ICE-E INFORMATION PACK

Refrigerants

The ideal "one-size-fits-all" refrigerant does not exist.

Table I: Ideal Cycle Performance for Several Refrigerants for Refrigeration.
T_{evap}: -15°C, T_{cond}: 39°C, COP_C=4.78

	q_L	COP	VCC
	kJ kg^{-1}	-	kJ m^{-3}
R-404A	99.9	3.15	1865
R-410A	151.7	3.38	2804
R-32	238.1	3.53	3177
R-290	253.7	3.54	1649
R-134a	134.7	3.59	1116
R-22	150.8	3.68	1946
R-600a	240.5	3.67	603
R-152a	227.1	3.79	1100
R-245fa	142.3	3.76	230
R-717	1058.6	3.82	2081

The working fluid of a refrigeration system is needed to obtain the refrigeration effect with high energy efficiency using components as simple, economic, reliable, and compact as possible.

The refrigerant has to be available at low cost, stable and chemically inert with the common materials used in the plants, and it has also to comply requirements related to safety (non-toxicity, non-flammability and environmental compatibility).

The purpose of a refrigeration system is to transfer thermal energy from a low-temperature source to a high-temperature sink while utilizing the least amount of work, i.e. to maximize the Coefficient of Performance (COP) for a given cooling capacity and for fixed source and sink temperatures.

The ideal cycle for achieving this goal (when both the source and the sink are isothermal) is the Carnot refrigeration cycle. The Carnot refrigeration cycle, however, cannot be realized via practical hardware. Therefore, the widely used reference cycle in practice is based on the so-called ideal vapor compression refrigeration cycle that contains two irreversibilities: (1) isenthalpic expansion and (2) superheating of the compressor discharge vapor (even considering an isoetropic compression process) to realize a constant-pressure heat rejection process in the condenser.

The most common method for evaluating the overall thermodynamic performance of these cycles is based on a First Law of Thermodynamics approach, namely, comparing the Coefficient of Performance (COP) and the Volumetric Cooling Capacity given by the product of the latent heat of vaporization (q_L) and the saturated vapour density at the evaporation pressure.

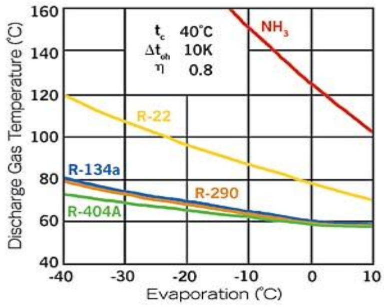
In Table I, values of COP, q_L, VCC are reported for several refrigerants and refrigerant mixtures, assuming constant condensation temperature (39°C) and constant evaporation temperature (-15°C). R404A and ammonia are the most widely used refrigerants in cold sores. Here the main advantages and disadvantages of the use of R404A and R717 (NH_3 – ammonia) in mechanical compression chiller systems for cold stores and food industry will be analyzed in details. The use of ammonia in these applications is growing up in Europe where, however, the use of R404A is quite common, whereas in North America the use of ammonia is somehow predominant, at least in large cold stores.

Note: considerations here proposed for R404A are readily applicable for R507 mixture, being the thermodynamic and thermophysical properties of the two refrigerants pretty similar.

The two fluids (R404A and R717) can be considered almost equivalent for the following reasons:

- Relationship saturation temperature/pressure. It is well known that in a refrigeration system, components which operate below the atmospheric pressure must be avoided, in order to avoid any air seepage (and thus humidity) through any sealing defects; on the other hand,

[1] *It is sufficient to split the gas in the lower part of the condenser and make it bubble in water: any not solubilized bubbles indicate the presence of uncondensable gases.*



Some refrigerants will be more suitable in some applications than others.

Table II: convective heat transfer coefficients range with R404A and ammonia in condensers and evaporators with smooth tubes (values in W/(m^2 K))

	CONDENSATION	
	Internal	External
R404A	950 – 1350	1150 – 1900
R717	4200 – 8500	7500 – 11000
	EVAPORATION	
	Internal	External
R404A	1100 – 2100	1000 – 1500
R717	3100 – 5000	2300 – 4500

a too high pressure at the condenser and at the related components could be a problem from the mechanical point of view. Ammonia and R404A have similar saturation curves, with R717 showing slightly lower saturation pressure, for a given temperature, having a normal boiling temperature of -33.4°C against -45.7°C (dew) or -46.5°C (bubble) for R404A. In terms of non-condensables tightness of the refrigeration system at low temperature, the use of R404A is favorite, though the ammonia behavior in the presence of water traces and the easy monitoring[1], for this fluid, of eventual air at the condenser limit the problems that could be caused by the sub atmospheric pressure of plant components.

- Volumetric cooling capacity. This parameter, with other ones (rotational velocity, volumetric efficiency), establishes the compressor size (displacement) for a given cooling capacity. This datum is very similar for the two fluids in normal operative conditions.

- Thermodynamic efficiency of the reference ideal cycle. For an ideal reference single stage compression cycle and for double stage compression/single stage throttling cycle, ammonia is slightly advantaged, especially at higher boiling temperature, whereas, for the cycle with a two-stage throttling, the use of R404A is more advantageous, especially, at lower boiling temperature. Anyway, differences between the two fluids are so small that they can be considered equivalent from this point of view.

Since the major efficiency lack in the ammonia ideal cycle is due to the remarkable desuperheating of the compressed gas, the recovery of desuperheating heat can be an option for energy recovery.

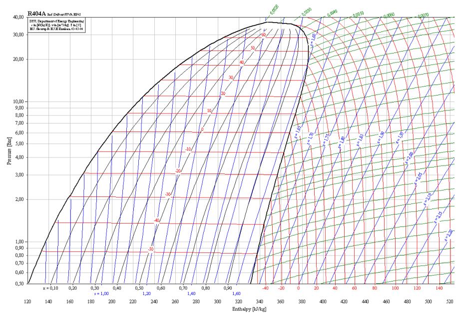
The advantages of ammonia when compared to R404A are the following:

- Cost: in case of purchasing of large quantities, the current cost per kilogram of product of the anhydrous ammonia for refrigeration systems is several times lower than that of R404A. A more meaningful indication of the cost ratio of the refrigerant charge for a plant should be based on the same volume of the liquid phase of the two alternative fluids, and in this case the advantage of the ammonia doubles because R404A has a double density than that of ammonia in the liquid phase.

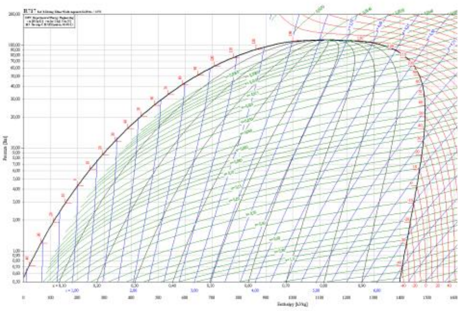
- Heat transfer coefficients: condensation and evaporation are the most important two-phase processes in vapor compressor chiller plants. The refrigerant side convective heat transfer coefficients achievable in condensers and evaporators depend on their geometry and on the particular thermo-fluid dynamic state; the following thermophysical properties of the fluid, listed roughly in order of importance, assume significant influence: thermal conductivity of the liquid phase, density of the liquid phase, latent heat of evaporation, dynamic viscosity and specific heats. The values of all these properties, except the density of the liquid phase, are favorable to ammonia in determining the highest heat transfer coefficients: in particular, the It is not possible to make any generalization, because the achievable value of the overall heat transfer coefficient depends on the different thermal convective resistances; therefore, the overall heat transfer coefficient is not proportional to the refrigerant side one. The best heat transfer performance using ammonia as refrigerant can be advantageously exploited, in comparison with the use of R404A, in a double direction: using equipments with a lower heat transfer area, thus saving plant costs, or diminishing the temperature difference with the external fluids, with an advantage in the plant thermodynamic efficiency and thus saving operating plant costs.
High efficiency surfaces (macro and micro finned surfaces) are now employed to improve the heat transfer performance of R404A.

- Efficiency of the compression process: as pointed out in the relevant info pack (Choice of compressors), ammonia, used in reciprocating compressors, leads to a higher compression isentropic efficiency. The energy saving is relatively modest and from a maximum value of about 10%, it ititidecreases as the pressure ratio

p-h chart for **R404A**



p-h chart for **R717**



decreases as the pressure ratio increases, up to zero at the operating limits of this fluid (pressure ratio of about 10). This behavior can be explained by considering the typical loss mechanisms of the compression process in reciprocating compressors; in fact, ammonia, as compared to R404A, presents lower losses in the fluid throttling through the compressor valves, due to a lower density of the vapor phase, but higher heat transfer losses with metal parts of the compressor in the suction, due to higher temperature of these parts, which is due to a higher superheating of the fluid in the compression. On the other hand, it is easily comprehensible how the first loss is important at low pressure ratio, whereas the second one is important at high pressure ratio.
Also with screw compressors, ammonia has advantages with regard to the compression efficiency, but, unlike reciprocating compressors, the energy saving increases as the pressure ratio increases.

- Plant pipes: the commonly used criterion for the design of pipes (and relative valves) that connect the various components of a refrigeration loop refers to pressure drops related to appropriate corresponding values of saturation temperature drop; with this criterion, different refrigerants can be compared with each others. From this point of view, ammonia is more advantaged than all of the other halogenated refrigerants because it needs pipes with a smaller diameter (both in vapor phase at high or low pressure and in liquid phase in the flooded evaporator fed by pump). For example, at a constant saturation temperature drop, a pipe of a fixed diameter fed by vapor is suitable to the production of a cooling capacity from two to three times higher for ammonia than that for R404A, keeping constant the other conditions. In ammonia systems with extensive network of working fluid distribution, a tube oversizing is often desirable, with a limited initial extra-cost, to take into account any future renovation/enlargement of the store with an increase of the required cooling capacity.

- Behavior in presence of water traces: under normal operating conditions, there could be water traces in the refrigerant either for an imperfect drying of the plant or for seepage in correspondence of leakages in any parts below the atmospheric pressure in the refrigerant circuit. With R404A, water separates and it can freeze at the orifice of the throttling device, thus blocking the operations. On the contrary, with ammonia, water stays in solution (as ammonium hydroxide) and it has not any drawbacks. Water traces should not exceed the concentration of 300 ppm also with ammonia, to avoid any chemical interactions with the lubricating oil, any formation of organic acids with the onset of corrosive phenomena also on iron materials, and any formation of deposits.

Leakage detection: ammonia presence is readily noticeable due to its sour smell already at concentration of 50 ppm in volume in the air; thus, ammonia leakages from a refrigerant plant can be easily noticeable, and the fault can be repaired. It is not uncommon that R404A leakages from a plant become noticeable only when most of the charge is lost, because it is odorless, with relative functional and economic damages. Levels of dangerousness of the two fluids will be discussed in the following.

Behavior with lubricating oil: the behavior between lubricating oil and refrigerants depends on the kind of fluid (ammonia or organic halogenated compound as R404A). With ammonia there is complete immiscibility, whereas with R404A there is complete miscibility with polyolester-oils, although the case of partial miscibility with other kind of synthetic oils could appear. Sometimes it is a question often debated, in different cold production applications, which behavior is better than the other one: anyway, the oil return to compressors must be guaranteed.
In large centralized direct expansion plant for food storage, with flooded evaporators and with scattered utilities, the ammonia behavior with oil is better: the complete non-miscibility eliminates the drawbacks related to the possibility of foaming of the

R404A and R717 can be considered almost equivalent in terms of: relationship saturation temperature/pressure, volumetric cooling capacity, thermodynamic efficiency of the reference ideal cycle.

The advantages of ammonia when compared to R404A are cost, heat transfer coefficient, plant pipes size, behavior in presence of water, leakage detection, environmental compatibility.

The advantages of R404A when compared to ammonia are compatibility with materials, final adiabatic compression temperature, safety.

oil in the crankcase of reciprocating compressors, whereas the few quantities of oil that enter into the refrigerant circuit can be periodically drained by special traps obtained in appropriate points of the plant, where oil deposits due to its higher density than that of the liquid ammonia, and reported to the compressor carter.

- Environmental compatibility: regardless of the possibility of formation of dangerous concentration at the release site, ammonia release does not create any environmental compatibility problems, because, reacting with CO_2 and H_2O in air, it leads to the formation of NH_4HCO_3 (ammonium bicarbonate), which is an harmless washed compound. On the contrary, R404A is under scrutiny for its relatively high greenhouse potential (GWP=3260). Therefore the use of R404A (and other HFCs) in large quantities is bounded by legislation, which is becoming more and more restrictive. Local legislation can be more restrictive than F-gas directive.

The use of R404A can be considered more suitable than that of ammonia for the following reasons:

- Compatibility with structural materials: whereas the use of R404A is fully compatible with common metals (steels, aluminum, copper and its alloys), ammonia (in presence of water traces) is aggressive on copper, zinc and their alloys. Thus, iron is the only suitable material for plants which use ammonia, and the use of traditional hermetic and semi-hermetic compressors is not allowed. In large centralized plants, this restriction has limited importance.

- Final adiabatic compression temperature: as a result of the considerable molar mass diversity of the two fluids (ammonia: M = 17 kg/kmol; R404A: M = 97.6 kg/kmol), at the same conditions, ammonia has a final adiabatic compression temperature which is much higher than that of R404A. Referring to the "Thermodynamic cycles" info pack, the reader may infer that high discharge temperature in general brings about high values of defects of efficiency due to desuperheating.

Moreover, superheating losses are not compensated by the opposite trend of the throttling losses. With reciprocating compressors, this behavior limits the maximum pressure ratio for single stage compression to values lower for ammonia, and often it requires water cooling of the cylinder head, or the use of arrangements as liquid injection in the suction phase. With screw compressors, this aspect of the ammonia behavior is almost negligible, due to the effect of the fluid cooling in the compression phase by the oil which is injected into the compressor.

It has been already noted that the higher ammonia superheating can be an advantage in the cases in which an energy thermal recovery from the superheated vapor is convenient. Using heat recovery from oil coolers on ammonia screw compressor packages is more and more common practice.

Flammability and toxicity: these are certainly the aspects that penalize the ammonia use as refrigerant.

R404A is classified A1 safety group according to ASHRAE ANSI/ASHRAE Standard 34-2010 (Designation and Safety Classification of Refrigerants), whereas R717 is classified B2 (flammable and toxic). The flash point of pure R404A is 728°C and that of ammonia is 630°C.

EN 378 (Refrigerating systems and heat pumps. Safety and environmental requirements) defines "practical limit" as the maximum concentration in an occupied room that does not create acute effects such that it is not possible a prompt evacuation of the occupants.

Practical limit for R404A is 0.48 kg/m^3, whereas for R717 is 0.00035 kg/m^3. On the other hand, ammonia due to its odour will give a warning signal, whereas concentration of R404A may increase without being noticed.