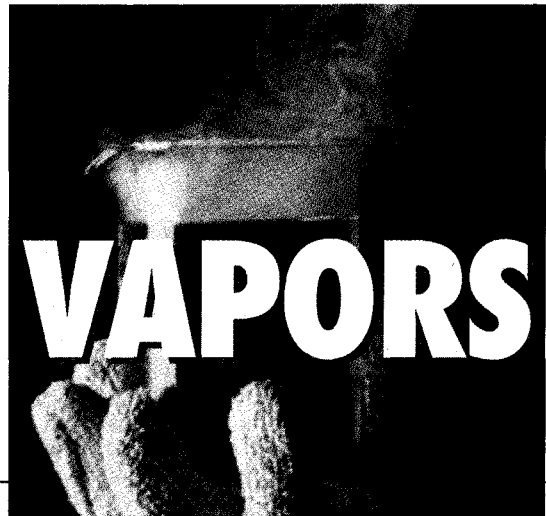


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CAPTURE ORGANIC VAPORS

Ann Christina Rasmuson, AGA AB



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Industrial operators worldwide expend considerable time and money to control the release of volatile organic compounds (VOCs) to the atmosphere. Such emissions react with nitrogen oxides to form photochemical oxidants in the troposphere. Resulting ground-level ozone or smog causes irreparable damage to crops and has been implicated in forest decline. Certain VOCs, particularly chlorinated compounds, are toxic to human health, and many VOCs are malodorous.

VOC emissions from a process are controlled in two fundamental ways: Operating conditions are changed to minimize the use of organic compounds. And, control equipment is installed to capture or destroy VOCs from the exhaust stream.

Process changes may involve switching to less harmful solvents, revising operating and maintenance practices, or installing upgraded versions of process equipment. Such modifications can drastically reduce VOC level. However, today's strict regulatory thresholds often call for the installation of end-of-pipe controls.

The most common VOC-control methods are adsorption, absorption, condensation and incineration. To choose the most applicable method for a particular application, the following parameters must be considered:

- Nature, number and concentration of VOCs in the effluent
- Exhaust stream flowrate and temperature
- Viability or desirability of VOC recovery
- Capital and operating costs
- Reliability of equipment
- Required operating time

It is not within the scope of this article to present detailed economic comparisons of the competing VOC-control techniques mentioned above. But the results from a recent study comparing adsorption, absorption and condensation are presented in Table 1.

Condensation is a well-known VOC-control technique, which is most often used for exhaust streams with relatively low flowrates or high vapor concentrations. To capture organics with relatively low volatility (such as toluene), conventional condensation systems typically use cooling water or refrigeration to attain temperatures to -40°C .

However, since most VOCs need substantially lower condensing temperatures, enhanced condensation is often required. Such systems typically rely on cryogenic coolants, or cascaded, refrigeration units based on chlorofluorocarbon chilling agents.

For years, cryogenic condensation with liquid nitrogen has been overlooked due to its perceived high operating costs. However, in certain cases, cryogenic condensation is competitive, both technically and economically, thanks in part to its relatively simple and straightforward operation, which requires very little operator attention.

Since the entire exhaust stream must be cooled to condense the offending vapors, the operating costs for a cryogenic condensation system may be prohibitive beyond a certain flowrate, or below a certain VOC concentration. As a general rule of thumb, cryogenic condensation is best suited for flowrates below roughly $1,000 \text{ Nm}^3/\text{h}$, or vapor concentrations above about $40 \text{ g}/\text{Nm}^3$. This limit is purely economic, however, because in principle nearly all VOCs can be condensed [1].

Versatile for mixed streams

VOC emissions are produced in a variety of industrial activities including the manufacture, storage, use or transportation of organic solvents, and operations such as evaporation, mixing and separation, cleaning and degreasing and coating. In many cases, solvent-laden exhaust streams have a wide range of pollutants, strongly varying concentrations and fluctuating flowrates.

