



Optimization of Benzene Production and Quality Enhancement

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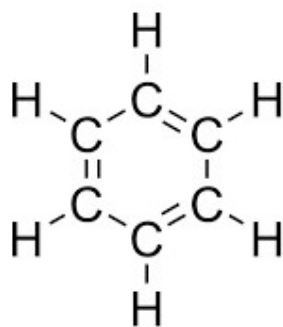
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Optimization of Benzene Production and Quality Enhancement

Report Summary

This research project addresses the critical challenge of substandard benzene quality in SAIL's Coal Chemicals Department (CCD). With rising competition from petroleum-based benzene (≤ 1 ppm sulphur) and stringent customer specifications (**Caprolactum grade: ≤ 2 ppm sulphur, ≤ 200 ppm moisture**), SAIL's current acid-washing-based benzene (60–80 ppm sulphur) faces market rejection. Leveraging RDCIS-developed technologies—Multistage Interstage Cooling (MIC) acid washing and molecular sieve drying—this project proposes an integrated pilot system to achieve ≤ 2 ppm sulphur and ≤ 20 ppm moisture in benzene. The project aims to enhance SAIL's market competitiveness, reduce revenue loss (₹30–40 crores/year), and align with global quality benchmarks.

Introduction



Benzene is a simple aromatic hydrocarbon with the chemical formula C_6H_6 . It is a **colourless, highly flammable liquid** with a sweet odour and is widely used as a precursor in the production of numerous chemicals. Structurally, benzene consists of six carbon atoms arranged in a hexagonal ring, with alternating double bonds, making it a stable and resonance-stabilized

compound. This unique arrangement of electrons gives benzene its characteristic **aromaticity**.

Benzene is a natural constituent of crude oil and is produced on a large scale through processes like catalytic reforming and steam cracking. It serves as a fundamental building block in the manufacture of plastics, resins, synthetic fibres (like nylon), rubber lubricants, dyes, detergents, drugs, and pesticides. Despite its industrial importance, benzene is known to be carcinogenic, and prolonged exposure can lead to serious health issues, including leukaemia. Therefore, strict safety measures are enforced during its handling and use.

Quality Of Benzene

Chemically pure benzene has a density of **0.879 gm/cc at 20°C** corresponding with a specific gravity at **15.5°C of 0.8847**. The boiling point is **80.099°C at 760 mm Hg**. The crystallization point is taken as **5.533 +0.010°C**.

a) Nitration Grade (NG Benzene)

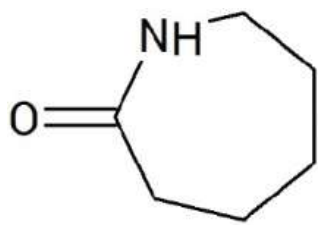
Nitration grade benzene is prepared to ensure a high-purity feedstock for the nitration process, which is a crucial step in producing various chemicals and explosives.

Specifically, it's done to minimize the presence of impurities that could interfere with the desired nitration reaction or lead to unwanted byproducts, produce high grade raw material to ensure consistent and predictable results.

SAIL plants produce benzene conforming to Nitration grade. N.G. Benzene as per **Indian Standard Specification No. 534, 1992** is given below with properties and values :

Property	Values
Specific gravity at 15.6°C/15.6°C	0.879-0.886
Distillation range 1-96%	All within 0.6°C including 80.1°C
Crystallisation point	5.3°C
Total Sulphur (max)	100ppm

b) Caprolactum Grade Benzene



Caprolactam

Benzene required for Caprolactam manufacture is of very **superior quality**. Specification of benzene with **low sulphur content and low aromatic & nonaromatic impurities** also known as Caprolactum grade benzene is required to produce Caprolactum. The specification is as follows :

Property	Values
Specific gravity 15.6/15.6°C:	0.879 to 0.886
Distillation range 1-96%	All within 0.6°C including 80.1°C
Crystallization point	5.3°C (min.)
Total sulphur	2 ppm (max.)
Acid wash colour	0.3 (max.) 50 ppm (max.) 10 (max.)
Aromatic impurities	300 ppm (max.)
Non-aromatic	3.0
Bromite index	0.879 to 0.886

Processing Of Crude Benzol

Crude benzol obtained in the recovery plant products by refining. The aromatic hydrocarbons present in crude benzol are the principal source of many commercial products. Most important of these hydrocarbons are Benzene, Toluene, Xylene, and solvent naphtha. The distribution is broadly as follows:

