



TECHNICAL BULLETIN

REFRIGERATED CONDENSERS FOR CONTROL OF ORGANIC AIR EMISSIONS

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REFRIGERATED CONDENSERS FOR CONTROL OF ORGANIC AIR EMISSIONS

Prepared by

Clean Air Technology Center (E 143-03)
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ACKNOWLEDGMENTS

This technical bulletin was made possible through the diligent and persistent efforts of Lyndon Cox, Senior Environmental Employee with the Clean Air Technology Center (CATC). Lyndon did an exceptional job identifying information sources, gathering relative data and putting this bulletin together. The CATC also appreciates the helpful and timely comments and cooperation of the following peer reviewers:

Randy McDonald, Organic Chemicals Group, Emissions Standards Division, Office of Air Quality Planning and Standards, Office of Air and Radiation, U.S. EPA

Dr. Cynthia L. Gage, Atmospheric Protection Branch, National Risk Management Research Laboratory, Office of Research and Development, U.S. EPA

In addition, the CATC thanks the individuals, companies and institutions who supplied information on refrigerated condenser technology used to prepare this Technical Bulletin. Contributors are indicated in the REFERENCES section of this bulletin.

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Refrigerated Condensers for Control of Organic Air Emissions

This Technical Bulletin describes both refrigeration and condensers that together form a control technology for organic emissions. These emissions may result from the evaporation of: Volatile Organic Compounds (VOC) that contribute to ozone formation in the troposphere; volatile organic Hazardous Air Pollutants (HAP) that may have a direct impact on our health and safety; or volatile stratospheric ozone depleting compounds. Terms like VOC and HAP are used in regulatory definitions to indicate specific chemical compounds and related emissions that are subject to a rule. The reasons for regulating specific groups of organic compounds may be very different. However, refrigerated condensers can be used to control vapors from most organic emissions that may be included in any of these regulatory definitions.

The types of refrigeration discussed are: absorption refrigeration; mechanical compression refrigeration (using sulphur dioxide (SO_2) , chlorofluorocarbons (CFC) and hydrofluorocarbons (HFC)); Reverse Brayton Cycle refrigeration; and cryogenic (liquid nitrogen) cooling. This Technical Bulletin also discusses how a condenser operates, advantages and limitations for each type of refrigeration system, safety precautions that should be taken, and the cost for each type of refrigeration system.

WHAT IS A REFRIGERATED CONDENSER?

A refrigerated condenser is a control device that is used to cool an emission stream having organic vapors in it and to change the vapors to a liquid. A refrigerated condenser condenses organic vapors just as moisture is condensed to water in an air conditioning system. However, while condensed water from an air conditioning system is disposed of via a drain, condensed organic vapors can be recovered, refined, and might be reused, preventing their release to the ambient air.

WHY IS REFRIGERATED CONDENSATION IMPORTANT?

Nitrogen oxides (NOx, the x is used because there are five oxides) and VOC react with each other in ultraviolet (UV) light from the sun to produce tropospheric ozone. Ozone in the troposphere (the air we breathe in the lower atmosphere) is the principle constituent of smog and is harmful to public health. Refrigerated condensers can reduce VOC emissions, which reduces the ozone generating potential of NOx. NOx reduction techniques are discussed in a separate CATC Technical Bulletin.

Many organic compounds have been designated as negligibly reactive with regard to ozone formation and are exempt from VOC regulations. Although some VOC may be HAP, compounds exempt from VOC regulations also may be HAP and need to be controlled. In addition, stratospheric ozone depleting chemicals are not considered VOC or HAP, but still need to be controlled. Stratospheric ozone protects us from the harmful rays in sunlight.

WHERE CAN YOU USE A REFRIGERATED CONDENSER?

A refrigerated condenser works best on emission streams containing high concentrations of volatile organic emissions. They are less effective on dilute streams (i.e., where there is much more air flow than organic vapor flow). For example, a paint spray booth requires a substantial amount of air flow through it to protect worker health and safety. As a result, most of the heat removed by a refrigerated condenser would come from air. The organic vapor content in a paint booth emission stream could be recovered by using a refrigerated condenser, but it would be very costly per ton of organic compound recovered. In addition, to reuse the organic compound, moisture condensation would probably need to be removed.

A refrigerated condenser could be a viable control option for any source of evaporative organic emissions if:

- there is minimal air flow carrying the organic emissions (i.e., the air stream is saturated with the organic compound)
- the organic vapor containment system limits air flow
- required air flow does not overload a refrigeration system with heat
- only one organic compound is emitted (or the system is designed for the compound that is the most difficult to control)

Refrigerated condensers often are used in the following applications:

- Dry Cleaning Industry used to recycle dry cleaning fluid (perchlorethylene or petroleumbase solvent) with virtually no air flow. The vapors are usually condensed without air being used to transport them.
- Degreasers using VOC or Halogenated Solvents some air is mixed with vapors because the solvent is uncovered (i.e., exposed to the atmosphere). Preparation (degreasing/cleaning) of parts prior to powder coating is one example of this.
- Transfer of Volatile Organic Liquid (VOL) and Petroleum Products (e.g., bulk plants, bulk terminals, and similar transfer operations).
- Vapors from Storage Vessels/Tanks

WHAT IS REFRIGERATION?

All refrigeration units are basically "heat pumps," absorbing heat on the "cold side" of the system and releasing heat on the "hot side" of the system. All refrigeration systems have a hot side and a cold side. Some have a compressor. The difference between refrigeration systems is whether the refrigerant is actually liquified within the apparatus and how low a temperature the "cold side" can reach.

HOW HAS REFRIGERATION CHANGED OVER TIME?