While other VOC-control systems may be daunted by stream variability, fluctuations in exhaust content or flowrate are quickly and easily handled in a cryogenic condensation system by quick-response controls on liquid-nitrogen injection. Not only do such controls provide precise vapor-removal efficiencies, but they ensure that nitrogen is only consumed when demanded by the process. Consumption is directly proportional to the required cooling performance.

Condensation with liquid nitrogen is a straightforward heat exchange process, which is not VOC specific. Organic compounds amenable to treatment include alcohols, ketones, chlorinated hydrocarbons and a variety of VOC mixtures. The purity of the effluent stream is a function of condensing temperature. Typically, the only constraint on the VOC itself is the freezing point, which ideally should be below -30°C .

Principles of operation

As an organics-laden vapor stream is cooled, the entrained compounds start to condense when their saturation temperature has been reached. At a given temperature, a larger fraction of highly volatile compounds (i.e., those with lower boiling points) will remain as a vapor. Such high-volatility compounds require lower temperatures for complete condensation. This is illustrated in Figure 1, using pure acetone as an example.

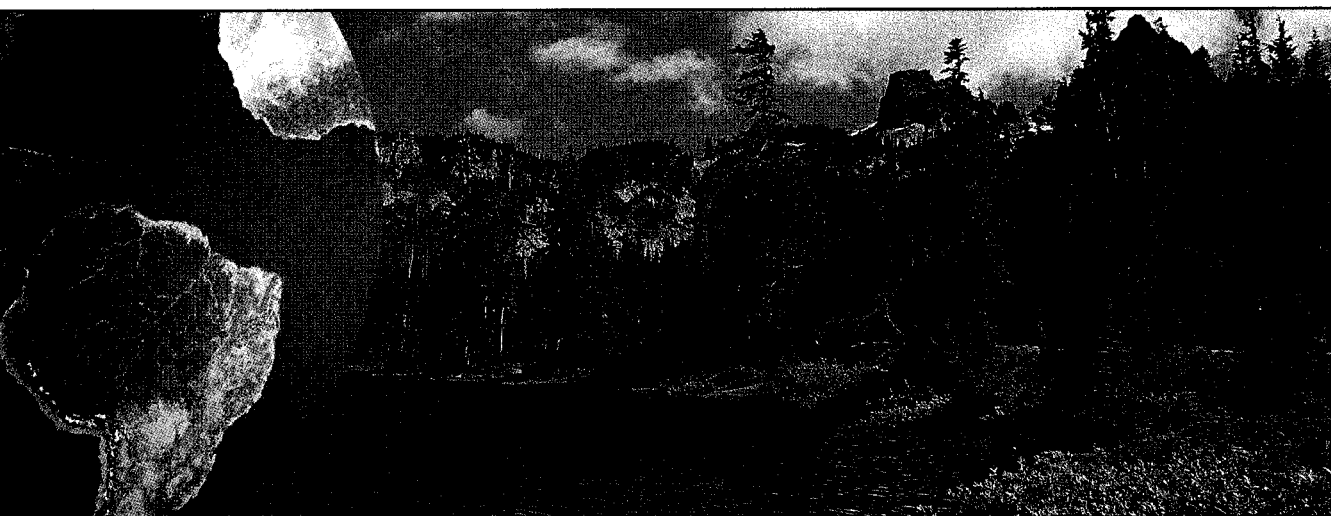
To condense low-boiling-point components to levels accepted by regulatory authorities, extremely low temperatures are often required. Table 2 shows several frequently used solvents, along with the temperature that must be achieved to fulfill the standards of TA-luft (the widely accepted emissions limits specified by the regulatory authorities in Germany). In the U.S., operators face similar thresholds under the various titles of the 1990 Clean Air Act Amendments, and state and local regulations.

