Industrial Emissions of 1,3-Butadiene by James A. Mullins*

Sources of industrial emissions of 1,3-butadiene are discussed both by process (production, consumers) and type (equipment leaks, point sources). Quantification of the emissions are presented, as reported by the U.S. Environmental Protection Agency in 1986. The reported emissions attributed to equipment leaks (also known as fugitive emissions) range from about 50 to 95% of the total, depending on the specific production process used. The methods by which these emissions were estimated are discussed, with particular emphasis on the fugitive sources. Industry studies to better quantify the fugitive emissions are described.

The previous paper discussed the production and uses of 1,3-butadiene. In this paper, a perspective is given on the atmospheric emissions of 1,3-butadiene resulting from these operations, both by the production process involved and by the specific types of operations that are potential sources of emissions. For the past few years the United States Environmental Protection Agency (USEPA) has been considering the need to establish regulations covering the emissions of 1.3-butadiene to the atmosphere under its Hazardous Air Pollutant program. As a part of that study, the USEPA collected emissions data from most of the producers and users of 1,3-butadiene. The data collected covered the year 1984 and serves as the primary basis for the material in this presentation. The paper describes available updated information and some of the industries' current activities that provide more accurate information about emissions resulting from equipment leaks.

Production of 1,3-butadiene in the United States is approximately 2.7 billion pounds per year almost totally as a by-product of ethylene production. Imports of 1,3-butadiene are about 0.5 billion pounds per year. Emissions to the atmosphere from the U.S. production segment, based on the 1984 USEPA survey (1), were approximately 3.8 million pounds per year or 0.14% of the amount produced. Equipment leaks were reported to be in 99.5% of these emissions.

The largest consumption of 1,3-butadiene (1.4 billion pounds in 1986) is for the production of styrene-butadiene copolymers, which accounts for over 40% of the total. In its study, EPA estimated that the total emissions of 1,3-butadiene to the atmosphere from this category were approximately 5 million pounds per year (2) or 0.3% of the amount consumed. Of this total, about 50% were attributed to equipment leaks and 50% to process venting. Based on recent information from several producers, some plants have been shut down and several have installed control devices on their process

vents that have reduced the 1984 reported emissions by 80 to 90%. It seems likely that losses due to process vents in this category may now be only about 50% of those reported by the industry for 1984.

The next largest category of 1,3-butadiene consumption is in the production of polybutadiene. This process consumed about 730 million pounds in 1986, or 23% of the total United States consumption. Based on the information submitted by eight of the ten polybutadiene producers in 1984, total atmospheric emissions of butadiene amounted to 900,000 pounds (3) or about 0.12% of the butadiene consumed for the year. Of this amount, 98% was reported to be equipment leaks.

While the above two consumption categories account for only about two-thirds of the total United States consumption, the remaining consumer categories, with the possible exception of neoprene/chloroprene, are not reported to have significant 1,3-butadiene emissions. In the case of neoprene/chloroprene, again the reported emissions of 1,3-butadiene are nearly all attributable to equipment leaks and amount to about 86,000 pounds per year or about 0.03 of 1% of the 1,3-butadiene consumption.

Table 1 summarizes the emission information just discussed. As indicated, the emissions, as reported by the USEPA, are mostly attributable to equipment leaks.

Losses of 1,3-butadiene because of storage and shipping are negligible since the material is stored and shipped as a liquid under pressure in vessels that are designed to contain the material under all normal conditions.

Table 1. 1,3-Butadiene emissions.

Source category	Equipment leaks		Process vents	
	Mm/lb/yr	% Feed	Mm/lb/yr	% Feed
BD production	3.8	0.14	0.013	< 0.001
SB copolymer	2.4	0.17	2.8	0.20
Polybutadiene	0.89	0.12	0.02	0.003
Chloroprene/neoprene	0.09	0.03	_	
Total	7.2	0.14	2.82	0.05

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To gain a better understanding of the meaning of equipment leaks, the difficulty in quantifying emissions of this type, the basis of the current USEPA emission estimates, and the industry position and activities to gain a better understanding of these estimates, the rest of this paper will be devoted to discussing equipment leaks, sometimes referred to as fugitive emissions.

Equipment leaks occur as the result of imperfect sealing at connections such as flanges, screwed fittings, sealing surfaces on rotating equipment such as pumps and compressors, and at devices designed to protect equipment from overpressure such as relief valves. The category also includes losses that may occur as the result of sampling process streams for quality control. Over the past several years, as the control of point sources such as process vents has been improved, the significance of equipment leaks as a potential major source of emissions to the atmosphere has increased. Because of this, the EPA in the mid-to-late 1970s conducted studies attempting to quantify these emissions. The primary thrust of the studies was the petroleum refining industry.

As a result of these studies, the USEPA developed average emission factors for the various types of equipment that could then be applied to large refining facilities. The approach was to use portable analyzers to measure the concentration of total organic material at the sealing surface such as the flange, valve stem packing, and pump or compressor seal. The measured concentration was then related to a mass emission rate by enclosing the leaking source in a bag and measuring the actual mass of organic material collected over a period of time. A large number of sources were studied at different refinery installations and average emission factors were developed for each type of source. Thus, it was concluded that in the typical refinery, all that one needed to do to determine emissions was count the number of sources of each type, multiply that number by the average emission factor for that type of source, and sum up the total organic emissions for the entire installation. Additional studies were run at a number of organic chemical process units and some adjustments were made in the average factors that were then applied to all chemical process units such as those producing and consuming 1,3-butadiene. In its 1984 study of 1,3butadiene emissions, the USEPA collected data from the industry on the number of potential equipment leak sources by type, and it applied the average emission factors, although some adjustments were made if the plant was located in an area where state regulations required a leak detection and repair program for these type of sources. This was the basis for the emission estimates previously discussed.

For some time the chemical industry has maintained

that the above-described method for estimating fugitive emissions is not valid when its is applied to specific installations that handle materials recognized as potentially toxic. Also, this method of estimation does not recognize the improvements made in the past 5 to 8 years in equipment design and maintenance practices. A number of 1,3-butadiene producers conducted screening studies to develop alternate emission rates for 1,3-butadiene. The Chemical Manufacturers Association also began developing a study protocol designed to provide better estimates of equipment leak emissions from the chemical process industry in general.

The emission estimates developed by two 1,3-butadiene producers for equipment leaks indicated that the average factor approach used to develop the emission estimates, published by the USEPA, could result in overstating the emissions by a factor of four to five. Since these estimates were developed by methods not fully approved by the USEPA and were from only two of the twelve producing facilities, the USEPA did not revise its estimates. Because the currently published information indicates that the most significant sources of 1,3-butadiene emissions result from equipment leaks, the industry, through the Chemical Manufacturer's Association, and the USEPA have agreed on a protocol for developing new equipment leak emission estimates. Plans are currently underway for the majority of 1,3butadiene producers to undertake the study and provide the revised emission estimates to the EPA later this

It is believed that this newer data will provide EPA with the best information available on 1,3-butadiene emissions, which can then be used for estimating the exposure of the public to 1,3-butadiene. Exposure estimates derived from dispersion modeling should be verified by actual monitoring data if possible. Coupled with the health data, which is the primary topic of this symposium, realistic risk management decisions can then be made on the need and/or degree of controls required to provide adequate health protection.

REFERENCES

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