Sl no.	Fraction	Distribution	Approx. boiling points
1	Pure Benzene	60-85%	80.1°C
2	Pure Toluene	12.0-17.0%	110.6°C
3	Pure Xylene	1.0 - 7.0%	135°C-145°C
4	Heavy solvents	0.5-3.0%	110°C-200°C

Processing of crude benzol consists of the following steps:

- Pre-treatment of crude benzol in the **forerunnings column**
- Acid washing/hydro-refining** of benzol
- The **final fractionation** to obtain the pure products

Forerunnings Column

Crude benzol is first distilled in a forerunnings column consisting of bubble plates, to obtain a top fraction called forerunnings (Boiling range 25°C to 80°C) boiling below benzene compounds like **carbon disulphide**, **cyclopentadiene** and **hydrogen sulphide** are separated in this column.

The **forerunnings column** is the **first distillation step** in the benzene purification sequence. It is called "forerunnings" because it removes the "fore" or **initial lighter boiling point fractions** — these are unwanted components that boil before benzene.

Purpose of the Forerunnings Column

1. **Remove light impurities** from crude benzene, such as:
 - Toluene (partially)
 - Sulphur compounds (e.g., thiophene)
 - Non-aromatic hydrocarbons (e.g., hexane, cyclohexane)
 - Acetone or other oxygenates (if present)
2. **Prevent contamination** of downstream columns (like the benzene column or toluene recovery column).

Crude benzol (from coke oven gas) is preheated and fed to the forerunnings column. Steam or reboiler heating is used to **drive off the light ends**. These light impurities are taken off at the **top of the column** (distillate). The **bottom product** contains purified benzene with heavier impurities, which is then fed to the next refining step.

Operating Parameters (Typical)

- **Temperature:** Around 80–100°C at the top; 120–160°C at the bottom.
- **Pressure:** Usually atmospheric or slightly above.
- **Reflux ratio:** Controlled to enhance separation efficiency.

Output Streams

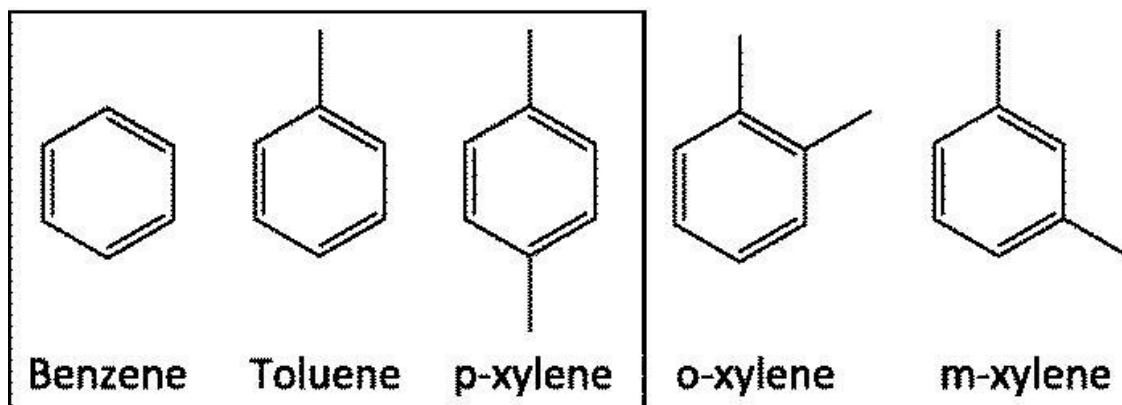
- **Top product (distillate):** Light hydrocarbons, sulphurous compounds — often sent to fuel or disposal.
- **Bottom product:** Partially purified benzene — sent for acid washing.

Importance in Benzene Refining

- Enhances **benzene purity** to >99.5% by ensuring upstream removal of low boiling impurities.
- Improves the efficiency of **downstream columns** and extends their operating life.

Acid Washing of Benzol

The bottom product containing heavier components like **Benzene, Toluene, Xylene, and solvents** from the forerunnings column are then treated with **sulphuric acid**. This removes impurities by chemical reaction of the acid with impurities, which cannot be removed by distillation.



The chemical reactions involve **oxidation, polymerisation, sulphonation, and other complex reactions with the unsaturated hydrocarbon olefins, diolefins, sulphur, nitrogen, and oxygen compounds**. Most reaction products remain in solution in the acid and removed with it by **gravity separation** from the washed benzol. Acid washing is done in conical bottom shaped agitators with capacities varying from **15m³ to 60m³**.