At atmospheric pressure, liquid nitrogen has a boiling point

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Cryogenic condensation recovers solvents, including alcohols, ketones and hydrocarbons, from air

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SUMMARY OF COSTS FOR ADSORPTION, ABSORPTION AND CONDENSATION

Method	Investment cost, TSEK*	Total annual cost, TSEK*
Absorption	3,500	1,410
Adsorption	4,000	1,525
Cryogenic condensation	2,400	1,625

Note: The VOC-laden gas stream evaluated is 400 Nm³/h containing 1,100 g of gasoline/Nm³. The total annual cost includes capital costs, operating costs at an average capacity utilization of 30%, monitoring and maintenance costs.
*TSEK = 1,000 Swedish crowns (7.5 SEK = \$1 U.S.) Annuity = 30%

TABLE 1. In a recent study comparing cryogenic condensation with adsorption and absorption, cryogenic condensation scored favorably on capital costs. In many cases, the slightly higher operating costs associated with cryogenic condensation can be offset by reusing nitrogen elsewhere onsite for blanketing, once its cooling capacity has been spent

of -196°C. As a nontoxic, noncorrosive, nonflammable substance that will not support combustion, liquid nitrogen is a versatile coolant for a wide variety of industrial operations. And, unlike the soon-to-be-banned chlorofluorocarbon coolants, nitrogen has no impact on the ozone layer.

Designing the system

Cryogenic condensation systems most often consist of surface, or indirect condensation equipment. Shell-and-tube heat exchangers are typically used.

The vapor-laden exhaust and the coolant are handled as two separate streams, and are not co-mingled. As liquid nitrogen flows through the tubes, vapors in the exhaust stream condense as a film on the cold, shell side of the tubes. These condensed vapors drain into a collection tank, where they can be recovered for reuse, or sent for disposal.

Many chemical process facilities buy and store liquid nitrogen, which they vaporize for use as a blanketing gas to minimize unwanted reactions, prevent fire and explosion, and reduce product degradation by exposure to air or moisture. All too often, the cooling capacity of this onsite supply of liquid nitrogen is wasted.

In these cases, an onsite supply of liquid nitrogen can be used for cryogenic condensation, to offset some of the operating expenses. Since nitrogen leaving the shell-and-tube condensation unit is uncontaminated, it can be reclaimed and used elsewhere in a facility for inerting, once its refrigerant value has been expended.

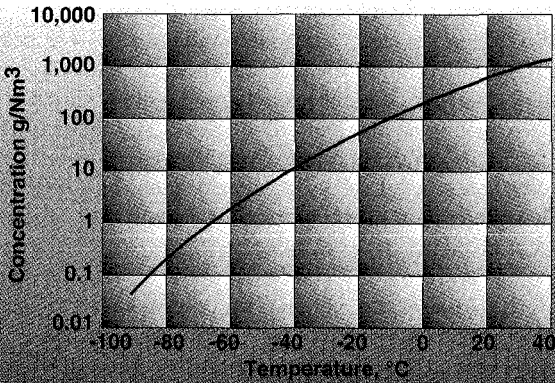
Beware: Ice and fog ahead

During cryogenic condensation, the presence of water vapor or VOCs with a high freezing point, may cause ice to form inside the condensation unit. Such a buildup could quickly foul the heat transfer area, reducing heat transfer capacity unless certain precautions are taken. One way to minimize buildup is to wash the pipes periodically with the condensed phase.

Another option is to install two condensers in series. In the first, pre-cool stage, the exhaust stream is cooled to about 1°C, to remove the majority of water before it freezes. The stream is then further cooled and condensed in the second condenser. Similarly, two condensers may be installed in parallel, so that one condenser is always in operation while the other is in standby, or defrost, mode.

Recently, a specially designed heat exchanger has become available for cryogenic condensation applications. The new unit is designed to maintain a layer of chilled, vaporized nitrogen between the liquid nitrogen inside the tubes, and the surface of the heat-transfer tubes in contact with the VOC-laden exhaust. This buffer layer, coupled with careful control of tube temperatures, minimizes the problem associated with VOCs freezing inside the condenser.