The most primitive refrigeration system was to cut ice in the winter and store it in sawdust insulation to chill items in the summer. There has been an evolution in refrigeration over time, and each type has different capabilities and limitations. Some pump heat directly from the material to be cooled. Other types use an intermediate material, such as brine or liquified nitrogen, to move the heat pump to a more remote location. This requires making deliveries of the cooled intermediate material by either pipe or truck. If the delivery is by truck, it makes the condenser somewhat like your great-grandparents icebox, an ice chest, or a picnic cooler - except it is often much colder.

Absorption refrigeration was invented circa 1850. In this refrigeration system, ammonia was boiled off from aqueous ammonia, liquified by cooling under high pressure, and then allowed to boil to generate a low temperature before again being absorbed by water. The cold side was frequently used to chill brine. The brine was then used as an intermediary to exchange heat between the material being chilled and the refrigerant. Because the ammonia was under high pressure, and because ammonia causes inflammation of the lungs and pneumonia at 25 parts per million in air, other refrigerants were used when they became available. There are still vendors for absorption refrigeration units, but these types of refrigeration units are sold mostly for use as air conditioning or refrigeration for rural homes or cabins that are without electricity. Because absorption refrigeration systems are rarely, if ever, used for control of organic vapors, they will not be discussed further in this Technical Bulletin.

Mechanical compression refrigeration initially used sulfur dioxide as a refrigerant. Sulfur dioxide is another noxious chemical. However, it could be mechanically compressed, condensed under high pressure (the hot side), and then boiled in a partial-vacuum to produce a low temperature (the cold side). Sulfur dioxide was replaced by chlorofluorocarbons (CFC such as Freon® which is both non-toxic and inert in the lower atmosphere) in most refrigeration units in the 1930's and 1940's. Because sulfur dioxide is rarely, if ever, used for control of organic vapors, it too will not be discussed further in this Technical Bulletin.

Mechanical compression of chlorinated fluorocarbons (CFC) became nearly the universal refrigeration system from the 1940's to the 1980's. These units had a mechanical compressor, which directed output to the hot side where the refrigerant was cooled and liquified under pressure, before being released by a throttling valve to the cold side where the refrigerant was boiled at low temperatures.

Reverse Brayton Cycle turbines, also called air-cycle machines, have been used as refrigeration systems since the 1940's, and they use an environmentally benign refrigerant - air. The cycle is different because the refrigerant (air) does not become a liquid. Reverse Brayton Cycle machines always lost economy battles to CFC mechanical compression refrigeration based on efficiency versus a controlled temperature. Efficiency was close when the temperatures of the hot and cold sides were the same, but the Reverse Brayton Cycle could not assure what the cold side

temperature would be. The Reverse Brayton Cycle machine became a winner in the 1990's when CFC ceased to be domestically manufactured, a large temperature change became desirable, and the use of a non-polluting refrigerant became necessary.

Cryogenic refrigeration also became an option after the 1960's. Cryogenic refrigeration does not use any machinery -- at least none at the plant where the liquid nitrogen is used for cooling. The machinery is at a central air separation plant, and the liquid nitrogen is delivered in the form of a cold liquid. This cold liquid is a liquefied fraction of air (nitrogen, which is 79-80% of air) that boils at -195.8°C (-352.44°F). When liquid nitrogen is used, the process is referred to as Cryogenic cooling. Release of nitrogen to the atmosphere is not considered pollution.

In the 1980's it became evident that ozone in the stratosphere was being destroyed by the breakdown of CFC. Their very "inertness" caused CFC to not break down molecularly until they received intense ultraviolet radiation after diffusing to the stratosphere. Stratospheric ozone shields us from the adverse effects of ionizing radiation (UV, x-rays, and gamma rays). This radiation penetrates to the troposphere (the air we breathe) when stratospheric ozone is insufficient. Ionizing radiation causes adverse health effects. As a result, manufacture of CFC has been phased out in the developed world, and CFC use is being phased out world-wide.

Hydrofluorocarbons (HFC) were developed to replace CFC as refrigerants in the 1990's. CFC have been replaced, in part, by reactive HFC which are less stable and some are even flammable. HFC do not persist in the atmosphere long enough to diffuse to the stratosphere. However, some recycled CFC was still being used in 2000 because refrigeration machinery requires expensive changes to be able to use HFC. HFC mechanical refrigeration operates on the same cycle that CFC systems do, but must use different elastomeric parts (hoses, gaskets, etc.). Use of HFC with the same elastomeric parts as used for CFC would cause either degradation, embrittlement, or dissolving of the elastomer with subsequent leakage.

In looking for a refrigeration cycle that could replace mechanical compression CFC refrigeration with environmentally safe refrigerants in the 1970's, HFC mechanical compression refrigeration, Reverse Brayton Cycle machines and cryogenics (liquid nitrogen) were all found to be workable and environmentally desirable alternatives.

WHAT MAKES THE REFRIGERATED CONDENSERS WORK?

Each type of refrigeration system chills a heat exchanger surface in a condenser, and organic vapor condenses on the cold heat exchanger (or heat transfer) surface. Condensation of organic vapor causes it to lose volume. This loss of volume produces a lower concentration of vapor near the heat exchanger (i.e., the condensation) surface. This produces a concentration gradient that causes the flow of the emission stream toward the heat exchange surface. Condensation is assisted by turbulence in the emission stream that also brings the emission stream close enough for heat transfer and subsequent condensation of the organic vapors. Usually, only a negligible fraction of a percent escapes this combined action when the condenser is sized large enough and

the refrigerant temperature is low enough. A finite vapor pressure is always present that allows some vapor to remain in the exhaust stream at all times.

