

# **Production of R-134a**

## **Background**

In the 1930's, chlorofluorocarbons (CFC's) were developed as a supposedly safe alternative to ammonia and sulfur dioxide refrigerants. While sulfur dioxide is toxic and ammonia is both toxic and highly flammable, CFC's were found to be nonflammable, nonexplosive, and noncorrosive. CFC's quickly became the compounds of choice for refrigeration as well as for cleaning and foam blowing agents.

However, the discovery of a hole in the ozone layer over Antarctica in 1985 led to a movement to reduce the use of CFC's. Due to their high ozone depleting potential, CFC's were scheduled to be phased out completely by 1996. This led to the need to find alternative refrigerants that are not ozone depleting substances. Some experts have suggested the use of hydrochlorofluorocarbons (HCFC's) for this use. Unfortunately, HCFC's also have some ozone depleting potential, and are scheduled to be banned by 2030. With this in mind, one replacement for CFC's in refrigeration is  $\text{CF}_3\text{CH}_2\text{F}$  (R-134a). R-134a is very attractive as a refrigerant because it has zero ozone depleting potential as well as a low direct global warming potential (GWP).

One factor limiting the use of R-134a had been the fact that conventional lubricants are not miscible with R-134a. However, new lubricants have been developed which allow R-134a systems to run efficiently and reliably long-term. This, along with the need to find refrigerants with a low ozone depleting potential, will greatly increase the market for R-134a in the future.

## **Environmental Significance**

production of an environmentally-friendly product alternative

## Process Description

The BFD and two PFDs shows a process to produce R-134a<sup>1</sup>. Liquid hydrogen fluoride (HF) enters the system at 25°C and 2 atm in Stream 1. It is pumped up to 3 atm by P-201 before being mixed with a recycle stream (Stream 16) consisting of HF, R-133a (CF<sub>3</sub>CH<sub>2</sub>Cl), R-134a (CF<sub>3</sub>CH<sub>2</sub>F), and trichloroethylene (TCE). The mixed stream (Stream 3) then enters H-201 where it is heated to 400°C before being fed to the R-134a reactor R-201. This isothermal plug-flow reactor converts 99.3% of the R-133a to R134a. The heat of reaction is removed from the process by means of a Dowtherm<sup>TM</sup> A cooling loop.

The product stream of R-201 (Stream 5) is then mixed with a feed of TCE (Stream 8). The mixed stream (Stream 9) is then fed through E-203 where it is cooled to 290°C. R-202 next converts HF and TCE to R-133a and hydrochloric acid (HCl). R-202 is quite similar in operation to R-201, including the use of a Dowtherm loop to remove the heat of reaction.

Stream 10 leaves R-202 and is then sent to E-205 where it is cooled to 30°C to reduce the costs associated with C-201. C-201 compresses the stream adiabatically to 9.8 atm, with a temperature increase to 595°C. The stream is then cooled to 30°C by E-206. The cooled stream (Stream 13) is then fed to T-201, the first of three distillation towers. T-201 operates at 9 atm, with the distillate temperature being 0.1°C and the bottoms temperature being 88.5°C. The reboiler uses low-pressure steam, with the bottom stream being recycled and mixed with the HF feed. The condenser uses a refrigerant mixture produced on site and processed in a refrigeration loop (not shown). In the loop, the refrigerant mixture removes heat from the process in the condensers of the towers. It is then compressed, cooled, and throttled back to the initial pressure.

The distillate (Stream 14) from T-201 consists mainly of R-134a, HCl, R-125, R-143a, and R-23. This stream is next compressed in C-202 to 20 atm before being fed into T-202. Here, R-

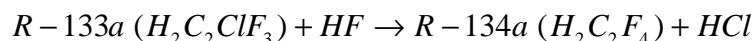
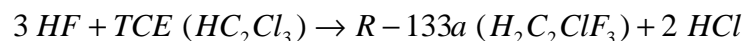
134a and trace amounts of HCFC-1133 are removed from the rest of the refrigerants and the HCl. The 99.99% pure R-134a bottom stream (Stream 20) is then fed to a zeolite column (A-201 A/B) where the toxic HCFC-1133 is adsorbed. A-201 A/B is two zeolite columns in parallel. This allows for continuous operation, with one operating while the other is being regenerated. E-207 then cools the R-134a to 40°C before P-205 pumps the stream to 28 atm (Stream 23) for storage.