(continues)



PETER MCMAHON

FIGURE 1. Condensation occurs when the temperature of a gas stream falls below the saturation point of the contained VOCs. Cryogenic condensation is particularly well suited for compounds with relatively low boiling points (high volatility)

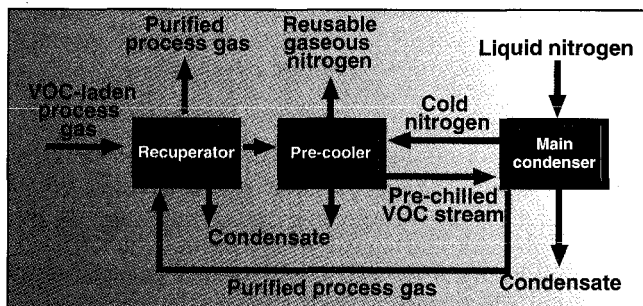
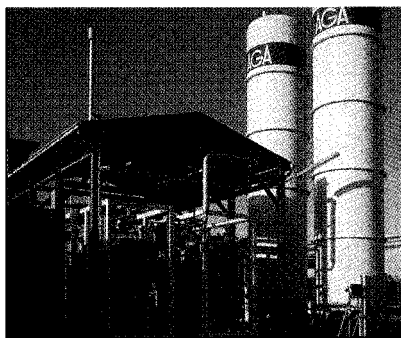


FIGURE 2. Thermal efficiency can be optimized and equipment costs minimized by varying the size and arrangement of the pre-cooler and main condensers. Using several precoolers minimizes ice formation. Condensation with liquid nitrogen is particularly well suited for exhaust streams with high VOC loads, strongly fluctuating flowrates and varying concentrations

FIGURE 3. The Solvay Duphar facility in Weesp (near Amsterdam) has successfully used cryogenic condensation to manage solvent vapors onsite since mid-1992



For some solvents, substantial cooling — to 40 to 50°C below the compound's dewpoint, for example — may also allow fog to form [2]. When the rate of heat transfer exceeds the rate of mass transfer, the bulk of the gas quickly cools below the dew point of the condensable vapor. If this happens, droplets will nucleate and condense in the bulk gas stream, rather than having time to migrate to a cold surface and condense. Such fog formation can be minimized by splitting the cooling process into successive steps. Using a series of heat exchangers instead of a single unit, the change in temperature across each component can be better controlled.

Similarly, a demister device can be used, or the gas velocity through the condenser can be reduced by increasing the diameter of the condenser. This allows droplets to fall instead of accompanying the gas stream out of the unit.

In most cases, cryogenic condensation systems are fairly straightforward, and require only condensers, collection tanks, valves and instruments. As a result, capital costs are modest in comparison to other traditionally used vapor control-systems (Table 1).

The main cost associated with operating a cryogenic condenser is that of the liquid nitrogen. Typical systems consume roughly 10 kg/h of nitrogen for each kW of cooling duty. However, as mentioned earlier, cryogenic condensation systems can often be integrated with an existing nitrogen supply onsite, to minimize costs.

Furthermore, cryogenic condensation requires neither power generation nor cooling water, and the units themselves are typically rather compact in space requirements. This, coupled with low maintenance requirements (since the system has no moving parts), makes cryogenic condensation suited for vapor control at remote locations.

Figure 2 shows a schematic flow diagram of a typical vapor-control unit based on indirect condensation with liquid nitrogen as the coolant. The VOC-laden effluent stream enters a recuperator, which initiates VOC removal using the cold purified stream leaving the main condenser as a chilling agent.

From the recuperator, the stream is routed to a pre-cooler, where further cooling is carried out, using the chilled, vaporized nitrogen return stream as the coolant. Both the recuperator and the pre-cooler are conventional shell-and-tube heat exchangers, in which the coolant flows through the tubes, and the vapors condense on the outer tube surfaces.

