Disposal of highly toxic wastes by means of liquid propellant rocket engine technology

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Introduction

World wide, there exists a problem of the destruction of highly toxic wastes like PCB's, pesticides, dioxins, chemical warfare agents, etc. These substances create a growing mountain of problematic waste that has to be disposed of properly. At present these wastes are being stored at various locations all around the world, or are being burned in waste disposal plants. A good storage of these materials for prolonged times does not exist as waste compounds generally have corrosive properties that damage the storage containers and lead to leakage into the environment. Consequently, this results in environmental problems (e.g. pollution of ground- and surface water that has to serve as drinking water). Storage, hence, can only be a temporary measure.

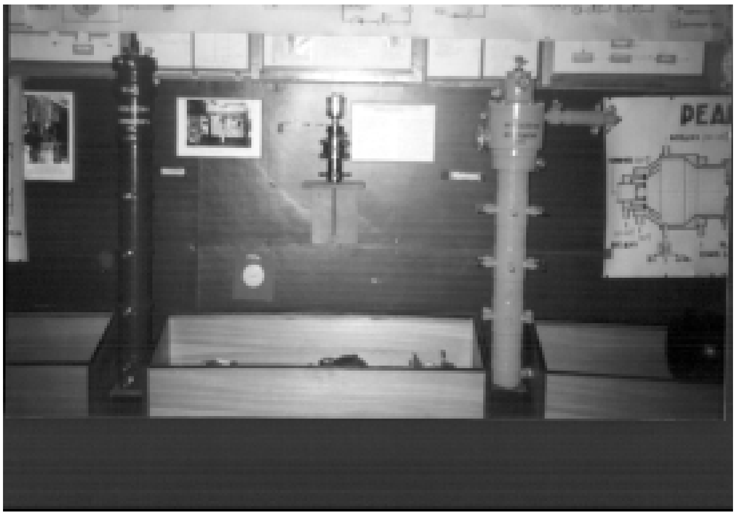

Figure 1. Examples of compact waste incinerators

A limited number of suitable waste disposal plants are available, for example in western countries, and the transport of highly toxic waste to these sites over long distances, poses serious safety risks. The technology that is the topic of this paper is very compact and could easily be implemented as part of a mobile facility. Other major parts of the mobile facility would be a flue gas cleaning and a fully automated control system.

In the former USSR, initial development has been carried out at the Topchiev Institute of Petrochemical Synthesis (TIPS) in Moscow (responsible party for this project) and the Baltic State Technical University (BSTU) in St. Petersburg, on a compact waste incinerator (CWI) based on liquid propellant rocket technology.

The technology is claimed to be capable of a very complete combustion of highly toxic waste, while unwanted secondary products like dioxins are not formed in the process. In the recent past, experiments carried out in Russia have shown the potential of the facility, although a western party did not yet independently verify this.

Conventional methods that are based on "common burning" (T < 1,500 °C) and plasma technology (T~10,000 K) do not satisfy two important boundary conditions:

- Complete combustion of the toxic waste,
- No formation of dioxins / furans, or other undesirable products in the process.

Not fulfilling one or both requirements demands for an additional clean-up of the exhaust products leading to higher operating cost. The operating conditions of the CWI are very suitable for the full combustion (conversion) of highly toxic wastes into products that can be conventionally handled, while no dioxins or other undesirable reaction products are formed in the process. The CWI cycle can hence treat toxic wastes and has emission boundary conditions that are expected to fulfil the most stringent requirements set by the environmental regulations. Another important aspect of the CWI is its compactness. The CWI cycle is more compact than for example a rotary kiln design, which is based on its operating principle quite bulky. The compact CWI is suitable for use in a mobile installation. A mobile installation could for example be composed of a number of containers that can be transported by conventional means, e.g. truck, train and ship. The operating cost is important for the full-scale engineering development of the mobile installation. To obtain an attractive system, the operating cost of the mobile installation should be below the cost of the packing, transport and proper disposal at a waste disposal facility in for example Europe. In this context it is important to note that the prices of waste disposal are decreasing due to the strong competition on the international waste market.