Mechanical Compression Systems

Mechanical Compression refrigeration has compressors that are driven by electric motors. They use the circulation of a refrigerant to chill organic vapor through a heat transfer surface. However, some units still use brine (discussed below) to transfer heat from the emission stream to the refrigerant. Fans may be used on the hot side to assist in heat transfer. Brine pumps and fans are also usually powered by electric motors.

Mechanical Compression refrigeration uses a compressor to pull a low pressure on the "cooling coils" to depress the boiling point of the refrigerant and then to raise the pressure at the compressor outlet to condense (liquefy) the refrigerant at above room temperature. As shown in Figure 1, the refrigerant in a mechanical compression refrigeration system goes through a "hot side" heat exchanger (called a refrigerant condenser) to cool and condense the refrigerant before it is cycled through a throttling valve to be exposed to the low pressure in the "cooling coils." The "cold side" has the "cooling coils" which are both a refrigerant evaporator and an organic vapor condenser. The "cooling coils" may be either a coil of copper tubing, a surface condenser, or a shell-and-tube condenser.

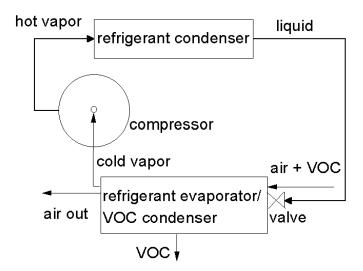


Figure 1. Mechanical Compression Refrigeration System

The valve that allows entry of refrigerant to the "cold side" is thermostatically controlled to maintain the flow of refrigerant to keep the temperature as constant as possible and as near optimum as possible for the desired organic vapor condensation. The appropriate CFC or HFC refrigerant is selected to meet the condensing needs.

All organic vapors are condensed and collected on the "cold side" heat exchanger surface and then drained off for either immediate recycling, further separation, purification, disposal, or sale.

Pre-cooling of the emission stream is sometimes used to remove moisture. Pre-cooling can use either a different refrigerant, the refrigerant leaving the cooling coils, or the cold exhaust stream from the condenser. For pre-cooling, the thermostatic expansion valve is set to a much higher temperature (~1°C or ~34°F) which would not be efficient for the same type of refrigerant that is used for condensation of an organic vapor.

Some types of CFC and HFC have lower boiling points than others. Those with the lowest boiling points are capable of condensing organic vapor at -30°F to -100°F. The CFC or HFC must have a lower boiling point than the dew point of the organic vapor. The temperature at which some organic vapors condense can be as low as -100°F.

When salt water brine is used, the condenser is known as a brine chiller. Brine chillers are of two kinds: <u>contact</u> condensers, in which the brine is sprayed directly into the gas stream; and <u>surface</u> condensers, in which the brine is separated from the gas stream by a metallic heat exchange surface. Contact condensers, as shown in Figure 2, are not used for organic vapor condensation because the organic vapor would get contaminated by salt in the brine.

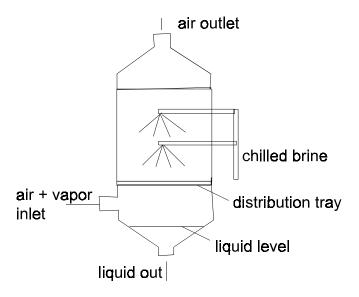


Figure 2. Contact Condenser

Surface condensers are used to recover organic vapors. In these condensers, the refrigerant is separated from the organic vapors and the atmosphere by a metal heat exchange surface. These heat exchange surfaces are needed to maintain the purity of both the refrigerant and the organic compound, and to maintain pressure differences between the refrigerant and the emission stream. In brine chillers, there is one heat exchange surface to transfer heat from the organic vapor to the brine, while a second heat exchange surface transfers this heat from the brine to the refrigerant, and a third heat exchange surface is used to reject the heat from the refrigerant to the atmosphere.

Reverse Brayton Cycle Systems

Reverse Brayton Cycle machines must be externally powered by an electric motor, a gas turbine, or an internal combustion (piston) engine. It is easier to reach the rotational speed of the turbine with either an electric motor or a gas turbine than with a piston engine.

Reverse Brayton Cycle turbines operate inversely from the normal operating cycle for gas turbines. Instead of converting heat to shaft horsepower, the Reverse Brayton Cycle system uses shaft horsepower to remove heat and reject it to the atmosphere. As shown in Figure 3, it does this by first compressing the refrigerant air, then rejecting the heat of compression at an elevated temperature, and finally expanding the refrigerant air through a turbine to get useful work from it. As a result of the lack of heat input, temperature rise from compression, followed by dissipation of heat, and the work that the refrigerant air flow does on the expansion turbine, exhaust from the expansion turbine is very cold, reaching about -73°C (-100°F). The expansion turbine assists the external power source in spinning the compressor turbine.

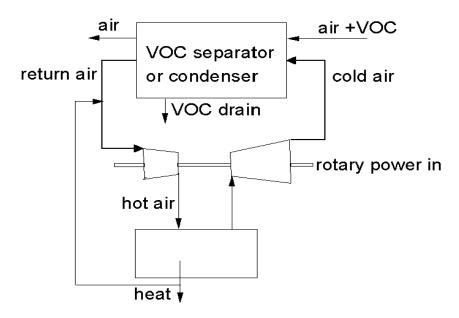


Figure 3. Reverse Brayton Cycle Refrigeration System

The refrigerant air never liquefies in this cycle. Organic vapors may go through the Reverse Brayton Cycle along with the refrigerant air and no heat exchanger surface would then be required. Reverse Brayton Cycle machines cool the refrigerant air (and organic vapors if they are contained in the refrigerant air) to a very low temperature in what appears to be a single step, although it may actually be several steps in the expansion turbine. All of the vapors condense essentially together. If the cold refrigerant air is used to chill a heat exchanger (surface condenser) as in Figure 3, the organic vapor can be condensed without going through the cycle. When organic vapor is exposed only to a heat exchange surface, the heat exchanger can be like any other refrigerated condenser.