A typical procedure involves charging of benzol fraction obtained from forerunnings column, followed by the slow introduction of strong **sulfuric acid (93% to 98%)**, the acid is added in stages each addition being followed by suitable agitation, settling and withdrawal of sludge. The acid reacts with nitrogenous bases and unsaturated compounds, forming heavy, viscous sludge known as "**acid tar**."

First step is a dehydration treatment. After complete washing (as judged by analysis) the batch is neutralised with aqueous caustic soda solution and then sent for further processing. In this step, **loss of Benzol is about 4 to 6% by vol. acid consumption is about 5% to 8% by wt.** Time required is about **5 to 8 hrs.**

The reactions occurring in acid washing are complex and include the following:

- a) Sulphur compounds are dissolved or oxidised.
- b) Nitrogen compounds (pyridine etc.) and some unsaturates combine with acid.
- c) Unsaturates are polymerised
- d) Aromatic compounds are sulphonated
- e) Some aromatics combine with unsaturated
- f) Some unstable hydrocarbons are oxidised

The optimum conditions are those in which the desired removal of unsaturated, thiophene etc. is accomplished with minimum sulphonation losses of aromatic hydrocarbons and minimum consumption of reagent acid and alkali.

Continuous acid washing:

Continuous acid washing process differs from batch acid washing in the absence of agitators. This has the provision of an interconnected row of mixers and tanks for various operations of treatment with acid, settling, neutralising etc.

Acid washing with additives:

Sulfuric acid washing with the addition of unsaturated compounds is incredibly helpful in reducing sulphur and thiophene in benzene. 92 to 93% H_2SO_4 is used for the purpose. In USSR two additives namely

- (i) **Piperylene ($\text{H}_2\text{C}=\text{CHCH}=\text{CHCH}_2$)** a by-product obtained during Isoprene production
- (ii) **Divinyl ($\text{H}_2\text{C}=\text{CHCH}=\text{CH}_2$)** used. The quantity of additive required depends on the initial thiophene content.

These unsaturated compounds are highly reactive and react much faster with thiophene than with hydrocarbons. Following figures indicate the reaction rates of additives:

Thiophene with Styrene	1
Thiophene with Piperiline	1.5
Toluene with Styrene	0.1
Toluene with Piperiline	0.062
Xylene with Styrene	0.166
Xylene with Piperiline	0.76

Because of the faster reaction rates of thiophene with additives, thiophene contents in the final benzene are reduced to exceptionally low level. Following table show the consumption of additives and sulphuric acid with respect to initial thiophene content.

Thiophene content	0.9-1.1%	1.1-1.2%	1.2-1.4%
Acid (92%) by wt.	5-6%	6-7%	7.8%
Consumption of additives	1.5-1.7%	1.7-2.0%	2.0-2.5%

Additives are mostly used with continuous washing schemes with several mixers. Additives are introduced at 3 points.

According to the data given in **Hyslop's paper**, with 98% sulphuric acid addition in two stages reduced thiophene sulphur from 5000 ppm to 100 ppm using 2.7% v/v of 98% sulphuric acid with 6 hrs agitation. A further 1.35% v/v of acid brought the sulphur down to about 3 ppm in 30 min. and further treatment with 1.35% v/v of acid to about 0.5 ppm in 10 min.

Use of oleum:

Oleum effects more efficient removal of Thiophene from BIX with large losses of hydrocarbons. Thiophene content of N.G. Benzene can be brought down to less than 1 ppm by treatment with oleum.

