

4. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

During the 1970s EPA moved to phase out leaded gasolines and to reduce the levels of air pollution from pre- or post-combustion vehicular emissions. This conversion to unleaded fuels tended to reduce the octane ratings. Additives such as benzene or toluene could increase octane levels, but these aromatic volatile organic compounds could lead to serious air pollution problems due to their known toxic properties. Various highly oxygenated blending agents, including several ethers and alcohols, can boost the octane of unleaded gasoline and, since they are less toxic, can mitigate many of the air pollution concerns. MTBE is one such product used in Reformulated Gasoline (RFG). Some states started requiring the seasonal use of RFGs in the 1970s, and this became a requirement for many parts of the country under provisions of the 1990 Clean Air Act. This requirement led to a rapid expansion in the production and use of MTBE starting in the late 1980s.

4.1 PRODUCTION

Typical production processes use feedstocks like isobutylene, often in combination with methanol, in adiabatic fixed reactors. The isobutylene and methanol react in the presence of ion-exchange resin catalysts at medium pressures and temperatures. Highly volatile by-products are removed through distillation, and methanol is reclaimed using water washing or molecular sieves. In a variant of this basic technology called reaction distillation, the catalysis and distillation steps take place simultaneously (Shanely 1990). There are numerous variants in these manufacturing processes, the details of which are protected under patents or license agreements (Lorenzetti 1994; Rhodes 1991).

Until the late 1980s isobutylene and other feedstocks could be readily obtained from existing refinery operations. With minor investments, these refineries could add MTBE production with yields in the range of 8,000-20,000 barrels per day. As demand for MTBE increased, large specialized production facilities were built. These larger specialized plants account for the vast majority of domestic production (Lorenzetti 1994). These plants are often close to other refineries, pipelines, or navigation shipping terminals. For instance, about 70% of the entire salable production capacity for MTBE is concentrated along the Houston Ship Channel near Beaumont, Texas (Anonymous 1992b). As MTBE production capacity begins to outreach the supplies of such feedstocks as isobutylene, various processes are being added to the conventional plant design to tap other petrochemical feedstocks. These processes include dehydrogenation of isobutane, dehydration of isobutanol, ethenolysis of branched alkenes, and catalytic

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isomerization of butenes or butane. A drawback to some new technologies is the production of large quantities of methyl isobutyl ether (MIBE), a low-octane MTBE isomer (Nicolaidis et al. 1993).

Nearly all the MTBE produced in the United States is used as octane boosters and oxygenating agents in reformulated gasoline, and these uses are the only ones for which reliable production figures are readily available. Starting in the late 1980s MTBE production increased rapidly. The 1990 Clean Air Act created a guaranteed market of some 400,000 barrels per day for all types of reformulated fuel oxygenated additives. Since other ingredients such as ethanol and other ethenes are alternative reformulation additives, MTBE is expected to command a market share of at least 250,000 barrels (about 64.8 million pounds or 29.4 million kg) per day (Lorenzetti 1994). Estimated production capacity in the United States during 1995 was 240,100 barrels (about 62.2 million pounds or 28.2 million kg) per day (CMR 1995).

Since some companies operate plants that make large contributions to the total annual U.S. production of MTBE, production estimate statistics may exclude figures from certain companies. In fact, such private providers of production information as SRI International (SRI 1995) no longer provide any MTBE production quantities for facilities or companies. Annual MTBE production estimates for 1991 were 9.57 billion pounds (4.34 billion kg), and estimates for 1992 were at 10.86 billion pounds (4.92 billion kg) (HSDB 1995; Reisch 1993). The U.S. International Trade Commission (USITC) solicits production estimates for a number of synthetic organic chemicals from companies suggested by government and industry representatives. MTBE has been included in this survey since 1993. The annual production estimates are subject to a series of revisions, so that it often takes at least a year for final figures to become stabilized. The most recent set of stable production statistics are for 1993, when the annual production was estimated to be 5.547 billion kg (12.229 billion pounds) (USITC 1995). Available statistics, therefore, show a dramatic increase in MTBE production from the 1980s to the early 1990s and a slower, but steady, increase in production during the 1990s).

Table 4-1 lists the facilities in each state that manufacture or process MTBE, the intended use, and the range of maximum amounts of MTBE that are stored on site. The amounts stored at these facilities ranges from amounts under the Toxics Release Inventory (TRI) reporting requirements to amounts at or above 1 million pounds (453,597 kg) per year (TRI93 1995). Four states (California, Louisiana, Michigan, and Texas) account for over 50% of the total number of reporting facilities in TRI93. The data from the Toxics Release Inventory listed in Table 4-1 should be used with caution, however, since only certain types of facilities were required to report (EPA 1995a). This is not an exhaustive list.