The refrigerant air in a Reverse Brayton Cycle system does not contaminate the organic compound, but several organic compounds may be mixed in the vapor state and therefore may be condensed together and mixed in a condensed liquid or slurry.

Reverse Brayton Cycle machines do not have a pre-cooling feature to separate moisture. To the extent that moisture is present in the vapor, it will be present in the condensed organic liquid. Some organic compounds can be separated by skimming, others require fractional distillation for purification.

After completing the Reverse Brayton Cycle, the refrigerant air can be either recycled or exhausted to the atmosphere. Because some organic compounds are actually frozen they should be separated as solid particles. To the extent that the refrigerant air recovers some of its heat before it is again compressed, or for some low melting point compounds, these organic compounds also may be recovered as a liquid. Multiple filter channels can allow one compound to warm up for recovery, while the other is chilled by cleaning the cold refrigerant air flow. While frozen organic particles must be captured by a filter, organic droplets can be captured by inertial impact or in a cyclone separator. In both cases the cut-off particle/droplet size depends on the design.

Cryogenic Cooling

Cryogenic Cooling uses no power at the plant where it is used for cooling, but the air separation plant that generates liquid nitrogen usually is electrically powered. The truck used to deliver liquid nitrogen to the user's plant will also use fuel. The distribution of liquid nitrogen in a plant is self-powered by the pressure of the gaseous nitrogen that results from heat leakage which causes the liquid nitrogen to boil.

Cryogenic Cooling starts at an air separation plant. Air is compressed, cooled and then expanded to atmospheric pressure. This expansion cools some fraction of the compressed air to make it a liquid. The air that has become liquid is then allowed to boil to give off Argon, Nitrogen,

Oxygen, etc. at their respective boiling point temperatures. Each gas is then collected and condensed again by compression and expansion just like the air originally was. This produces relatively pure liquid nitrogen that is used for cryogenic cooling. A cryogenic cooling system is shown in Figure 4.

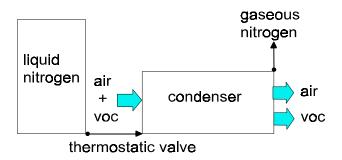


Figure 4. Cryogenic Cooling

In a very real sense, the refrigeration system is at the air separation plant, which can be in a totally different plant than the one condensing the organic vapor. Liquid nitrogen is delivered to the condensing plant as a very cold liquid stored in a Dewar flask (a large, stainless steel, double-walled vacuum bottle similar to a Thermos bottle). Liquid nitrogen has a lot in common with the commercial manufacture of ice. Both occur in a central plant with a refrigeration system that is too large to be portable and is too expensive for smaller users.

Cryogenic cooling simply boils off the liquid nitrogen. The flow of liquid nitrogen is in response to a thermostatic valve which controls its flow. Liquid nitrogen flows and boils to cool a shell-and-tube or other type of surface condenser. A pressure release valve for the nitrogen may be necessary at several points to allow gaseous nitrogen to exhaust at a safe pressure in the event that the main venting path becomes blocked. Organic vapor will condense as a film on the inside of the tubes in a typical shell-and-tube condenser.

Cryogenically cooled condensation systems often have a pre-cooler before the condenser. It may be cooled by a separate refrigeration system, a flow of cold gaseous nitrogen exiting from the condenser, or the exhaust air leaving the main condenser. By staging the condenser temperatures, most water vapor can be collected separately.

WHAT LEVELS OF CONTROL ARE ACHIEVABLE?

Destruction or Removal Efficiency (DRE, also known as the control efficiency) is a measure of the effectiveness of a control device. The DRE reflects the percentage of organic compound recovered by a refrigerated condenser. When emissions of organic vapors are controlled by mechanical compression refrigeration with the condenser chilled by way of a brine heat exchanger, a DRE in the range of 50 to 90% can be expected. This wide range occurs because brine cannot be circulated below -14 °C (0°F). CFC or HFC in mechanical compression refrigeration systems chilling a condenser directly can achieve a temperature of -53°C (-65°F), which can give the condenser a DRE of 90% or better for organic compounds that condense above this temperature. Special CFC refrigeration systems can reach -73°C (-100°F), but are not highly efficient at this temperature. The Reverse Brayton Cycle can raise the DRE of a condenser to 98% by having a cold side temperature of -73°C (-100°F). Cryogenic refrigeration can raise the upper limit of the DRE of a condenser to 99+% by having a cold side temperature as low as -195°C (-352°F). The DRE of refrigerated condensers can be either higher or lower than many other competing control technologies (e.g., adsorbers, incinerators, etc.), depending on the lowest temperature in the condenser, and therefore the lowest vapor pressure attained by the organic compound.

WHAT FACTORS AFFECT THE PERFORMANCE OF REFRIGERATED CONDENSERS?

Any refrigerant can be used to cool the surface of a heat exchanger. The only requirements are that the temperature is low enough and that the cooling capacity is sufficient. When organic compounds are recovered along with moisture and other contaminants, an impure organic compound may require too much effort to purify and might be destroyed by burning. However, recovery and recycling of the organic compound is the preferred outcome.