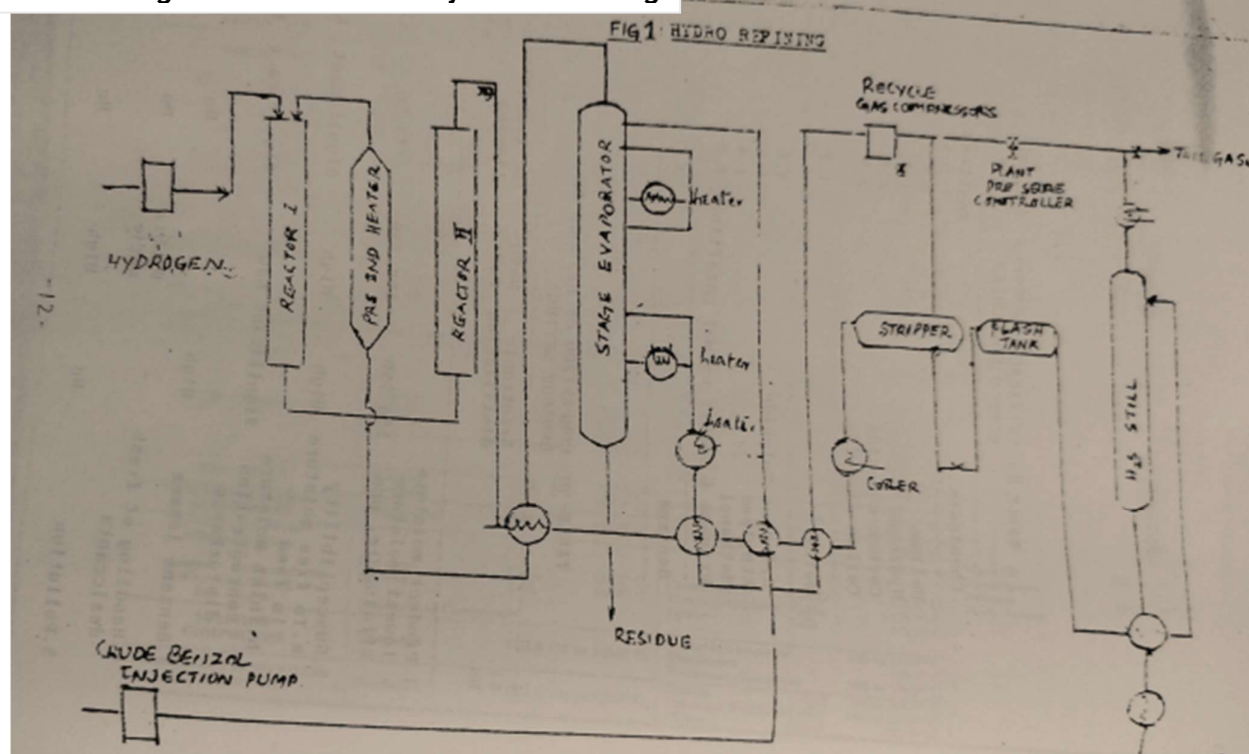
Hydro-refining:

Hydro refining of crude benzol effectively removes sulphur compounds. Hydrogen from the coke oven gas, compressed to 30 to 40 atm pressure, is circulated in the installation. Benzol vapours are heated to 305 - 320°C and sent to the reactor which facilitates reaction between benzol vapours and hydrogen on a catalyst made up of cobalt and molybdenum supported on Alumina. The raffinate obtained is distilled to obtain final products. The important reactions are-

- (1) Sulphur compounds are hydrogenated to H_2S .
- (2) Nitrogen is converted to ammonia and
- (3) Unsaturated compounds become saturated.



Technological Scheme for Hydro-Refining



The benzene obtained by this process has the following properties:

Distillation range	0.5°C
CS₂	Nil
Thiophene	0.0001%
Crystallisation temperature	5.32 °C

Elevated temperature hydrogenation:

Hydro-refining done at temperatures 600-650°C is called elevated temperature hydro-refining. It was developed by USA as '**Littol process**'. 35 to 40atm. hydrogen is used. this facilitates cracking of Paraffins olefins and sulphur compounds, which convert to low molecular weight compounds. Alkyl aromatics convert to Benzene. By this benzene with following specification can be obtained:

Thiophene content	0.00002%
Yield	99.8%
Crystallisation point	5.45°C
Total sulphur	0.00005%
Benzene yield	120%

Udex process

To get synthesis grade benzene raffinate from medium temp. hydro refining is extracted with **Diethylene glycol** (solvent for extraction). This solvent selectively dissolves only **chromatics but not paraffins**.

Extraction is done at 7 atm. pressure and at 175°C. Benzene obtained from this process has 99.9% purity and a crystallisation point of 5.5°C.

Extractive distillation

The refined benzene obtained from medium temperature hydro refining has a low crystallising point because of the presence of saturated hydrocarbons and so is not suitable for synthesis. This problem is resolved by extractive distillation with N-formyl morpholine or Dimethyl pyrrolidine as solvent for separation of aromatics from non- aromatics. First, the raffinate is treated in a pre-distillation column to separate into a Benzene-Toluene fraction and a Xylene-solvent fraction. Top B/T fraction is then treated in the extractive distillation column, along with the solvent N-Formyl-morpholine (NFM) which dissolves most of the aromatics from the vapours. Subsequently the solvent containing benzene and toluene is stripped off in a stripping column to recover Benzene- Toluene fraction from the top. Later Benzene and Toluene are separated by distillation.