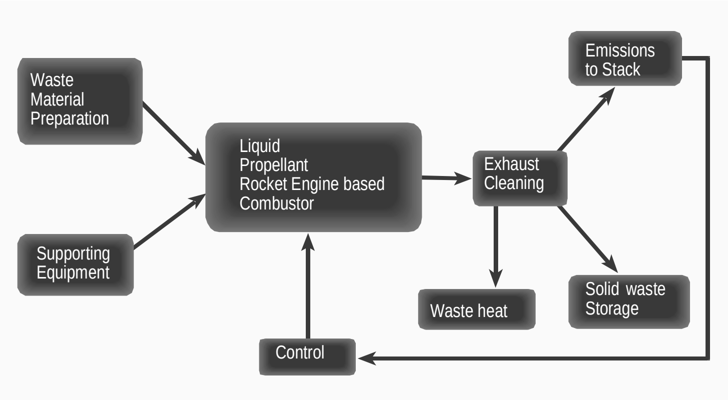

Figure 2. Overview of the installation

Available technology

The TNO - Prins Maurits Laboratory (PML) in close co-operation with the TIPS in Moscow, Russia has developed and verified a chemical reactor operating on liquid fuel and oxygen. The installation has completely (better than 0.999999) destroyed a number of highly toxic compounds that were introduced into the fuel flow, while other highly toxic substances like dioxins were not formed in the process. Numerous experiments and accurate analysis of the exhaust products support the reliability of the apparatus. The CWI incorporates special features of liquid rocket engines and is operated at elevated pressure and temperature; conditions that are ideal for the complete destruction of extremely toxic substances. With rocket technology, reliable operation at high combustion temperatures and pressures is state-of-the-art.

Configuring the waste disposal installation as a mobile facility allows for treatment at sites all over the world while preventing the dangers of transport.

Process description

An overview of the installation in which the liquid propellant rocket engine based chemical reactor is integrated is given in Figure 2. The toxic waste to be disposed of is supplied to the chemical reactor under suitable conditions (Input/Support equipment). After combustion, additional steps may be needed to clean the exhaust gases before releasing them into the atmosphere (Emission). These steps cannot be prevented as the toxic waste contains hazardous ingredients that have to be captured and cannot be emitted into the atmosphere. However special provisions can be made to introduce certain cleaning steps already within the reactor. Moreover, there may also be solid waste collection for certain types of waste and waste heat recovery in order to economise on the energy that is accompanying combustion.

Due to the extremely complete conversion of highly toxic substances to common combustion products, the need for additional cleaning for remnants of the toxic waste in order to meet the most stringent emission requirements set by the respective Environmental Protection Agency will be moderate.

Due to the compactness of the chemical reactor as compared to for example a rotary kiln oven: design, construction and operating cost will be relatively low; supporting the economical credibility of the concept; particularly for a mobile layout.

Concept validation

The concept validation has been carried out in Russia: at the TIPS in Moscow and at the BSTU in St. Petersburg. TIPS was responsible for the work carried out at BSTU.

Validation test plan

A validation test plan was prepared comprising the following major goals:

