to free N_2. This reaction is thermodynamically favorable at 800 °C with a Gibbs free energy change of -268 kJ/mol (-64 kCal/mol) of NO. The measured N_2:O_2 ratio was, at 5.72:1,

Table 3. Results: Gas Analysis, Port A - Argon and Energetics Feed.

	Experimental Conditions		
Species	Pure Ar	Energetics (Expt)	Energetics (Theory)
Ar	94.5%	89.4%	85.3%
CO	0.2%	1.2%	5.1%
CO_2	0.1%	0.6%	-
N_2	1.5%	2.0%	0.1%
NO_x	200 ppm	300 ppm	-
H_2	-	1.8%	9.5%
O_2	0.9%	0.4%	-
H_2O Vapor	0.2%	0.2%	-
CH_4	0.0%	0.2%	-
C_2H_4	0.0%	Trace	-
C_2H_2	0.0%	Trace	-
Total:	97.4%	95.8%	100.0%

Table 4. Results: Gas Analysis, Port A - Ar/Water and Ethylene Diamine Feeds.

	Experimental Conditions		
Species	Ar/Water	E-D Sol'n (Long RT)	E-D Sol'n (Short RT)
Ar	89.9%	70.8%	73.8%
CO	0.1%	6.9%	7.6%
CO_2	0.0%	0.1%	0.5%
N_2	5.5%	14.7%	10.3%
NO_x	142 ppm	4 ppm	N/A
H_2	0.2%	6.9%	7.2%
NH_3	-	3.5%	N/A
O_2	1.2%	3.1%	1.8%
CH_4	0.0%	0.6%	1.1%
C_2H_4	0.0%	0.6%	0.7%
Total:	96.9%	103.7%	103.0%

Note: Total gas mass balances are accurate to within 6%.

greater than the normal ratio for air (3.76:1), which supported this hypothesis. Higher than expected levels of free N_2 and O_2 were attributed to air ingress *via* leaks.

4.3 Chemical Agents/Malathion

Analysis of gas sampled from Port B is summarized in Table 5. Cooled off-gas from the secondary reactor was passed through a wet scrubber containing 1N NaOH. The pH of the scrubber solution decreased from an initial value of 14 to 10.8 during the 45 min. feeding period. Titration of the scrubber solution showed that 0.33 gm equivalent of NaOH was consumed by the product acid gases, believed to be HCl and H_2S. Analysis of the scrubber solution by EPA Test Method 505 [9] indicated a residual Malathion concentration in the scrubber solution of < 25 μgm/liter. Based on the total flow rate and mass balance, the amount of unreacted Malathion leaving the system was determined to be < 0.000001%. Assuming that no unreacted feed remained inside the reactor, this corresponded to a destruction efficiency (DRE) of 99.99999% ("7 nines").

Table 5. Results - Gas Analysis, Port B - Malathion/Water Feed.

Species	Malathion/Water
Ar	75.6%
CO	4.0%
CO_2	Trace
N_2	12.0%
NO_x	57 ppm
H_2	3.2%
H_2S	0.4%
O_2	3.3%
SO_x	0.0%
CH_4	0.1%
C_2H_4	0.0%
Total:	98.6%

5. Conclusions

The use of an induction coupled plasma heated reactor for the pyrolytic conversion of military wastes, or chemically similar surrogates, to potentially useful products such as CO and H_2 has been demonstrated. A 15 kW demonstration-scale PERC™ system has been developed and used to convert energetics, rocket fuel and chemical agents to simple molecules at conversion efficiencies in excess of 99%, with low NO_x, thus making PERC™ a viable alternative to incineration.

6. References

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