Purity of Benzene obtained by this process is 99.95% with a crystallising point 5.45 to 5.5°C and a sulphur content less than ppm.

Fractional Distillation

After acid washing or hydro refining the product obtained is distilled to obtain the final products. This step is achieved by Batch distillation or continuous distillation or a combination of both.

Batch distillation

Batch distillation is done in an installation consisting of one still connected to a distillation column, by means of a vapour pipe that carries vapour to the column and a liquid pipe which permits return liquid from

the column to the still. The column contains 30 to 40 plates with bubble caps. The still is provided with steam coils to supply required heat energy for the predetermined rate of evaporation of the batch. Sometimes, the still is provided with live steam supply also for facilitating steam distillation. The column is fitted with a condenser, separator, reflux controller pumps etc. In batch still operation, the top temperature gradually changes. As distillation proceeds, first low boiling components are collected and replaced by heavier components as time proceeds. Intermediate components are produced in between principal components and are stored separately. Factors which control batch still operation are temperature of vapor leaving the top of the column and volume of reflux or the reflux ratio. The vaporisation rate is controlled by amount of steam introduced into heating coils by means of regulator valves. Reflux is controlled by reflux control regulators.

Continuous operation

A continuous operation is performed in continuous distillation columns. Continuous column consists of a reboiler of smaller capacity than that of still of batch columns. because the feed material is being constantly pumped into the unit and residue pumped out of the reboiler. The fractionating column consists of 30 to 40 plates. It is provided with a condenser, separator, reflux controller, pumps etc. The feed is pumped into the column at a specified feed plate, unlike batch stills. In continuous columns only one product can be obtained at the top from a single column. Accordingly, there must be as many columns as products. Conditions of temperature and pressure are constant throughout its operation. If requires more control than the batch columns, all factors must be kept constant. Uniform feed, its composition, optimum reflux ratio, constant top temperature and bottom temperature are to be maintained to obtain products with high purity and good yield.

Improvement In the Quality of Benzene Produced

Benzene is produced in all the coal chemical plants of SAIL. However major share of benzene belongs to Bhilai and Bokaro Steel Plants, SAIL benzene conforms to LS. specification in all respects except in sulphur content. Rourkela Steel Plant produces benzene with low sulphur content as it uses hydro refining of crude benzol instead of sulphuric acid washing for the removal of sulphur compounds and unsaturates. Hence, benzene from SAIL needs to be improved with respect to its sulphur content to retain its market share. Though I.S. specification for benzene does not stipulate any limit on moisture content of benzene, presently some of the customers have imposed stringent limit on this value not exceeding 200 ppm. Normally, benzene contains about 700 ppm moisture which is soluble in benzene at room temperature.