The distillate from T-202 (Stream 19) is then sent to T-203 where HCl and R-23 are removed from the refrigerant mixture. The refrigerant mixture obtained as the bottoms from T-203 (Stream 25) is cooled in E-208 to 15°C and pumped to 25 atm in P-206. It is then stored.

The distillate of T-203 (Stream 24) contains mainly HCl and R-23. The HCl is absorbed into water in T-204. The result is a stream of HCl in water that is 99.99% pure HCl at a concentration of 35.12 weight percent (Stream 30) which is stored. The unwanted R-23 stream (Stream 29) is sent to the waste incineration facility.

### **Necessary Information and Simulation Hints**

R-134a is produced by the following series of reactions:



These reactions are based on limited data found in US Patent 5,243,105. It was determined that the activation energies for the two main reactions were as follows:

167 kJ/mol for TCE to R-133a

237 kJ/mol for R-133a to R-134a

Using data from the patent the rate constants were determined from the following equations:

$$-r_A = kC_A C_B$$

$$\tau = C_{A0} \int \frac{dX}{-r_A}$$

These were found to be:

$$k = 10.94 \text{ l/(mol s)} \text{ for R-133a to R-134a}$$

$$k = 11.82 \text{ l/(mol s)} \text{ for TCE to R-133a}$$

and the preexponential factors were found to be:

$$A = 6.5 \times 10^{18} \text{ l/(mol s)} \text{ for TCE to R-133a}$$

$$A = 5.5 \times 10^{20} \text{ l/(mol s)} \text{ for R-133a to R-134a}$$

These values account for the two primary reactions for the process. However, the patent demonstrated that side reactions also occur in the R-134a reactor. This has been accounted for by adding a component separator and a small feed stream to the simulation immediately following this reactor, specified to correlate with the patent.

A major difficulty in simulating the process outlined in the patent is the lack of available data for R-133a. The simulation is based on R-133a as a user-added component, with all properties based on the normal boiling point<sup>2</sup> and the UNIFAC group contribution method. All simulations were run using ideal vapor pressure for  $K$  values and latent heat for enthalpy except for the HCl absorber (T-204). In T-204, PPAQ (partial pressure aqueous) was used for the  $K$  values which automatically accesses the library heats of solution for enthalpies (in Chemcad).

The nomenclature for refrigerants is as follows. For saturated hydrocarbon refrigerants, the nomenclature is R $xyza$ . The  $a$  denotes a specific stereoisomer. The  $x$  is the number of carbons minus one (which means  $x = 0$  for old, single-carbon refrigerants). The  $y$  is the number of hydrogens plus one, and the  $z$  is the number of fluorines. The remaining number of atoms needed to saturate the molecule are chlorines. Therefore, R-134a has two carbons, two hydrogens, 4

fluorines, and no chlorines. R-133a has two carbons, one hydrogen, one fluorine, and one chlorine. R-125 has two carbons, one hydrogen, and five fluorines.

### **Equipment Descriptions**

P-201 A/B	HF Pumps
H-201	Fired Heater
P-202 A/B	TCE Pumps
E-201	TCE Vaporizer
R-201	R-134a Reactor
P-203 A/B	R-134a Reactor Dowtherm Pump
E-202	R-134a Reactor Dowtherm Cooler
E-203	R-133a Reactor pre-cooler
R-202	R-133a Reactor
P-204 A/B	R-133a Reactor Dowtherm Pump
E-204	R-133a Reactor Dowtherm Cooler
E-205	Reactor Effluent Cooler
C-201	Compressor
E-206	Reactor Effluent Cooler
T-201	TCE Recycle Tower
E-209	TCE Tower Condenser
V-201	TCE Tower Reflux Vessel
P-207 A/B	TCE Tower Reflux Pumps
E-210	TCE Tower Reboiler
C-202	Compressor

T-202	R-134a Tower
E-211	R-134a Tower Condenser
V-202	R-134a Tower Reflux Vessel
P-208 A/B	R-134a Tower Reflux Pumps
E-212	R-134a Tower Reboiler
A-201	HCFC 1122 Adsorber
T-203	Mixed Refrigerants Tower
E-213	Mixed Refrigerants Tower Condenser
V-203	Mixed Refrigerants Tower Reflux Vessel
P-209 A/B	Mixed Refrigerants Tower Reflux Pumps
E-214	Mixed Refrigerants Tower Reboiler
E-207	R-134a Cooler
P-205 A/B	R-134a Pumps
E-208	Refrigerant Mixture Cooler
P-206 A/B	Refrigerant Mixture Pumps
T-204	HCl Absorber

## References

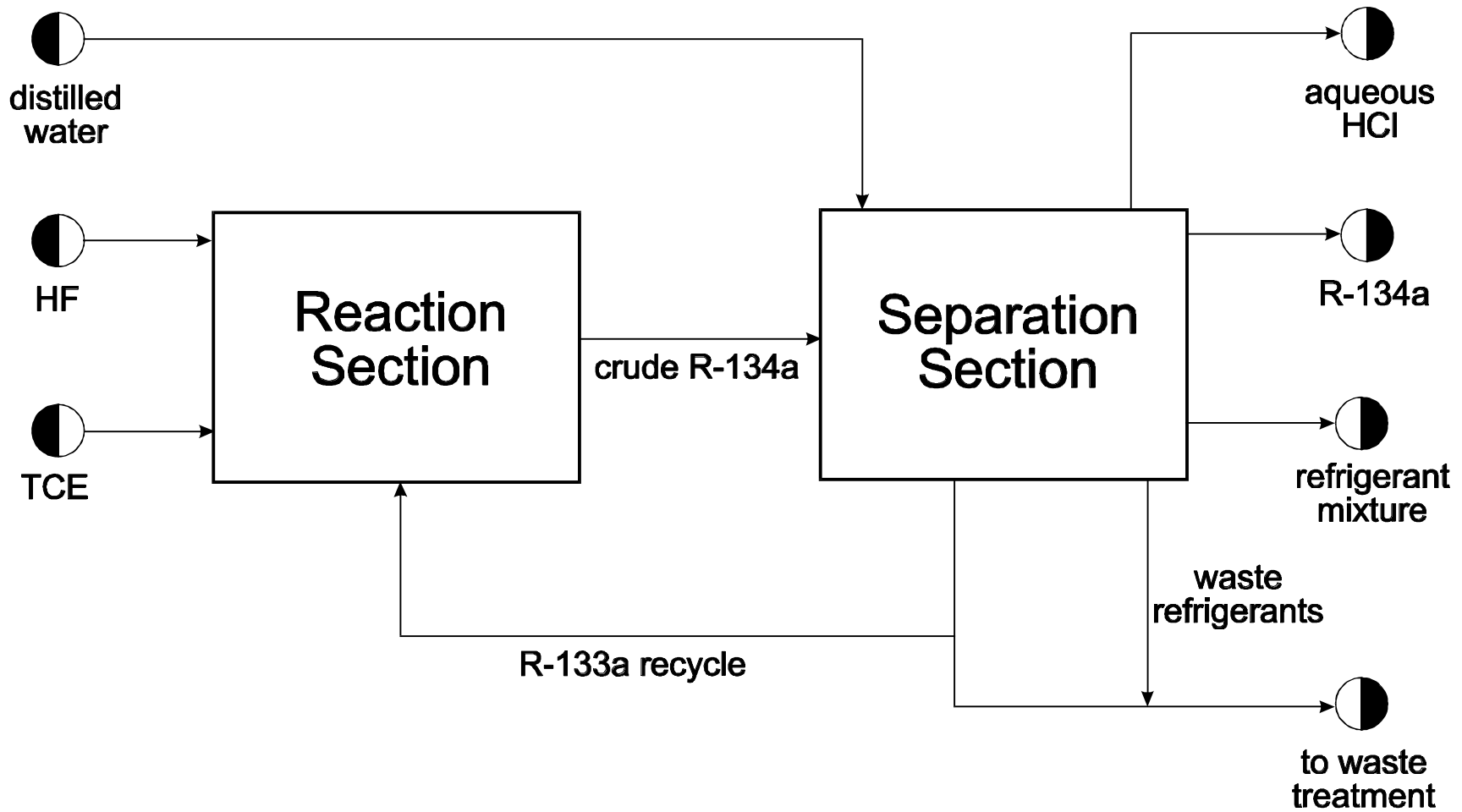
1. Scott, John D. and Racheal Steven. U.S. Patent 5,243,105. Imperial Chemical Industries. 1993
2. Chemfinder Web Site

## Stream Flow Table for R-134a Production

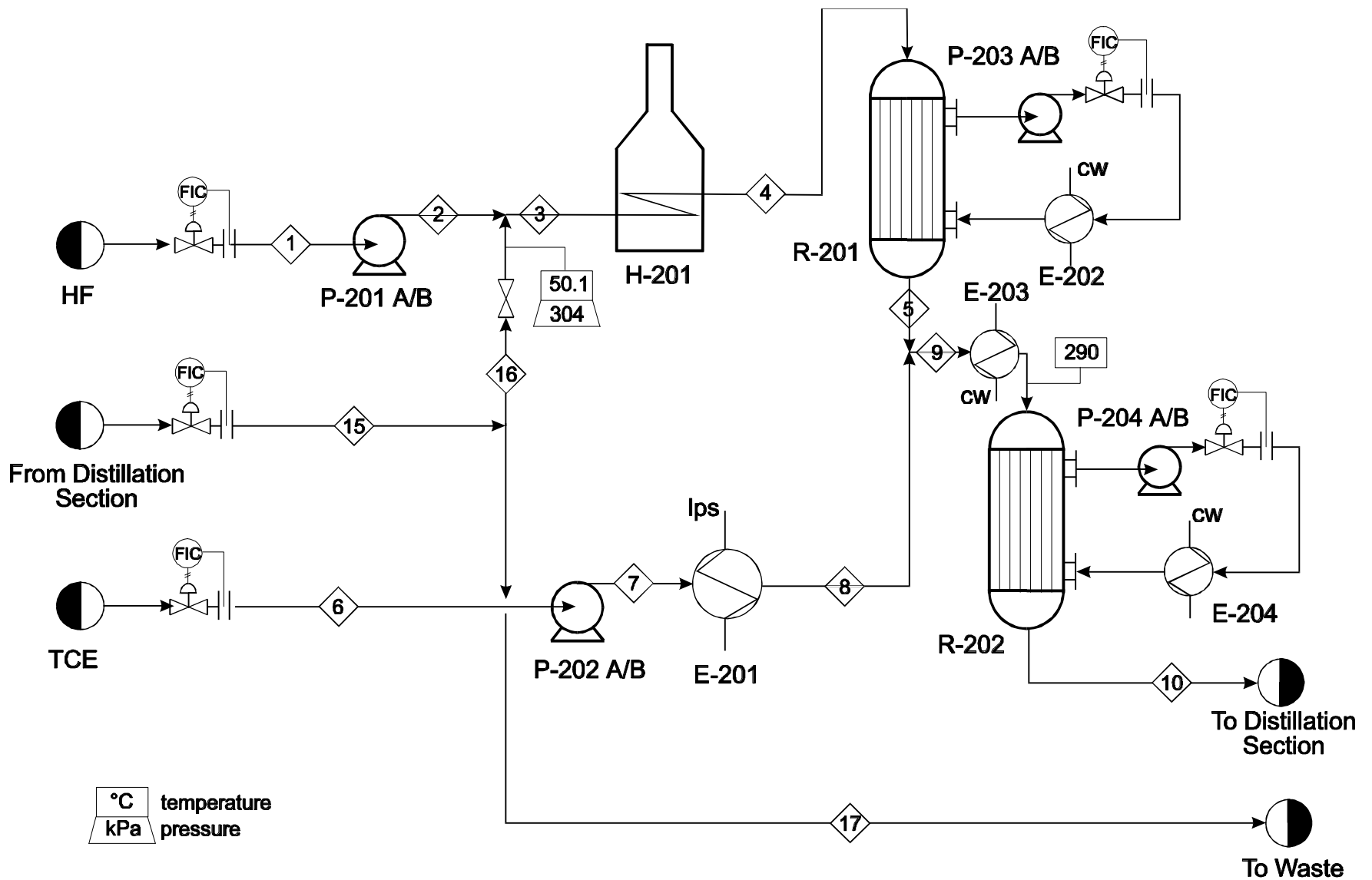
Stream No.	1	2	3	4	5	6	7	8	9	10
Temperature (°C)	25.0	25.1	51.3	400.0	399.3	25.0	25.0	114.9	290.0	290.0
Pressure (kPa)	202.6	304.0	304.0	263.4	243.2	202.6	222.9	222.9	222.9	1.6
Vapor mole fraction	0.0	0.0	0.1	1.0	1.0	0.0	0.0	1.0	1.0	1.0
Total Flow (kg/h)	1833.4	1833.4	7220.8	7220.8	7222.7	2924.8	2924.7	2924.7	10147.5	10147.6
Total Flow (kmol/h)	91.6	91.6	236.2	236.2	234.7	22.3	22.3	22.3	257.0	234.7
Component Flowrates (kmol/h)										
1112-4F-Ethane	--	--	3.6	3.6	23.9	--	--	--	23.9	23.9
TriCl-Ethylene	--	--	0.2	0.2	0.2	22.3	22.3	22.3	22.4	0.2
Hydrogen Fluoride	91.6	91.6	210.3	210.3	186.8	--	--	--	186.8	120.1
Hydrogen Chloride	--	--	0.001	0.001	21.8	--	--	--	21.8	66.3
111-3F-Ethane	--	--	0.001	0.001	0.2	--	--	--	0.2	0.2
PentaF-Ethane	--	--	0.006	0.006	1.5	--	--	--	1.5	1.5
Trifluoromethane	--	--	--	--	0.2	--	--	--	0.2	0.2
Water	--	--	--	--	--	--	--	--	--	--
R-133A	--	--	22.2	22.2	0.2	--	--	--	0.2	22.4

Stream No.	11	12	13	14	15	16	17	18	19	20
Temperature (°C)	30.0	594.8	30.0	5.38	92.8	50.1	92.8	75.6	-6.2	78.3
Pressure (kPa)	1.6	993.0	993.0	932.2	952.5	304.0	952.5	2026.5	2026.5	2046.8
Vapor mole fraction	1.0	1.0	0.2	1.0	0.0	0.2	0.0	1.0	1.0	0.0
Total Flow (kg/h)	10147.6	10147.6	10147.6	4698.8	5447.9	5387.4	60.5	4698.8	2619.5	2079.3
Total Flow (kmol/h)	234.7	234.7	234.7	88.5	146.2	144.5	1.6	88.5	68.1	20.4
Component Flowrates (kmol/h)										
1112-4F-Ethane	23.9	23.9	23.9	20.3	3.6	3.6	0.04	20.3	0.002	20.3
TriCl-Ethylene	0.2	0.2	0.2	--	0.2	0.2	0.002	--	--	--
Hydrogen Fluoride	120.1	120.1	120.1	--	120.0	118.6	1.3	--	--	--
Hydrogen Chloride	66.3	66.3	66.3	66.3	0.001	0.001	--	66.3	66.3	--
111-3F-Ethane	0.2	0.2	0.2	0.2	0.001	0.001	--	0.2	0.2	0.002
PentaF-Ethane	1.5	1.5	1.5	1.5	0.006	0.006	0.0001	1.5	1.5	0.005
Trifluoromethane	0.2	0.2	0.2	0.2	--	--	--	0.2	0.2	--
Water	--	--	--	--	--	--	--	--	--	--
R-133A	22.4	22.4	22.4	0.02	22.4	22.2	0.2	0.02	--	0.02





R-134a Production Block Flow Diagram



R-134a Reaction Section