Each organic compound becomes liquid below its dew point, and becomes a solid "frost" below its freezing point. This "frost" must be removed from a condenser periodically, especially in cryogenic condensers because they are so cold, to allow free flow of the emission stream containing organic vapor and to permit heat transfer to occur as designed. The "frost" can be removed by flushing the condenser with the condensed organic compound in its liquid phase. However, the liquid organic compounds are always mixed in the frost and slurry, just as the organic vapors were mixed.

Cryogenic condensers can be the coldest and therefore are capable of the highest DRE. Fluctuations in heat load caused by fluctuations in emission stream flow and organic vapor concentration are offset by a thermostatically controlled valve modulating the nitrogen flow. However, if cryogenic cooling is operated at a temperature well above the boiling point of liquid nitrogen, there will be locations within the condenser that will be somewhat warmer than the thermostat setting because gaseous nitrogen has a low specific heat and is warming up as it passes through the shell of the condenser.

The DRE is limited by the amount of organic vapor that escapes with the exhaust from the condenser. The amount of organic vapor that escapes is determined by both the vapor pressure of the condensed liquid (i.e., the partial pressure of the organic vapors in the emission stream) and the amount of air present in the emission stream. We cannot always eliminate the air from the emission stream, but we can minimize both the amount of air in the emission stream and the vapor pressure of organic compounds. Therefore, condensation technology needs to:

- 1. Maximize the portion of the organic vapor that is affected by the cold surface in the condenser (i.e., make the residence time large enough and the flow sufficiently turbulent).
- 2. Minimize the partial pressure of the organic vapor after it comes in contact with the heat exchanger (i.e., make the condenser cold enough and the refrigeration capacity large enough).
- 3. Reduce the temperature of the organic compounds below the freezing point, if possible, because vapor pressure becomes a minimum when organic compounds are frozen. (This should be done even though frozen organic compounds must be removed periodically.)
- 4. Minimize the amount of air in the emission stream that contains organic vapors. Heat load is greater when you must chill a lot of air. Minimizing the amount of air mixed with the organic vapors will reduce the heat load and increase the useful cooling (i.e., the cooling available for condensation). Reducing the heat load will reduce the cost of refrigeration. Increasing the useful cooling will improve the DRE.

Temperature versus Flowrate

Along with the size of the condenser, adequate cooling capacity must be provided for the maximum emission stream volume to be chilled. If air is mixed with the stream of organic vapor, much of the cooling capacity will be used to chill the air which does not condense (except at liquid nitrogen temperatures). Placing an adsorber before the condenser can separate the streams of air and organic vapor and allow the volume of the emission stream through the condenser to be minimized. This reduces the heat load and increases the useful cooling which raises the DRE.

As shown in Figure 5, a pre-cooling heat exchanger placed before the main condenser in the emission stream can cool the emission stream and remove moisture before the emission stream reaches the main condenser. The fact that the main condenser has to chill the emission stream less and does not have to condense the moisture, makes the emission stream flow a less dominant factor in sizing the main condenser. In effect, the pre-cooling isolates the main condenser from moisture fluctuations. That is because most of the water is condensed in the pre-cool heat exchanger. The principal concern is that the pre-cool heat exchanger have sufficient efficiency and flow capacity to handle the required flows.

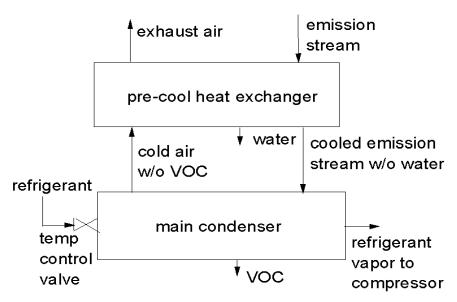


Figure 5. Flow Through Pre-Cooling Heat Exchanger

Refrigerated condensers come in various temperature ranges, heat transfer areas, and heat transfer capacities, as needed for various refrigeration or cooling systems. The achieved temperature must be low enough that the organic vapor will condense, and the refrigeration and heat transfer capacity must be sufficient for both the condensation of volatile organic compounds and for chilling the entire emission stream. It is sometimes overlooked that the refrigeration or chilling capacity must handle the heat load of air present in the emission stream as well as the heat load of the organic vapor in the emission stream.

Sometimes flow rates are made artificially greater than necessary just to dilute organic vapors. This may be done to meet OSHA requirements regarding the Permissible Exposure Limit for an organic compound (PEL, the concentration that workmen can breathe safely). Where such large air flows are not absolutely necessary, organic vapor should be captured before it gets diluted in air. This may be done by ducts bringing the organic vapor directly from the points of emission. This would enable condensation of organic vapors without cooling excessive amounts of air. The consequence of eliminating a large portion of the heat load would be to reduce the cost of energy consumed as well as the cost of more refrigeration capacity.

Material Compatibility

Material compatibility can sometimes be a problem. Cooling coils are often made from aluminum or copper alloys. Anything that will react with any of these metals gives an indication that you should not use that type of condenser. Some condensers are made of stainless steel, which usually does not present any material problems. Some condensers are made of carbon steel, which may be subject to rust and reaction with organic compounds, or brittleness below a brittle transition temperature. Brine chillers usually require a metal that will not react with the brine (usually sodium chloride, potassium chloride, calcium chloride, or a mixture of these in water). If a brine chiller is used, the organic compounds must be compatible with monel or similar metals.

Reverse Brayton Cycle machines have turbine blades that are made of high strength alloys. Part of the "air cycle" is to experience moderately high temperatures in the "hot side" heat exchanger. These alloys, the heat exchanger, the temperatures, and the organic compounds all must be mutually compatible. Separation or filtration of crystals and droplets of organic compounds must occur adequately if the refrigerant air is to be recycled. Both compression and expansion turbines get eroded when the organic vapor condenses and droplets or solid particles impinge on rotor blades.