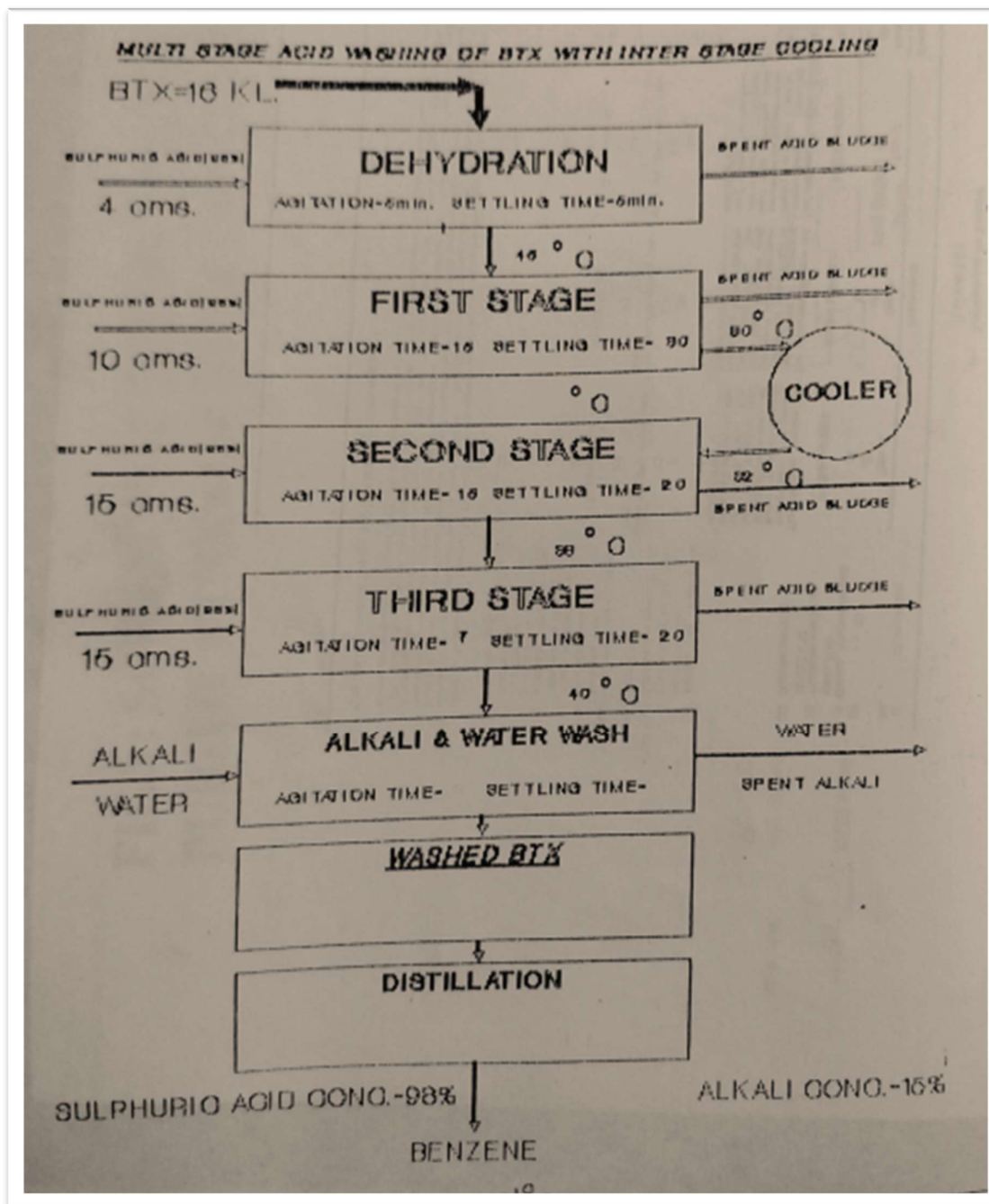
Measures Taken at BSP for Quality Improvement of Benzene

BSP had taken a decision in 1993 to implement multistage acid washing with inter-stage cooling (MIC) developed by RDCIS for sulphur reduction and molecular sieve technology for drying of benzene as recommended by RDCIS.

MIC process

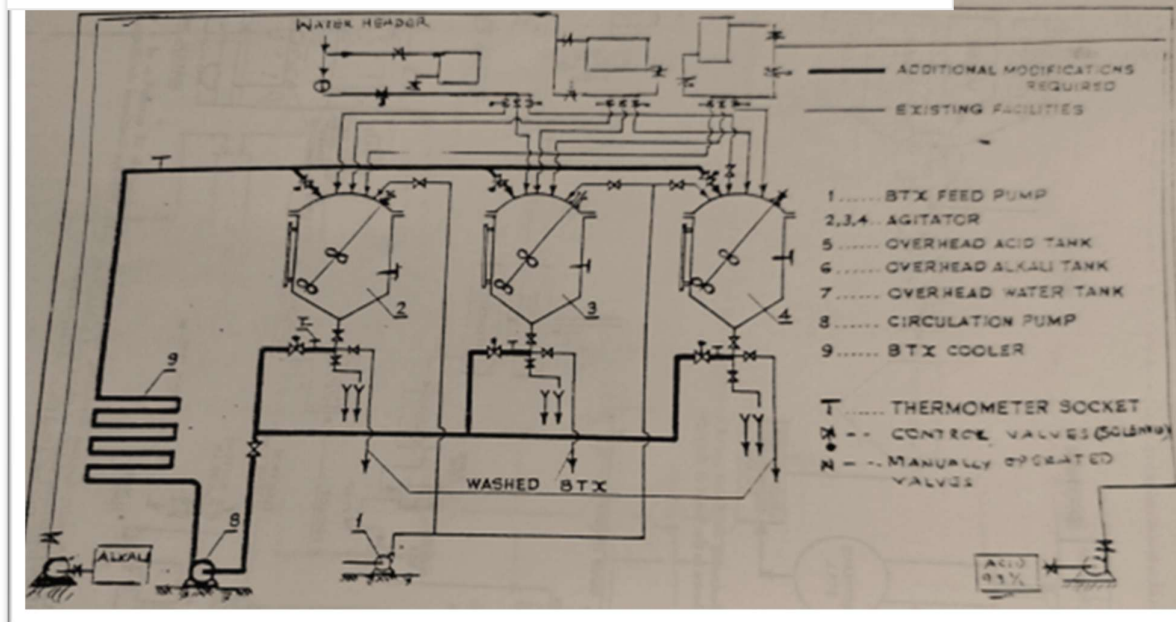
Conventional acid washing followed at BSP was to add about 450 litres of 95-98% Sulphuric acid in single stage after Dehydration of BTX using sulphuric acid of the same strength in Agitators of 17MT capacity. Washed