1. The main goal of test plan is to illustrate the possibilities of liquid rocket engine based technology for high efficiency destruction of chosen simulant toxic testing compounds (TC).
2. The validation study is based on similar work, which was carried out previously by the Russian co-partners and relied on experimental facilities that already existed. Modifications to installations were proposed to adjust the equipment to the particular testing conditions. Analytical methods were matched to the particular TC.
3. Two set-ups were employed for experiments: one in Moscow and the second in St. Petersburg. The facilities were different by: the means of ignition, the cooling system, etc. This will demonstrate independence of the CWI on the particular features of the installation. Answers to questions on what will be better for a pilot plant in terms of reliability/simplicity/cost, what materials will be preferable for manufacturing etc. were not part of the studyand should be considered in a following Engineering Manufacturing and Design phase.
4. The number of positive experiments (experiments which illustrate the efficiency of the technology) should be sufficient to substantiate the reliability of the results. Questions related to the dependency of the results on the fuel + TC composition, etc. should be solved during a following phase.
5. A TC used for the validation study should represent the major features of wastes like: elemental composition, energies of the bonds, etc. During the validation study phosphorous and chlorine contained compounds will be tested.
6. For the validation study, the TC should not be extremely hazardous in order to minimise health risks during the study.
7. The TC should be low cost and relatively easy to analyse. The same applies for the fuel.

Testing at BSTU in St. Petersburg and analysis of results

Tests were held during September - October 1999 in the laboratory of the department "Engines of Flying Apparatus" of the BSTU. The test compound (chlorobenzene) was dissolved in gasoline with a concentration of 10%. Oxygen was the oxidant. In Table 1, the process parameters that were valid for the tests are presented.

Table 1. Main parameters of the experiments

Parameter	Unit	1st run	2nd run
Mass flow rate of ethanol	g/s	3	3
Mass flow rate of disposed mixture (90 % of the gasoline + 10 % of chlorobenzene	g/s	3.3	3.3
Mass flow rate of oxygen (waste disposal)	g/s	20	20
Excess coefficient for the oxygen α		~1.8	~1.8
Pressure in the combustion chamber	Pa (*10^5)	3.5	3.5
Pressure in the chamber of quenching and sampling	Pa (*10^5)	2.7	2.7
Flow rate of the quenching liquid (water) 1st level 2nd level	g/s	24.7 13.3	24.7 13.3
Sampling time	S	120	420

The exhaust gases were sampled in the combustion chamber of the reactor. The results of the analyses are presented in Table 2. The presence of chlorine in the combustion process resulted in high temperature corrosion of the inner chamber walls. This problem was successfully solved.

Analysis showed that the degree of conversion achieved for chlorobenzene was 0.9999987 or better.

The formation of dioxin was assessed twice. The analysis showed that the amount of dioxin present in the effluent was below the measurement threshold of the equipment (< 0.2 ng/l), and dioxin was not detected.

Table 2. Combined results of chlorobenzene analysis

Number of protocol	Number sample	Date of sampling	Analysis results [mg/l][1]	Comments
Protocol ХБ-02	9A	18.09.99	1.80 ± 0.45 mg/l	1st bulb, 120 ml
	10A	21.09.99	0.70 ± 0.20 mg/l	Two fire experiments without replacing of the sampler. 1st bulb, 350 ml
	10Б	21.09.99	0.10 ± 0.03 mg/l	Analysed in the presence of Dutch visitors. 2nd bulb, 80 ml
	14A 14Б	30.09.99 30.09.99	1.09 ± 0.30 mg/l 0.25 ± 0.12 mg/l	1st bulb, 350 ml 2nd bulb, 3 ml
Protocol ХБ-03 Dioxin meas.	6	15.09.99	< 0.2 ng/l	20 % of chlorobenzene in gasoline. 1st bulb
	10A	21.09.99	< 0.2 ng/l	1st bulb (sampling in the presence of Dutch visitors)
Protocol ХБ-04	16-в	22.10.99	50 ± 12 μg/l	Experiment with water shield Quenching water
	16-б	22.10.99	28 ± 8 μg/l	Distillated water after several days exposition in next to the test room
	16-д	22.10.99	40 ± 9 μg/l	

1. Samples numbers 6 and 10A were dioxin analysis.

Testing at TIPS in Moscow and analysis of results

The facility at TIPS was specially prepared and fully adapted to the requirements of the validation study. The facility is remotely operated from a dedicated PC. The PC defines the operation cycle. This operation cycle can be smoothly varied from the PC control panel. The PC controls the operating of all valves and initiates the sampling for subsequent further analysis of the exhaust flow. The PC also controls measurements of some process parameters during the experiment. The screen of the PC shows the operating cycle of the process real time and the variation in time of the measured parameters (an example will be presented in the final report). During the experiments some changes were made in the facility, which were necessary in order to obtain a high degree of test compound decomposition.