Stainless steel is routinely used for both the tubing and shell of the condenser in cryogenic service. Carbon steels are not suited to cryogenic temperatures because all carbon steels have a brittle-failure-transition temperature well above the liquid nitrogen temperature range. Because most stainless steels avoid this brittle transition, and organic compounds are compatible with most stainless steel, there are virtually no material compatibility issues with cryogenic cooling using a stainless steel condenser.

Contaminants

Any single organic compound cannot be recovered with high purity from a mixture of organic vapors by condensing it, because all of the organic compounds are condensed and collected together. This is a limitation of all condensers. Subsequent purification by another process such as fractional distillation, skimming, or membrane separation must be performed before recycling or selling recovered organic compounds.

If there are a lot of solid particles or fibers in the emission stream that would form sludge when recovered along with the condensed organic vapor, the particles should be filtered out before they reach the condenser. When enough particles have been filtered out, either the mixture will not form a sludge on the "cooling coils," or the condensed organic compound will wash the particles off (or out of the condenser tubes). The emission stream is clean enough for condensation when particles and fibers in the emission stream will not form a sludge on the cooling coils.

Reliability

Mechanical Compression refrigeration systems using CFC or HFC have a rather long life between overhauls. How long depends upon the type of compressor used. Rotary vane compressors often exceed ten-thousand hours mean-time-between-failure (MTBF). Piston compressors may have only about a thousand hours MTBF.

Reverse Brayton Cycle machines are competitive up to about 2,000 cubic feet per minute (cfm). The crystals or droplets that are not captured before the compressor inlet in recycling the refrigerant air, or are created before the turbine outlet, will erode the turbine blades. This will limit the service life of Reverse Brayton Cycle machines between overhauls. In spite of this, the MTBF of a Reverse Brayton Cycle turbine is well over a thousand hours, and depending upon the amount of particles in the emission stream, the MTBF might extend from ten thousand hours to a hundred thousand hours.

Cryogenic Cooling is principally applicable to emission streams smaller than 10,000 cfm, although it has been applied to larger flows. Plants that already use liquid nitrogen for other purposes will find that using it as a refrigerant is economical. Because nitrogen is inert and makes up about 80% of air, releasing nitrogen to the atmosphere is not considered pollution. The major concern is that nitrogen be returned to the atmosphere in a stream mixed with air. If returned unmixed, asphyxiation could occur without warning to people who may be exposed to that stream. The reliability extends to a very long and indeterminate time because failures have been so rare. However, obstruction of venting has occurred where safeguards were ignored.

WHAT SAFETY PRECAUTIONS MUST BE OBSERVED?

Consult with an industrial hygienist and a safety officer, and review the material safety data sheets (MSDS) for both the organic compound and the refrigerant before selecting <u>any</u> refrigerated condensation technology.

Mechanical Compression

The widespread use of CFC in refrigeration was largely based upon its being non-toxic and inert. CFCs and their replacements, the HFCs, have become the standard for home refrigeration for over sixty years. As a result, these safety rules have become known to almost everyone. The safety precautions are:

- 1. Do not breathe the vapor, or the aerosol cloud if you can see it.
- 2. Do not let liquid CFC/HFC get in your eyes, mouth, nose, or on your skin.
- 3. Do not touch very cold surfaces with your skin. Do not touch anything that frost forms on.

4. Make sure that clothing does not get caught in the rotating machinery.

Allowing liquid refrigerant to contact the body in any way could lead to loss of the contacted tissue by freezing. Touching cold surfaces may result in a prompt loss of tissue. Getting clothing caught in rotating machinery could promptly cause injury or death.

If sprayed with a liquid CFC or HFC, an exposed person is also subject to breathing an aerosol of compressor oil (a silicone oil) which was dissolved in the escaped refrigerant. This compressor oil will form an aerosol of tiny droplets in CFC, HFC, or air. Breathing the aerosol cloud means getting the compressor oil (a silicone oil which is mixed with the refrigerant) as an aerosol into your lungs. Also, breathing the CFC or HFC vapor can produce effects ranging from euphoria, to unconsciousness, or even asphyxiation.

This aerosol indicates where a break is located because both CFC and HFC are colorless. Avoid breathing the aerosol and turn off the compressor motors, because without refrigerant to carry the oil, the compressors would operate without lubrication -- leading to damage and possibly a fire. Promptly evacuate the area after shutting down the compressors. Remain in a well-ventilated area outside the building until the refrigerant vapor has dispersed.

Reverse Brayton Cycle

Safety with this externally powered gas turbine requires the following:

- 1. Do not breathe the cold air, touch the cold duct work, or let it the cold air touch your skin.
- 2. Do not touch the "hot side" heat exchanger or duct work.
- 3. Keep clothing from being caught in rotating machinery.
- 4. Do not allow the turbines to "run dry" (without oil).

Contact with the cold air or metal duct directing the flow could lead to frostbite and/or loss of tissue. Contact with the "hot side" heat exchanger or metal duct could cause burns or blisters. Getting clothing caught in rotating machinery could cause prompt injury or death. Allowing turbines to "run dry" (i.e., without oil) could lead to either damaging the turbines or a fire.