BTX thus obtained was able to produce benzene with sulphur content of 60-80 ppm.



MIC process basically differs from the conventional batch acid washing process in addition of sulphuric acid in **three stages** instead of one and removal of exothermic heat generated during its stage acid washing. The MIC process is depicted in a block diagram which is self-explanatory.

Technological Scheme for Multistage Acid Washing of BTX



Moisture removal in benzene

The methods of moisture reduction in benzene essentially fall into two headings:

1. Azeotropic distillation
2. Methods based on desiccants.

Azeotropic distillation cannot be used economically to remove the moisture to the desired level of 200 ppm.

Desiccants normally used for drying of benzene are:

- Caustic soda pellets
- Anhydrous calcium chloride lumps
- Activated alumina/silica gel
- Molecular sieves

Caustic soda and anhydrous calcium chloride lumps have noticeably short life and are highly **hygroscopic**. Granular silica gel is generally not preferred for liquid drying due to its tendency to shatter. The degree of

dryness obtained with activated alumina ranges from 0-5% of the saturation water content whereas molecular sieves have the capability liquids to ultra dry levels 0-0.2% of saturation moisture content. Due to regular crystalline structure molecular sieves are employed for ultra drying operations. Molecular sieves preferentially adsorb compounds which are more polar and have critical diameter smaller than its pore size. Critical diameter of some common molecules is given in Table-II. Critical diameters of water and benzene are 3.2A and 6.7A. Thus, molecular sieve of 4A type is ideally suitable for drying of benzene.

Principle of molecular sieve drying is essentially a process of preferential collection of molecules of water on the surface of solid (M.S. adsorbent). The adsorbed water is called adsorbate. When molecular sieve reaches its saturation with water molecules, it is heated with elevated temperature nitrogen which desorbs the moisture from the molecular sieve.

Comparison Of Methods of Benzene Drying

Sl. No.	Criteria	Azeotropic Distillation	NaOH / CaCl_2	Activated Alumina	Molecular Sieve
1	Product moisture (lowest moisture attainable, ppm)	150-250	150-250	40-50	<20
2a	Susceptibility to free moisture in feed	High	High	Significant	Low
2b	Inlet moisture concentration disturbance	Significant	Low	Significant	Low
3	Benzene losses	High	-	No	No

4	Handling of fresh desiccants	–	Problematic	No	No
5	Pollution	No	High	No	No

Process Description

Molecular sieve technique of benzene based on two column adsorption process. At any given time one column packed with molecular sieve will be on drying service and the other column will be on regeneration service.

Drying Cycle

In drying cycle, feed benzene from the existing storage tanks through a rotameter into an adsorption column is pumped and dry benzene (moisture <20ppm) will be obtained in a single pass. This cycle continues for 24 hours, and dry benzene is stored in the product tank.

Regeneration Cycle

During the same time second column is under regeneration. The benzene in the void space between molecular sieve pellets as well as the adsorbed moisture is driven out by passing hot and dry nitrogen as purge gas for regeneration. Steps of regeneration are as under:

1. Draining of liquid from the column
2. Benzene recovery by heating up to 100°C by nitrogen in a closed loop.
3. Moisture desorption by heating nitrogen up to 240-250°C and circulating the same through a blower.
4. Cooling of the molecular sieve bed up to 45°C by circulation of (via. column) cold nitrogen

Regeneration cycle is completed in 24 hours and regenerated column is ready for drying cycle. Column changeover is achieved with the help of manually controlled valves.