An example of a PC control screen plot of a test is presented in Figure 3. The horizontal axis represents the time axis.

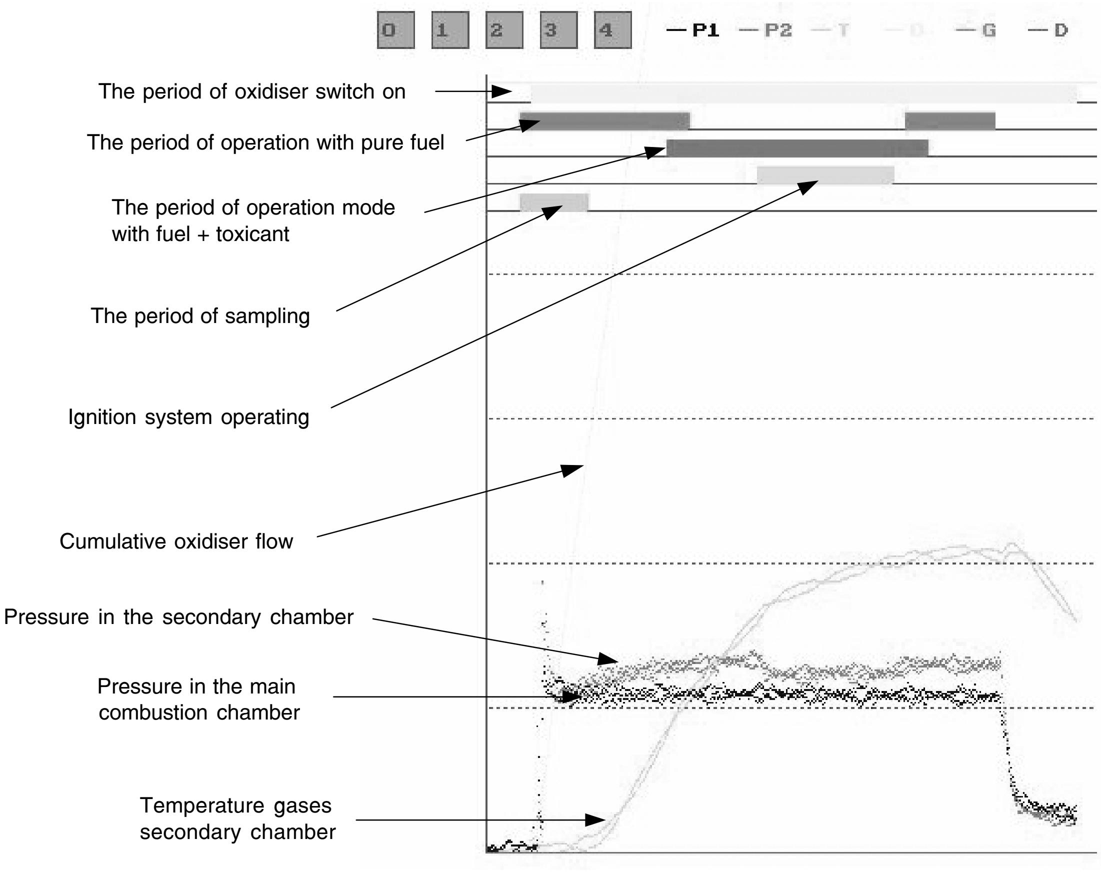

Figure 3. PC control screen plot of test

The gases were sampled automatically and were subsequently analysed at TIPS using a Gas Chromatograph. The calibration curve for triethylphosphate is presented in Figure 4.

