

Production of the Isomers of Mono-Nitrotoluene by Nitration of Toluene

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Introduction:

Toluene reacts with Nitric acid in sulfuric acid to give 3 isomers of mononitrotoluenes:

- **2-Nitrotoluene**
o-nitrotoluene is a clear yellow liquid that crystallizes at lower temperatures to solid α - or β -forms. It has a melting point of -9 deg C and boiling point of 222.3 deg C at standard conditions. 2-Nitrotoluene derivatives are used mainly as colorant intermediates. One of its main derivative, toluidines are used to produce agrochemical intermediate.
- **3-Nitrotoluene:**
m-nitrotoluene is a yellow liquid with melting point of 16.1 deg C and boiling point of 239.9 deg C. 3-nitrotoluene is produced in very small quantities upon nitration of toluene. Catalytic hydrogenation or reduction with iron converts 3-nitrotoluene to m-toluidine, which provides important components for azo dyes.
- **4-Nitrotoluene:**
p-nitrotoluene forms colorless to light yellow rhombic – bipyramidal crystals, which have a melting point of 44.5 deg C and boiling point of 238.3 deg C. 4-Nitrotoluene derivatives are used as intermediates for colorants and related products.

Description of Flowsheet:

- The nitrating mixture used for the production of mononitrotoluene is typically 20% nitric acid, 60% sulfuric acid, and 20% water referred to as 20/60/20 mixed acid.
- Toluene is added so that the molar ratio of toluene to nitric acid is slightly above 1 in the reacting mixture. Toluene and mixed acid are fairly insoluble into each other and form separate phase. Efficient agitation is required to maximise contact and reduce resistance to mass transfer.
- The agitated phase is sent to a series of 3 CSTRs. In the first reactor the reaction is conducted at 40-50C in isothermal conditions. The reaction doesn't require use of a separate catalyst as the sulphuric acid acts as a catalyst for the reaction.
- In the 2nd and 3rd reactor, the reaction is conducted at the same conditions but the conversion achieved are higher due to higher space time. The reason behind using a

series of CSTRs inspite of a single large reactor is owing to easy operability of 3 small reactors, better agitation in small reactors and easy process control.

- The resulting mixture of o-nitrotoluene, p-nitrotoluene, m-nitrotoluene, very little dinitrotoluene, spent acid containing high concentrations of sulphuric acid, water and little nitric acid is sent to decanter where the organic and aqueous phase are separated.
- The sulphuric acid from the spent acid is regenerated in sulphuric acid regenerator where the excess water is evaporated and the concentrated stream of sulphuric acid is filtered to remove of impurities. The clean stream is recycled back into the reactor to ensure maximum utilisation of sulphuric acid and reduce its wastage.
- The organic phase is fed to a tall distillation column where the distillate is 99.9% pure o-nitrotoluene while the bottoms product consists of all the para, meta nitrotoluene and dinitrotoluene product. The distillation column works under atmospheric pressure.
- To separate the para and metanitrotoluene products, we take advantage of their different melting points. The feed is sent to melt crystalliser which is first cooled to 40C when all the para and DNT product crystallises while the meta product still remains in liquid state.
- The crystals are scraped off from the crystalliser. The liquid product is sent to another crystalliser which is cooled to 0C where the meta product also crystallises and is scraped off. This way, we can produce almost pure isomers of nitrotoluene.

Results:

In the first CSTR, 88-90% conversion of the reagents take place. In the 2nd and 3rd reactor, the reaction is conducted at the same conditions but the conversion achieved are 94-95% and 99% respectively. This produces a mixture of 60% o-nitrotoluene, 36% p-nitrotoluene, 4% m-nitrotoluene which are separated to produce 98% pure o-nitrotoluene from the distillation column and almost pure p-nitrotoluene from the melt crystallizer. We were adding 5 kmol/h of fresh sulphuric acid for every 500 kmol/h of sulphuric acid recycled.

References:

Henry M. Brennecke and Kenneth A. Kobe, *Mixed Acid Nitration of Toluene*(1956)