This pre-cooled stream then passes into the main condenser, where it is cooled to the temperature needed to completely condense the entrained vapors. VOC condensate drains by gravity to different collection tanks for recovery or disposal.

The purpose of this successive cooling procedure is three-fold:

- To minimize the overall liquid nitrogen consumption by making the most efficient use of available nitrogen
- To condense the largest amount of components with a high freezing point (e.g., water) before freezing occurs
- To minimize fog formation

If recovery for reuse is the desired objective, the condensate can be recovered at successively lower temperatures, to provide

VOLATILE ORGANIC COMPOUNDS

Volatile organic compound	Emission limit according to TA-lüft	Corresponding condensation temperature, °C
Dichloromethane	20 mg/Nm ³	<-95
Toluene	0.10 g/Nm ³	-65
Methyl ethyl ketone	0.15 g/Nm ³	-75
Acetone	0.15 g/Nm ³	-56
Tetrahydrofuran	0.10 g/Nm ³	-90
Methanol	0.15 g/Nm ³	-60

TABLE 2. Very low condensation temperatures are required to meet Germany's TA-lüft standards for VOC emissions

TABLE 3. Using cryogenic condensation, operators at Solvay Duphar have been able to consistently remove greater than 99.9% of vapors from operations handling a variety of solvents

SUMMARY OF TECHNICAL DATA AT THE SOLVAY DUPHAR FACILITY

Flow of exhaust gas	40-70 Nm ³ /h
Temperature	Ambient
Relative humidity	10-90%
Concentration of main VOCs:	
Dichloromethane	0-800 g/Nm ³
Toluene	0-50 g/Nm ³
Methyl ethyl ketone	0-110 g/Nm ³
Tetrahydrofuran	0-140 g/Nm ³
Purification degree	>99.9%
Outlet concentration	<20 mg/Nm ³
Operation	Continuous 6,000 h/yr
Cooling duty	2 x 37 kW

further separation based on the relative volatilities of the VOCs in a mixed stream. This is especially useful if the VOCs in the exhaust stream differ widely in boiling point.

The temperature (and hence the purity) of the gas stream inside the condenser is easily controlled using a control valve located on the outlet line of the gaseous nitrogen. As cooling requirements increase, the valve opens and liquid nitrogen is injected. As cooling needs taper off, the flow of nitrogen is throttled. This simple control scheme allows the system to meet required VOC-removal efficiencies while responding quickly to changing refrigeration load requirements caused by fluctuating flowrates or changing gas composition.

For most VOCs, cryogenic condensation removes 99+% of existing VOCs. However, for organic compounds whose freezing point would otherwise preclude them from cost-effective cryogenic condensation, a zeolite adsorption unit can be added as a final polishing step to capture residual vapors.

The adsorption capacity of a zeolite bed increases substantially with decreasing stream temperature, so the most cost-effective approach is to route the cold exhaust stream from the cryogenic condensation unit directly to the zeolite bed. For continuous operation, dual zeolite beds can be used, so that one bed is always in operation while the other is being regenerated. Desorbed VOCs are routed to the solvent-collection tank.

Case in point

Solvay Duphar manufactures a host of active ingredients for pharmaceuticals at a batch facility in Weesp, near Amsterdam. A variety of organic solvents, including dichloromethane (DCM), methyl ethyl ketone and toluene are routinely used at the plant.

Over the last few years, operators have worked to improve operating procedures, and upgrade certain equipment components. Nonetheless, to meet strict emissions limits set on VOCs at the plant, the firm needed to add end-of-pipe vapor controls.