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Table 4-1. Facilities That Manufacture or Process Methyl *tert*-Butyl Ether

State ^a	Number of facilities	Range of maximum amounts on site in thousands of pounds ^b	Activities and uses ^c
AK	1	100-1000	8
AL	2	1-10000	2, 4, 8, 13
CA	15	1-500000	1, 2, 3, 8, 13
CO	2	1000-10000	8
DE	1	1000-10000	8
FL	1	10-100	8
GA	1	1000-10000	1, 2, 4, 10
IL	4	0-500000	1, 3, 8, 13
IN	6	1-10000	1, 3, 4, 8, 9, 11, 13
KY	2	1-10000	1, 3, 4, 8, 9
LA	11	10-100000	1, 2, 3, 4, 5, 6, 7, 8, 10, 11, 13
MI	10	1-10000	1, 3, 5, 8, 9, 10, 11, 12, 13
MN	2	1-10000	1, 4, 9
MS	1	10000-50000	1, 3, 4, 8
MT	1	100-1000	8
NJ	9	1-100000	1, 3, 4, 8, 9, 10, 11
NM	2	100-1000	1, 4, 8
NY	1	10-100	9
OH	1	10-100	9, 13
OK	2	1000-10000	1, 2, 3, 8, 13
PA	7	100-100000	1, 2, 3, 4, 8, 13
PR	1	10000-50000	8
SC	2	10-100	13
TN	4	1-50000	9, 11, 12, 13
TX	36	0-500000	1, 2, 3, 4, 5, 6, 7, 8, 10, 11, 13
UT	2	10-10000	8
VA	1	1000-10000	9
VI	1	1000-10000	2, 4
WA	1	50000-100000	8
WI	4	1-100	10, 11, 13
WY	3	100-100000	1, 2, 3, 4, 8

Source: TRI93 1995

^a Post office state abbreviations used^b Data in TRI are maximum amounts on site at each facility^c Activities/Uses:

- | | |
|-------------------------------|----------------------------------|
| 1. Produce | 8. As a formulation component |
| 2. Import | 9. As a product component |
| 3. For on-site use/processing | 10. For repackaging only |
| 4. For sale/distribution | 11. As a chemical processing aid |
| 5. As a by-product | 12. As a manufacturing aid |
| 6. As an impurity | 13. Ancillary or other uses |
| 7. As a reactant | |

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4.2 IMPORT/EXPORT

The USITC and the U.S. Department of Commerce only started to document import information for MTBE in 1993 and export information in 1994. Therefore, only limited quantitative estimates on annual import and export levels for MTBE are available for years prior to 1994. For 1994, the level of MTBE imports is 1.753 billion kg (3.865 billion pounds); the level of exports for 1994 is estimated as 0.405 billion kg (0.893 billion pounds) (NTDB 1995). For imports, the 1993 figure is 0.919 billion kg (2.026 billion pounds) (NTDB 1995). In earlier published U.S. production figures, the statistics would often combine MTBE used domestically with MTBE exports (Reisch 1993). While there has been substantial construction of new MTBE production facilities worldwide (Anonymous 1992b; Otto 1993) large U.S. production facilities are reported to export a substantial percentage of their output (Lorenzetti 1994). One reason that MTBE has only recently attracted interest for purposes of official import and export statistics (as opposed to overall, production estimates) is that the vast majority of MTBE output is first blended into reformulated gasolines. Foreign producers will generally seek markets for products like finished gasoline, so that most MTBE would be imported not as a bulk product but as an ingredient in gasolines (Anonymous 1992b; HSDB 1995; Lorenzetti 1994).

4.3 USE

Nearly all the MTBE produced in the United States is produced for use in reformulated gasolines. MTBE can be thermally decomposed into methanol and isobutene and in the past has been used to produce isobutene (HSDB 1995). MTBE is used in small quantities as a laboratory reagent to extract semi-volatile organic compounds from such sample types as leachates or solid wastes (EPA 1984a). MTBE is also a pharmaceutical agent, which can be used as an alternative to surgery in dissolving gallstones when injected intraductally (Angle 1991; Bergman et al. 1994; Eidson et al. 1993; Gilbert and Calabrese 1992).

4.4 DISPOSAL

Since most MTBE is used as a component in reformulated gasoline, provisions for its disposal are generally subsidiary to regulations for disposing of gasolines or similar volatile or such semi-volatile organic compounds as benzene or toluene. MTBE is likely to be encountered in waste sites or NPL sites where blended gasoline has been disposed of, or at NPL sites around pipelines, large tank batteries, or refineries and other facilities involved in the manufacture of reformulated fuels. Once dissolved in water, MTBE can readily leach into groundwater supplies. MTBE from past disposal in dumps and waste sites or

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from spills, leakage from underground storage tanks, or other releases to the environment is being increasingly recognized as a pollutant to groundwater supplies (Schorr 1994; USGS 1995). Chapter 7 contains an overview of regulations and guidelines regarding disposal practices for MTBE. No information was located on the quantities of MTBE disposed of by each disposal method, or on trends in disposal amounts or practices.