Cryogenic Cooling

Liquid nitrogen cooling has a somewhat more elaborate set of precautions. This is only because cryogenics is the newest technology, and the safety precautions are unknown to many people. Liquid nitrogen is usually liquefied at a supplier's plant and delivered in a Dewar flask for storage on-site. It is very cold, and will freeze things seemingly instantaneously. However, if liquid nitrogen is used currently in a plant, workers should find these safety rules easy to follow:

- 1. In damp weather conditions, the top of the Dewar flask must be checked to assure that it is free of ice, and that venting paths are not obstructed. Ice could block the relief valves, which operate at a pressure within the Dewar flask of 1 psi and 10 psi, or the rupture disk which is set to actuate at 80 psi.
- 2. Promptly evacuate all personnel when a rupture disc actuates. This is clearly indicated by the noise and the aerosol plume (actually it is moisture in the air being condensed) which appears to be coming from the Dewar. When a rupture disc actuates, the noise will drown verbal orders, so make all arrangements for evacuation before this occurs. Evacuate to avoid excessive inhalation of nitrogen. You cannot see or smell nitrogen. The effects of inhalation of nitrogen can range from harmless, to drowsiness, headache, dizziness, excitation, vomiting, moderate respiratory discomfort, or even to death by asphyxiation. Nitrogen gives no warning signs.

Establish a buffer zone around the venting and keep <u>all</u> personnel outside of it. Allow people to enter the buffer zone only if they are equipped with a mask supplied with either breathing oxygen or breathing air. Admit people without breathing apparatus to the area <u>only</u> after venting has stopped and adequate ventilation has resumed.

- 3. Assure adequate ventilation outside the buffer zone. Although nitrogen is not toxic, it can produce death by asphyxiation if it is not mixed with enough air. Liquid nitrogen expands to 3700 times its liquid volume when it becomes a gas and must be diluted with at least ten times that volume of air to reach both a concentration and a temperature that causes minimal health effects. A cubic foot of liquid nitrogen requires the space of a large house to dilute enough that it can have the least severe health effects. Even then health effects would still be noticeable.
- 4. A fire hazard may be present from air frozen on pipes in the presence of combustibles (such as paint). Fire may occur when nitrogen boils off first (it has a lower boiling point than oxygen), leaving behind frozen oxygen which then evaporates and reacts with the combustible material. This requires that plant personnel and firefighters plan in advance how they are to respond when a rupture disk actuation vents the Dewar flask.
- 5. All attempts to save the remaining inventory of liquid nitrogen should be abandoned, because there is chance of asphyxiation, freezing, frostbite, or loss of tissue to surfaces that are not normally cold. The reason for the rupture disc actuation is probably a blockage, since continued flow would have relieved the pressure. This blockage may clear upon thawing.
- 6. Suitable safety equipment (face shields, goggles, aprons, and gloves, etc.) must be worn by everyone near enough to be within range of splashes or spills when handling liquid nitrogen (such as when transferring it between containers). Every person who is near enough to the Dewar to get splashed can experience frostbite or "cold burns" to skin, delicate tissues, and eyes if safety equipment is not properly used. Drops of liquid nitrogen can fly unexpectedly long distances as though shot from a gun, so the safe distance may be much farther than expected.

- 7. Do not allow oxygen in the emission stream to freeze in the condenser. Oxygen and organic compounds frozen together could react violently upon thawing. The only other restriction on suitable organic compounds for cryogenic cooling condensation is that the freezing point of the compound should be below -30°C, to avoid excessive buildup of "frost" in the condenser. This "frost" consists of any water vapor that came through the pre-cooler stage, plus any organic compounds with a higher freezing point than the temperature at that point in the condenser. If it is not collected (or removed) this frost could block heat transfer and block the flow of the emission stream containing organic vapors. The diameter of the tubes is important in defining the schedule for cleaning. This cleaning may be done by flushing the tubes with the liquid organic compound.
- 8. Anyone who receives a "cold burn" or frostbite should promptly seek proper medical attention. Handling high pressure gases or materials at cryogenic temperatures requires special training. Just as important, safe handling requires both that the training be kept current and that the training be used.

HOW MUCH DO THESE SYSTEMS COST?

The Control Cost Manual and the CO\$T-AIR spread sheets (available from the CATC web page at www.epa.gov/ttn/catc) both use the EPA's model for calculating the cost of CFC mechanical compression refrigerated brine chillers for control of organic compounds. A new HFC refrigeration system should cost a similar amount, within the 30% probable error of the cost estimate. However a retrofit might cost more than half the cost of a new system. The adjustment for inflation should be made in accordance with the inflation factors found on the CATC website.

The cost of Reverse Brayton Cycle machines also varies widely. NASA has used some Reverse Brayton Cycle machines on space flights, and EPA has used them to recover solvents from soil remediation projects. The cost of equipment for space does not accurately reflect the price when these systems are used to control organic vapors in a factory. Similarly, soil remediation costs are not often limited by competition. However, NUCON has installed a Reverse Brayton Cycle machine at a 3M Corporation tape coating plant. If the cost of this Reverse Brayton Cycle machine is amortized over 10 years, the sum of operating and capital cost to recover solvent vapors should be about \$300/ton plus labor and maintenance costs. The labor and maintenance costs should be near zero until a breakdown occurs.

The capital cost of a liquid nitrogen condenser for a 500 cfm emission stream is about \$500,000. The operating cost is about 10 kW of electricity and 300 scfm of nitrogen. Using the national average (in 1998) of \$0.084/kW-hr and \$0.50/gal for liquid nitrogen delivered in bulk, we can calculate the operating expense. Based upon a 10 year life for the equipment, and operating two 8 hour shifts per day, the total cost would be in the range of \$200 to \$1000 per ton of organic compound recovered. However, a number of factors had to be assumed in computing this cost. Each facility should determine costs based on their own site-specific circumstances.