A flexible system was needed to cope with strongly fluctuating flowrates and substantial changes in exhaust gas composition, due to the batchwise operation of the facility. Several technolo-

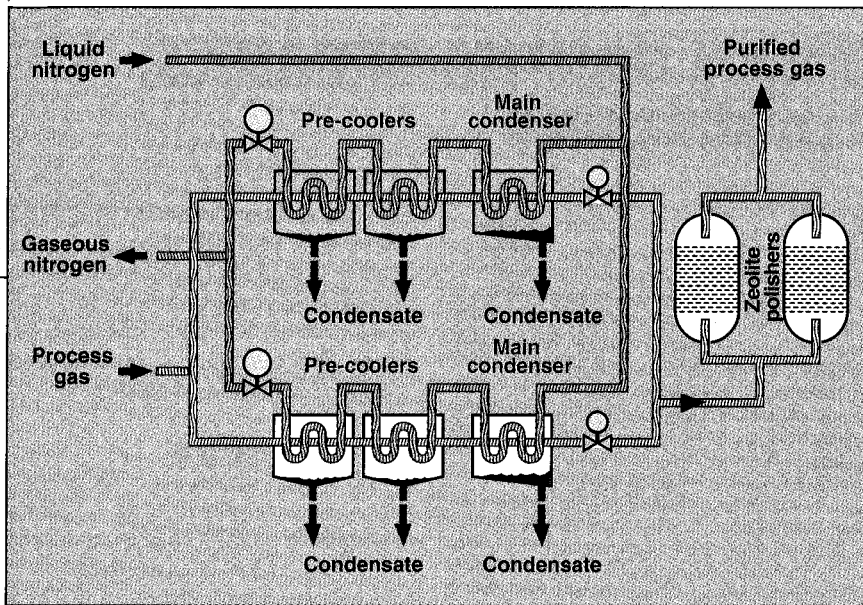


FIGURE 4. At Solvay Duphar, solvent-laden exhaust is cooled to -85°C in the condensers. To cost-effectively remove DCM vapors to meet regulatory thresholds, the plant installed a zeolite polishing unit. The gaseous nitrogen leaving the unit is recycled to the production processes onsite for inerting

gies were assessed for the task. Incineration was rejected due to the risk of secondary dioxin formation. Adsorption on activated carbon was rejected for safety reasons: The presence of ketones, which are readily oxidized to peroxides, increases the risk of spontaneous combustion in the carbon bed.

Similarly, pilot tests using absorption with phthalic ester showed that the approach could reduce solvent vapors to an acceptable level. However, the operators did not want to introduce a new solvent to the site, and the relatively high operational costs ruled against this technology.

Ultimately, Solvay Duphar opted for cryogenic condensation, and in 1992, in-

stalled a Cirrus CD vapor-control system from AGA AB (Figure 3). Using liquid nitrogen, the solvent-laden exhaust stream is cooled to about -85°C (Figure 4). This removes roughly 97% of the solvents. To reach the regulatory thresholds of $20\text{ mg}/\text{Nm}^3$ for DCM, the system would have needed to achieve temperatures far

below the freezing point of DCM (-95°C). To minimize overall costs and nitrogen consumption, Solvay Duphar chose instead to route the post-condensation exhaust stream through a zeolite adsorption bed, which effectively captures residual DCM, meeting regulatory thresholds.

The use of a dual-condenser system ensures continuous operation by allowing operators to alternate the condensation and thaw cycles. After the liquid nitrogen has performed its cooling duty, vaporized nitrogen is routed to other processes onsite, where it is used for inerting.

Operating conditions and results at the Solvay Duphar facility are summarized in Table 3. This vapor-recovery scheme has helped the facility to reduce solvent consumption and lower the total volume of VOCs discharged to the atmosphere. ■

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The author

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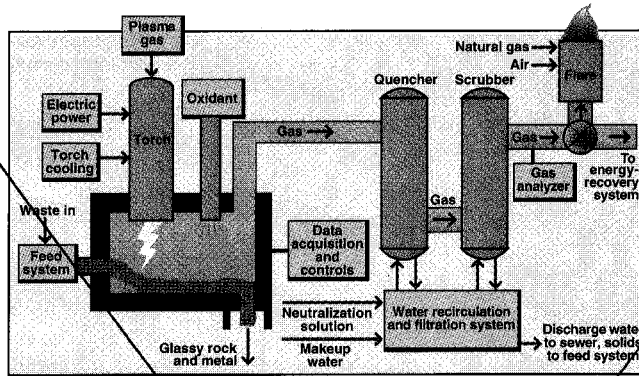
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PLASMA TORCH GASIFIES ORGANICS, VITRIFIES INORGANICS

For years, plasma torches have been a versatile source of industrial heat in metals and glass-processing operations. Now, these torches, which use a high-voltage field to turn any number of gases into a hot, high-speed jet of partially ionized gas, are finding application in waste treatment.

Plasma processing of waste offers the potential for material recovery, competitive economics and improved environmental compliance. A plasma-based system, the Thermal Destruction and Recovery (TDR) system, has been developed by Plasma Energy Applied Technology (PEAT; Huntsville, Ala.). Using a plasma torch to carry out controlled pyrolysis at



The TDR system uses controlled pyrolysis to treat a wide array of industrial, military and medical wastes, producing fuel and glassy aggregate as the byproducts

2,500 to 3,000°F, the patent-pending TDR system treats organic and inorganic debris as varied as contaminated soil, infectious medical waste, ammunition and other weapons components, flyash, electronic scrap, asbestos and a variety of other solid and liquid waste streams.

For organic wastes, the system restricts oxygen to just the amount needed to

gasify the carbon. Compared with direct combustion, the TDR system generates smaller gas volumes (typically 20% of the gas volume generated by combustion in an incinerator), so smaller gas scrubbers can be used to capture particulates and acid gases from the exhaust stream.

Organics to fuel gas

By pyrolyzing organics in an oxygen-deprived environment, the gaseous atmosphere remains highly reducing. Steam can then be added as an oxidant to reform organics into a hydrogen-rich fuel.

Fuel-gas generation rates are inherently limited by steam availability. As a result, unlike aspirated combustion systems, the TDR system can handle surges in feed rate or variations in feed composition without large changes in gas volumes overwhelming the gas-treatment system.

The fuel produced by this gasification (or steam reformation) process is composed primarily of H₂ and CO. It can be used to power a gas or steam turbine, or as a feedstock for methanol production, hydrogen extraction or fuel cell operation. And, combustion of this 300- to 400-Btu/std. ft³ fuel typically requires no scrubbing to meet regulatory emissions requirements, says the company.

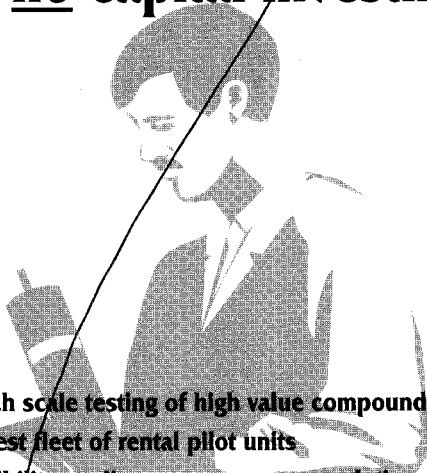
Vitrify inorganics, too

When handling inorganic streams, the plasma torch produces molten metal, which can be recovered in alloy form, and vitrified slag. Using the appropriate fluxing agents, this ceramic slag can be either formed into construction aggregate, or spun into mineral wool fiber for use as insulation. In the wide variety of materials tested to date, the glassy residue has passed strict, U.S. government-mandated leachability testing.

For treatability testing, a pilot unit currently produces either a 70-kW or 170-kW plasma torch, using a variety of ionized gases. The chamber can be equipped with any of five feeder mechanisms and a variety of refractory linings. Instrumentation and data-acquisition capabilities are expandable. PEAT is in the process of permitting a 1,000-lb/h TDR unit for a hospital in California, and is in the proposal stage for 25-ton/d units for several industrial and medical clients.

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