Heating of Nitrogen

The regeneration temperature of molecular sieve is 230-240°C to achieve desired drying and this temperature cannot be achieved by the medium pressure steam of 12-14 atm available in Benzol Rectification Plant. Hence hot oil unit is required for heating nitrogen. Hot oil unit is electrically heated.

Desulphurisation of Benzene at BSL

BSL has a continuous acid washing (CAW) system for removal of thiophene and other unsaturated compounds from BTXS fraction obtained after defrosting operation of LCB. RDCIS studied the system and found that a level of 30 ppm of sulphur in benzene could be achieved by optimising the parameters of CAW. To achieve a sulphur content less than ppm of sulphur, a modified process namely single pass double stage (SPDF) process was proposed by RDCIS after carrying out laboratory investigations. BSL has awarded the job of introducing the facilities for SPDF process to RDCIS. The job is envisaged to be completed by the end of 1998.

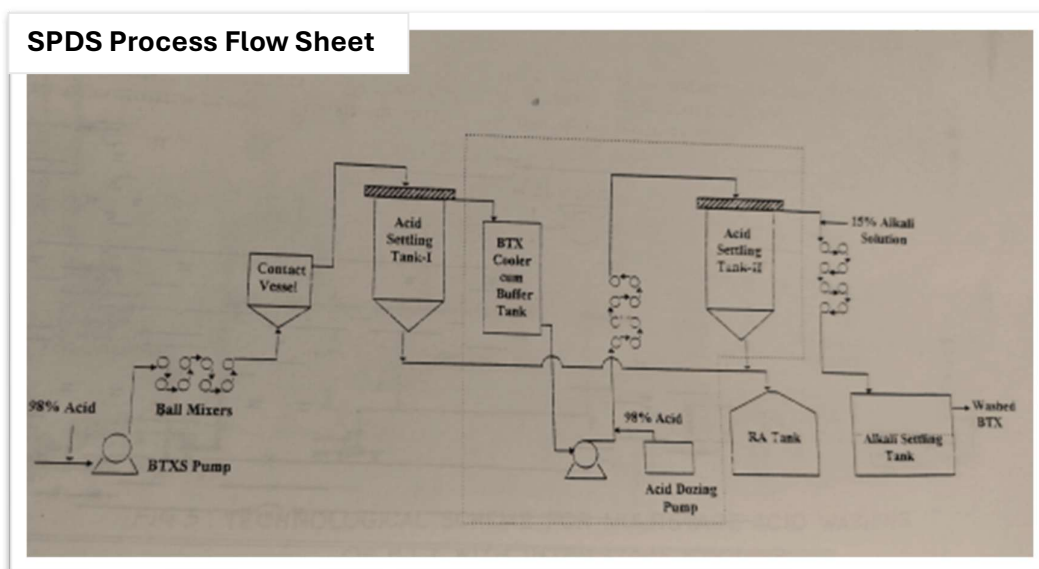
SPDS Process Simulated Moving Bed Parex Process (sometimes referred to as Simulated Moving Bed Distillation Separation)

In this system, BTXS fraction after defrosting in CS₂ column is pumped through a series of ball mixers, along with 98% sulphuric acid (dozed into suction line of the pump) and enters a contact vessel. The reaction between acid and thiophene of BTXS reaches equilibrium conditions by the time the mixture leaves contact vessel. However, due to exothermic

reactions, the temperature rises by about 20°C, i.e., to about 50°C to 56°C which prevents sulphur levels of final benzene going below 30 ppm.

After leaving contact vessel, acid-BTXS mixture flows to the existing spent acid settler where spent acid sludge separates out. BTXS with small quantity of residual acid overflows through the settling vessel to a cooler cum buffer tank and gets cooled to 34- 35°C. It is then pumped through a series of 8 ball mixers & after the second acid dozing at a point just before the ball mixers. The BTXS acid mixture at about 36 to 38°C passes to a second acid settler where BTXS and acid are separated. BTXS fraction then flows into the existing alkali washing circuit consisting of 4 ball mixers. Dilute sodium hydroxide solution is dozed into BTXS stream and mixing of alkali and BTXS takes place in ball mixers. Neutralized BTXS flows to existing alkali settling tank from which overflows washed BTXS to the storage.

Spent acid from both acid settlers flows to existing regenerated acid storage tank. Spent alkali from settling tank is stripped by steam to recover benzol trapped in it. BTXS thus obtained when distilled can give benzene of sulphur less than 5 ppm.



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