Look for the use of liquid nitrogen in a plant: where there is purging of the vapor in a container, where there is blanketing in places where oxidation must be avoided, where low pressure gas must be used for transferring substances between containers, where drying must be accomplished without oxidation, where there is deep freezing of foodstuffs, where grinding is being done in an inert atmosphere, where deburring or grinding of rubber or plastic is being done, where there is shrink fitting of parts, or where there is cooling of blown or molded glass. If liquid nitrogen is used in a plant, the additional expense of using liquid nitrogen for organic vapor control is greatly reduced.

WHAT DOES THE FUTURE HOLD?

What could be coming up next? There are gases other than nitrogen, such as carbon dioxide, that might be more economical to liquefy, and may even be used as a solid. Liquid carbon dioxide or "dry ice" might be an option where it costs less than liquid nitrogen.

A major use for refrigerated condensers today is in dry cleaners to capture either the petroleum or the perchlorethylene dry cleaning fluid vapors. A less commonly known use is in remediation of soils.

In situations such as printing plants and coating operations, large amounts of air mixed with the organic vapors have made use of refrigerated condensers prohibitively expensive. Use of adsorbents to concentrate the organic vapors may allow refrigerated condensers to be more economical where the emission stream is dilute. The hot side of a refrigerated condenser could be used to pump heat into the bed of an adsorber to assist in desorbing the organic compound for recovery on the cold side of the condenser.

In other situations, using a refrigerated condenser on an emission stream containing a mixture of organic vapors results in a mixture of liquid organics that require further processing to separate. Adsorbers might be used to selectively separate each organic compound into its own recovery stream. The hot side of a refrigerated condenser could be used to pump heat into the bed of an adsorber to assist in desorbing the organic compound for recovery on the cold side of the condenser. Alternatively, such mixing might be greatly reduced by using separate condensers at progressively lower temperatures for different organic compounds that condense at temperatures more widely separated than the temperature variations in any single condenser. This separation might provide organic compounds of adequate purity for immediate recycling.

Semi-Volatile Organic Compounds (SVOC) are liquids or solids at room temperature. Use of refrigerated condensers on SVOC have proved difficult because the "frozen" SVOC adheres to the condenser. Perhaps the next step will be to use intermediate higher temperatures which will condense SVOC without freezing them and/or wash off the frozen SVOC with liquid SVOC.

Whatever the next step will be, we can expect that it will address - and maybe solve - at least one of today's problem areas.

CONCLUSIONS

Refrigeration has gone from no moving mechanical parts except fans and brine pumps, to reciprocating pistons, to rotary vane compressors, to rotating gas turbines, and then back to no moving mechanical parts (on-site) except throttling valves. Reliability, toxicology, regulations, and cost were the principal factors driving each of these changes. Each of these options have advantages and disadvantages, and all of these must be considered when selecting any one.

You should be aware of materials that are incompatible with the organic compounds at the temperatures involved, and you should avoid them. You should also be aware of material properties.

While there are hazards associated with the use of this type of equipment, handling CFCs, HFCs, rotating machinery, oil aerosols, and liquid nitrogen are really low in risk, as long as proper training is given and used, the employee is properly equipped, and the proper safety precautions are taken. None of these control technologies would have ever been put into use if the risk in using any of them were too great.

With trained personnel, proper supervision, and adequate precautions, each refrigerated condensation technology can be very safe. Refrigerated condensation can then be an effective and economical control technology.

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TECHNICAL REPORT DATA (Please read Instructions on reverse before completing)					
1. REPORT NO. EPA-456/R-01-004	2.	3. RECIPIENT'S ACCESSION NO.			
4. TITLE AND SUBTITLE		5. REPORT DATE			
Refrigerated Condensers for Control of Organic Air Emissions		December 2001			
		6. PERFORMING ORGANIZATION CODE			
7. AUTHOR(S)		8. PERFORMING ORGANIZATION REPORT NO.			
9. PERFORMING ORGANIZATION NAME AND ADDRESS		10. PROGRAM ELEMENT NO.			
Clean Air Technology Center (E 143-03)					
Information Transfer and Program Integration Division Office of Air Quality Planning and Standards		11. CONTRACT/GRANT NO.			
U.S. Environmental Protection Research Triangle Park, NC					
12. SPONSORING AGENCY NAME AND ADDRESS		13. TYPE OF REPORT AND PERIOD COVERED			
Office of Air Quality Planning and Standards Office of Air and Radiation U.S. Environmental Protection Agency Research Triangle Park, NC 27711		Final			
		14. SPONSORING AGENCY CODE			

15. SUPPLEMENTARY NOTES

For more information, call the CATC Information Line at (919) 541-0800 or access the CATC Web page at www.epa.gov/ttn/catc

16. ABSTRACT

The purpose of this document is to provide information on refrigerated condensers as a control technology to reduce organic air pollution emissions. Several types of refrigerated condensation systems are discussed, including mechanical compression, Reverse Brayton Cycle, and cryogenic cooling. This document describes the different systems, how they work, where they can be used, how effective they are, safety precautions, and how much they cost.

17. KEY WORDS AND DOCUMENT ANALYSIS					
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group			
refrigeration, condensers, mechanical compression, reverse brayton cycle, cryogenic cooling	Air Pollution control, volatile organic compounds, refrigerated condensers				
18. DISTRIBUTION STATEMENT	19. SECURITY CLASS (Report) Unclassified	21. NO. OF PAGES			
Release Unlimited, available from NTIS and the OAQPS TTN Web page	20. SECURITY CLASS (Page) Unclassified	22. PRICE			

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE