

## 5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

### 5.1 PRODUCTION

Tetrachloroethylene is a commercially important chlorinated hydrocarbon solvent and chemical intermediate. It is used as a dry cleaning and textile-processing solvent and for vapor degreasing in metal-cleaning operations. Tetrachloroethylene was first commercially produced in the United States in 1925 via a four-step process using acetylene and chlorine as raw materials (IARC 1979). By 1975, only one U.S. plant was using this process because of the high cost of acetylene.

Currently, the majority of tetrachloroethylene produced in the United States is made by one of three processes: direct chlorination of certain hydrocarbons, chlorination of ethylene dichloride, and oxychlorination. The first process involves the reaction of chlorine with a hydrocarbon such as methane, ethane, propane, or propylene at high temperatures, with or without a catalyst. A chlorinated derivative of a hydrocarbon may also be used. The reaction forms a crude product, which can be purified to yield a marketable grade of tetrachloroethylene. This is easier and more economical than the acetylene process. In addition, the hydrocarbon wastes from other processes can subsequently be used as feedstocks for this process. However, large quantities of hydrogen chloride can be produced. The second process, chlorination of ethylene dichloride, involves noncatalytic chlorination of ethylene dichloride or other C<sub>2</sub> chlorinated hydrocarbons. The third process, oxychlorination of ethylene via ethylene dichloride, is widely used to coproduce trichloroethylene and tetrachloroethylene without any net production of hydrogen chloride (Chemical Products Synopsis 1985; Keil 1985; Hickman 2000).

In 1993, the manufacture of tetrachloroethylene via reaction of a hydrocarbon having three or less carbon atoms with a partially chlorinated hydrocarbon, chlorine gas, and carbon tetrachloride at 500–700°C was proposed in a patent. The introduction of carbon tetrachloride to the reaction in a closed system (as opposed to it being formed in the reaction) was to monitor and prevent carbon tetrachloride production in the manufacturing of tetrachloroethylene (Hoshino et al. 1993).

Tetrachloroethylene is produced in the following grades: purified, technical, U.S. Pharmacopoeial (USP), spectrophotometric, and dry cleaning (ACGIH 1991). The dry cleaning and technical grades meet specifications for technical grade, differing only in the amount of stabilizer added to prevent decomposition. Stabilizers, which include amines or mixtures of epoxides and esters, are added to prevent decomposition. Tetrachloroethylene, which is thus stabilized and not easily hydrolyzed, is transported in tanks and drums (ACGIH 1991).

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Historical U.S. production volumes of tetrachloroethylene have been reported as follows (C&EN 1994): 547 million pounds in 1983 and 271 million pounds in 1993, respectively. These data show that there was an overall decline of about 50% between 1983 and 1993. According to the U.S. EPA Inventory Update Reporting for 2006, the total U.S. production volume of tetrachloroethylene was between 500 million and < 1 billion pounds (EPA 2013f). The overall demand for tetrachloroethylene was expected to grow at a rate of approximately 1.5% per year from 2007 to 2011 (CMR 2008), but data show that the total annual capacity has decreased. In 2011, the directory of chemical producers in the United States listed three major manufacturers with a total annual capacity of 458 million pounds (SRI 2011).

Some of the facilities that manufactured or processed tetrachloroethylene in 2011 are listed in Table 5-1 (TRI11 2013). Toxics Release Inventory (TRI) data should be used with caution since only certain types of industrial facilities are required to report. This is not an exhaustive list.

Tetrachloroethylene was reported to be produced naturally by several temperate and subtropical marine macroalgae at the rate of 0.0026–8.2 ng/g fresh weight/hour. These species of algae have also been reported to produce trichloroethylene, usually at greater rates. It should be noted, however, that there are results that show that tetrachloroethylene was not detected in cultures of the same algae when the methods of Abrahamsson et al. (1995) were done in the laboratory (Murphy et al. 2000).

## 5.2 IMPORT/EXPORT

In 1990, about 75.0 million pounds of tetrachloroethylene were imported into the United States, and in 2012, about 26.5 million pounds were imported in the United States (USITC 2013). Exports from the United States were about 55.1 million pounds in 1990 and about 83.8 million pounds in 2012 (USITC 2013).

## 5.3 USE

Tetrachloroethylene is commercially important as a chlorinated hydrocarbon solvent and as a chemical intermediate. An estimate of the current end-use pattern for tetrachloroethylene is as follows: 60% for chemical intermediate, 18% for dry cleaning and textile processing, 18% for surface preparation and

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**Table 5-1. Facilities that Produce, Process, or Use Tetrachloroethylene**

State <sup>a</sup>	Number of facilities	Minimum amount on site in pounds <sup>b</sup>	Maximum amount on site in pounds <sup>b</sup>	Activities and uses <sup>c</sup>
AL	3	1,000	99,999	2, 3, 12
AR	5	1,000	999,999	9, 10, 11, 12
CA	21	0	99,999,999	1, 3, 4, 6, 7, 9, 10, 11, 12
CO	2	10,000	99,999	12, 14
CT	1	10,000	99,999	9
DE	1	10,000	99,999	10
FL	1	10,000	99,999	11
GA	9	1,000	999,999	7, 9, 12, 14
HI	1	1,000	9,999	10
IA	1	100,000	999,999	7, 9
IL	10	100	999,999	7, 9, 10, 11, 12
IN	11	100	9,999,999	1, 2, 7, 9, 10, 12, 13, 14
KS	12	0	999,999	1, 2, 3, 4, 7, 8, 9, 10, 11, 12, 13, 14
KY	4	10,000	999,999	1, 3, 6, 9, 12
LA	22	0	499,999,999	1, 2, 3, 4, 5, 6, 7, 9, 10, 11, 12, 13
MA	5	1,000	99,999	2, 3, 9, 11, 12
MI	4	100	999,999	1, 5, 7, 10, 12
MN	4	10,000	999,999	6, 10, 11, 12
MO	7	100	99,999	7, 9, 11, 12
MS	2	10,000	999,999	7, 10
MT	3	0	99,999	10, 12
NC	2	100,000	999,999	7, 9
ND	1	1,000	9,999	10
NE	2	10,000	99,999	7, 12
NJ	2	10,000	99,999	2, 3, 8, 9, 10, 12
NM	1	10,000	99,999	10
NY	7	100	999,999	2, 4, 9, 10, 12, 14
OH	15	100	9,999,999	2, 3, 7, 9, 11, 12, 14
OK	5	1,000	99,999	6, 10, 11, 12
OR	2	1,000	99,999	10, 12
PA	12	1,000	9,999,999	2, 3, 7, 8, 9, 10, 11, 12
RI	1	100,000	999,999	7, 9
SC	2	10,000	99,999	11, 12
TN	2	100	99,999	2, 3, 6, 9, 10, 12
TX	45	0	499,999,999	1, 2, 3, 4, 5, 6, 7, 9, 10, 11, 12, 13, 14
UT	3	10,000	999,999	10, 12
VA	1	10,000	99,999	12
VI	1	100,000	999,999	10

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State <sup>a</sup>	Number of facilities	Minimum amount on site in pounds <sup>b</sup>	Maximum amount on site in pounds <sup>b</sup>	Activities and uses <sup>c</sup>
WA	6	100	999,999	2, 4, 7, 9, 10, 11, 14
WI	6	10,000	99,999	7, 9, 11, 12
WY	1	100	999	10

<sup>a</sup>Post office state abbreviations used.

<sup>b</sup>Amounts on site reported by facilities in each state.

<sup>c</sup>Activities/Uses:

- |                          |                             |                            |
|--------------------------|-----------------------------|----------------------------|
| 1. Produce               | 6. Reactant                 | 11. Manufacturing Aid      |
| 2. Import                | 7. Formulation Component    | 12. Ancillary/Other Uses   |
| 3. Onsite use/processing | 8. Article Component        | 13. Manufacturing Impurity |
| 4. Sale/Distribution     | 9. Repackaging              | 14. Process Impurity       |
| 5. Byproduct             | 10. Chemical Processing Aid |                            |

Source: TRI11 2013 (Data are from 2011)

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cleaning, 2% for oil refining catalyst regeneration, and 2% for miscellaneous use (Dow 2008). Beginning in 2020, federal regulations are scheduled to begin eliminating the use of tetrachloroethylene in dry cleaning in urban locations (CMR 2008).

In textile processing, tetrachloroethylene is used as a scouring solvent that removes oils from fabrics after knitting and weaving operations, as a carrier solvent for sizing and desizing, and for fabric finishes and water repellents. Tetrachloroethylene is able to dissolve fats, greases, waxes, and oils without harming natural or human-made fibers. However, because of the growing popularity of wash-and-wear fabrics, improved efficiency of dry cleaning equipment, and increased chemical recycling, the demand for tetrachloroethylene as a dry cleaning solvent has steadily declined (EPA 1995). There are three types of tetrachloroethylene dry cleaners as regulated by the EPA's Clean Air Act: large industrial and commercial dry cleaners; freestanding small dry cleaners; and small dry cleaners in apartment buildings. The EPA has required operators to reduce emissions from dry cleaners and has enforced a final rule on the phase out of tetrachloroethylene use in dry cleaners that are in residential areas by December 21, 2020 (EPA 2006). Currently, approximately 28,000 U.S. dry cleaners use tetrachloroethylene (EPA 2013g).

Another major use of tetrachloroethylene is as a vapor and liquid degreasing agent. Since tetrachloroethylene dissolves many organic compounds, select inorganic compounds, and high-melting pitches and waxes, it can be used to clean and dry contaminated metal parts and other fabricated materials. It is also used to remove soot from industrial boilers (Verschueren 1983). Tetrachloroethylene was used as an anthelmintic in the treatment of hookworm and some nematode infestations, but it has been replaced by drugs that are less toxic and easier to administer (Budavari 1989; HSDB 2013).

#### 5.4 DISPOSAL

The chemical industry has responded to increased environmental and ecological concerns with efforts to improve recovery and recycling of tetrachloroethylene. One method of disposal involves absorption in vermiculite, dry sand, earth, or a similar material and then burial in a secured sanitary landfill (HSDB 2013). A second method involves incineration after mixing with another combustible fuel. With the latter method, combustion must be complete to prevent the formation of phosgene, and an acid scrubber must be used to remove the haloacids produced. The gas-fired type of incinerator is optimal for the total destruction of tetrachloroethylene (HSDB 2013).

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Tetrachloroethylene is also a potential candidate for fluidized bed incineration at 450–980°C, rotary kiln incineration at 820–1,600°C, and liquid injection incineration at 650–1,600°C (HSDB 2013).

Federal regulations prohibit land disposal of various chlorinated solvent materials that may contain tetrachloroethylene. Any solid waste containing tetrachloroethylene must be listed as a hazardous waste unless the waste is shown not to endanger the health of humans or the environment (EPA 1985b, 1988). Destruction and removal efficiency of tetrachloroethylene that is designated as a principal organic hazardous constituent must be 99.99%. Discharge of tetrachloroethylene into U.S. waters requires a permit (WHO 1987). Before implementing land disposal of waste residue, environmental regulatory agencies should be consulted for guidance on acceptable disposal practices (HSDB 2013).