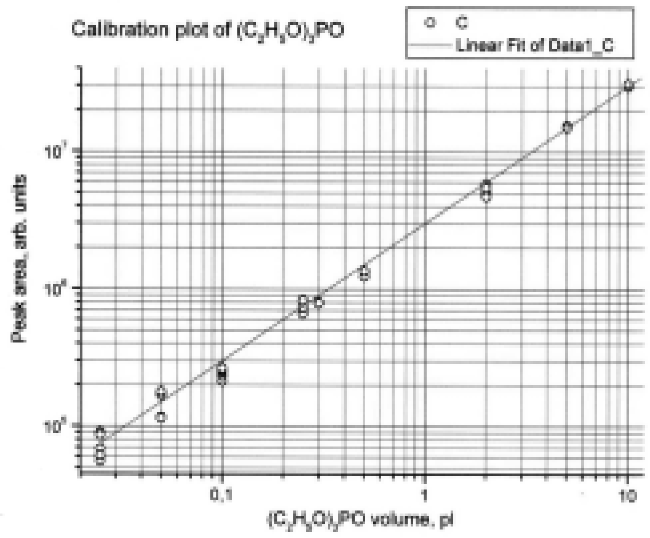

Figure 4. GC calibration curve for triethylphosphate.

A number of sample chromatograms are presented in Figures 5 and 6. The sampled gas from the reactor was dissolved in alcohol, but to be sure that all the triethylphosphate remnants were actually dissolved, the gas in the sampling vessel was also analysed. A result of such an analysis is given in Figure 5. The absence of any peaks shows that no TC was present in the gas phase. In Figure 6, a zero experiment (a); i.e. an experiment where only clean alcohol was injected to measure the zero response of the gas chromatograph, and three chromatograms (b - d) are presented. The left-hand peak is due to P_2O_5, a common reaction product for a phosphor compound, while the second peak is due to non-combusted triethylphosphate.

The procedure for determination of the degree of triethylphosphate decomposition was discussed with representatives of TNO-PML and AVR-Chemie and agreed to be sound. Results on triethylphosphate decomposition tests (10 % solution of triethylphosphate in the gasoline) together with the degrees of conversion are presented in Table 3.

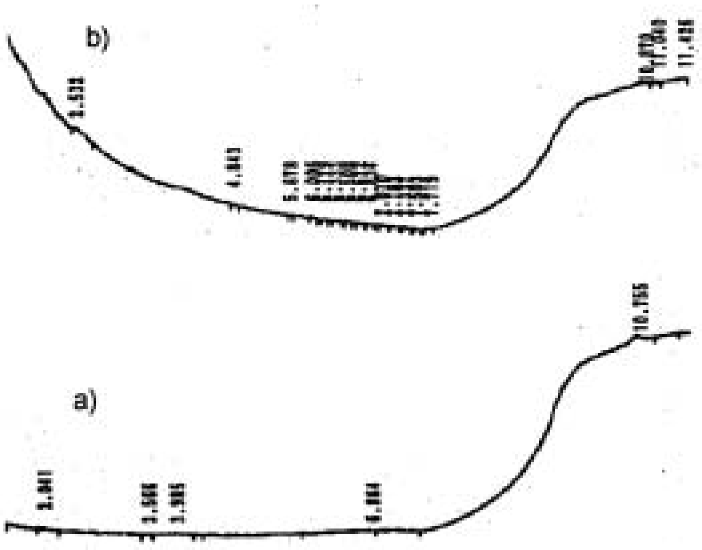

Figure 5. Analysis of gas phase, 24.09.99, NPD.

a) 300 µl Ar (blank experiment), $Rt_{(C2H5O)3PO}$ = 3,985 min, $S_{(C2H5O)3PO}$ - ;
b) 300 µl gas phase, $Rt_{(C2H5O)3PO}$ - , $S_{(C2H5O)3PO}$ -.

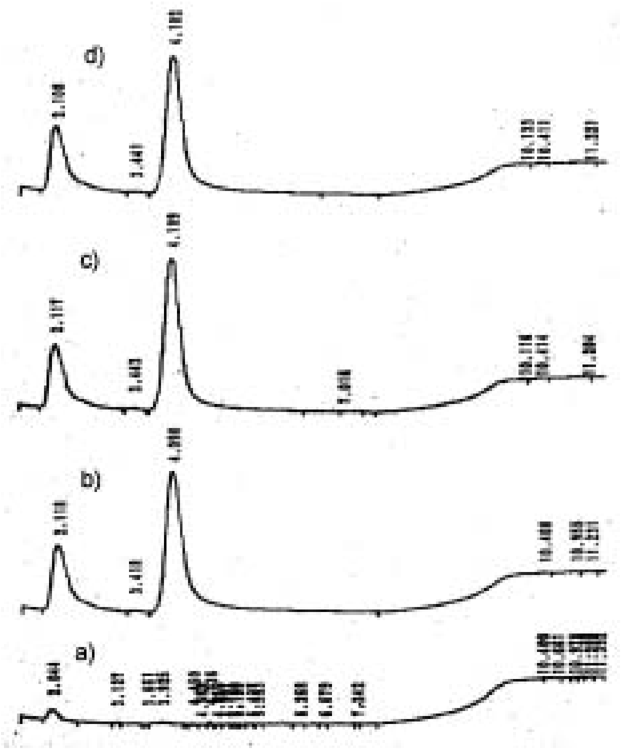

Figure 6. Analysis of liquid phase, 24.09.99, NPD, 1 ml liquid phase.

a) C_2H_5OH (blank experiment), $Rt_{(C2H5O)3PO}$=3,925min, $S_{(C2H5O)3PO}$=9846 (arb.units)
b) sample 1, $Rt_{(C2H5O)3PO}$=4,090min, $S_{(C2H5O)3PO}$=1284493, Y=0,99999991;
c) sample 2, $Rt_{(C2H5O)3PO}$=4,109min, $S_{(C2H5O)3PO}$=1257980, Y=0,99999991;
d) sample 3, $Rt_{(C2H5O)3PO}$=4,102min, $S_{(C2H5O)3PO}$=1176067, Y=0,99999991.

Table 3. Analysis of the mixture of triethylphosphate high conversion products (selected results)

No	Date	Date, Files	Conversion	Comment
1	06.09.99	TETPH1B	0.99999999	
4	17.09.99	TETPH9B	0.99999999	With TNO
6	23.09.99	TETPH11B	0.9999998	With TNO + AVR
7	24.09.99	TETPH12B	0.9999999	With TNO + AVR

Conclusions

At the Topchiev Institute of Petrochemical Synthesis (TIPS) in Moscow and the Baltic State Technical University (BSTU) in St. Petersburg, combustion experiments were carried out with two chemical reactors based on liquid propellant rocket engine technology. At TIPS and BSTU, respectively triethylphosphate and chlorobenzene (both representative compounds) were combusted.

The experimental results showed a high efficiency of the process. The degree of conversion was 0.99999999 - 0.999999, which is considerably better than the best rotary-kiln facility can produce (0.99999). During the validation study, it was discovered that the presence of hydrogen chloride (HCl) caused high temperature corrosion of the inner walls of the combustion chamber. This problem was successfully solved.

The combustion of chlorobenzene may result in the formation of dioxin in the process. This was for example a problem with rotary kiln and other oven types. The combustion products were analysed on dioxin. No measurable amount of dioxin was found.

The results show that a combustor bearing specific features of liquid rocket engine technology is a validated tool for the disposal of highly toxic waste, and has good potential when applied to the destruction of extremely toxic wastes like chemical warfare agents.