

INTRODUCTION

Toluene is a colorless, mobile liquid with a distinctive aromatic odor somewhat milder than that of benzene. The name toluene derives from a natural resin, balsam of Tolu, named for a small town in Colombia, South America. Toluene was discovered among the degradation products obtained by heating this resin.. Toluene is widely used as raw material in the production of organic compounds and as a solvent. It is readily absorbed from the gastrointestinal and respiratory tracts and, to a lesser degree, through the skin. Toluene is distributed throughout the body, with accumulation in tissues with high lipid content. It is metabolized in the liver, primarily to hippuric acid and benzoyl glucuronide, compounds that are rapidly excreted in the urine .

Prior to the World War I, the main source for toluene was coke ovens. At that time Trinitrotoluene (TNT) was the preferred high explosive and large quantities of toluene was required for its manufacture. To augment the supply, toluene was for the first time obtained from petroleum sources by subjecting narrow cut naphtha's containing relatively small;; amount of toluene to thermal cracking. The toluene concentrate so produced was then purified and used for manufacture of trinitrotoluene. Production from petroleum was discontinued shortly after world war I. Petroleum again became the source for toluene with the advent of catalytic reforming and the need for large quantities of toluene for use in aviation fuel during World War II. Since then manufacture of toluene from petroleum sources has continued to increase and manufacture form coke ovens and coal tar products has continued to decrease.

Toluene is generally produced along with benzene, xylenes, and C₉ aromatics by the catalytic reforming of C₆-C₉ naphtha's. The resulting crude reformat is extracted, most frequently with sulfolance, to yield a mixture of benzene, toluene, xylenes, and C₉ aromatics, which are then separated by fractionation. About 90-95% of the nearly 31 x 10⁶ metric tons (9.4 x 10⁹ gal) of toluene produced annually in the United States is not isolated but is blended directly into the gasoline pool as a component of reformatted and of pyrolysis gasoline. Capacity exists to isolate ca 5.3 x 10⁶ t (1.6 x 10⁹ gal) per year of which about half is used for chemicals and solvents. The remainder is blended into gasoline to increase octane number.

Toluene Market

World toluene production in 2001 is forecast to be worth \$2.9 billion and reach almost 10 million tons.

Utilization of toluene

About 17% of the total production capacity for toluene is isolated in extraction units: about half of the isolated material is used in chemicals production, and half is returned to the gasoline pool for blending to increase the octane numbers of premium fuels. During the past few years, the use in fuels has increased and the used in chemicals has shown a slight decline. By far the greatest use of toluene for chemicals (about two thirds of the total) is conversion by demethylation into benzene. The use of toluene as a solvent in surface coatings and other formulations is expected gradually to diminish because of substitutions required by environmental considerations.

As a blending component in automotive fuels, toluene has several advantages. First, it has a high octane number compared to regular and premium unleaded gasoline. Secondly, its relatively low volatility permits incorporation into gasoline blends of other less expensive and available materials, e.g. N-butane, with relatively high volatility. Since the main use of toluene is in gasoline, with only ca 9% or less used in chemicals, there will always be an available supply for chemicals manufactures at a price essentially fixed by the value of toluene as a blending component in gasoline.

Manufacture of Benzene. Toluene is converted to benzene by hydrodemethylation either under thermal or catalytic conditions. Benzene produced from this source generally supplies 25-30% of the total benzene demand.

Use as Solvent. Toluene is more important as a solvent than either benzene or xylene. Solvent use accounts for ca 14% of the total U.S. toluene demand for chemicals. About two thirds of the solvent use is in paints and coatings; the remainder is in adhesives, inks, pharmaceuticals, and other formulated products utilizing a solvent carrier. Use of toluene as solvent in surface coatings is declining and is expected to continue to decline primarily because of various environmental and health regulations. It is being replaced by other

solvents such as esters and ketones and by changing of product formulation to use either fully solid systems or water-based emulsion systems.

Toluene Diisocyanate. Toluene Diisocyanate is the basic raw material for production of flexible polyurethane foams . It is produced by the reaction sequence shown below in which toluene is dinitrated, the dinitrotoluene hydrogenated to yield 2,4-diaminotoluene, and this diamine in turn treated with phosgene to yield toluene 2,4-diisocyanate.

Benzoic Acid. Benzoic acid (qv) is manufactured from toluene by oxidation in the liquid phase using air and a cobalt catalyst.

Benzoic Chloride. Benzyl Chloride is manufactured by high temperature free-radical chlorination of toluene. The yield of benzyl chloride is maximized by use of excess toluene in the feed.

Miscellaneous Derivatives. Other derivatives of toluene, none of which is estimated to consume more than ca 3000 t (10 6 gal)of toluene annually, are mono- and dinitrotoluene hydrogenated to amines; benzotrichloride, and chlorotoluene, all used as dyeintermediates *tert*- butylbenzoic acid from *tert*- butyltoluene, used as a resin modifier; dodecyltoluene converted to a benzyl quaternary ;ammonium salt ;for use ;as a germicide; and biphenyl, obtained as by-product during demethylation, use in specialty chemicals. Toluene is also used as a denaturant in specially denatured alcohol (SDA) formulas 2-B and 12-A.

Potential Uses of Toluene.

Because much toluene is demethylated for use as benzene, considerable, effort has been expended on developing processes in which toluene can be used in place of benzene to make directly from toluene the same products that are derived from benzene, such processes both save the cost of demethylation and utilize the methyl group already on toluene. Most of this effort has been directed towards manufacture of styrene. An alternative approach, currently near commercialization, is the manufacture of *para*-methylstyrene by selective ethylation of toluene followed by dehydrogenation. Resins from this monomer are expected to displace polystyrene because of price and performance advantages. Another approach to developing large-scale uses of toluene is

to find a reagent that reacts selectively in the *para* position to yield a derivative readily converted to a carboxylic acid. Such a process would provide a feedstock for manufacture of terephthalic acid and eliminate the need; for separation of *para*-xylene, the current feedstock, from mixed C₈ aromatics.

Specifications, test Methods, and Analysis

Toluene is marketed mostly as nitration and industrial grades. The general accepted quality standards are given by ASTM D 841 and D 362. Although the actual concentration of toluene in samples is not stipulated by these specifications, the purity is in fact controlled by the specific gravity and the boiling –range requirements of the method.

Purity of toluene samples as well as the number, concentration, and identity of other components can be readily determined using standard gas-chromatography techniques. Toluene content of high purity samples can also be accurately measured by freezing point as outlined in ASTM D 1016. Toluene exhibits characteristic UV, Ir., nmr, and mass spectra which are useful in many specific control and analytical problems.