Category – II : Brochure on Major Technology Development

Title

Aromatic extraction for production of benzene and toluene (B, T) using sulfolane solvent

Slogan: Make in India

General Introduction:

Pure aromatics like Benzene, Toluene and Xylenes are the primary feed stocks /major building blocks for the petrochemical industry. Benzene is essential raw material for the production of Linear Alkyl Benzenes (LAB), polystyrene, nylon, phenol, caprolactam etc. It is a basic raw material used by most chemical manufacturing companies and the base chemical for all types of dyes and dye intermediates. It is also used for the production of pharmaceuticals, pesticides, cosmetics, paints and detergents. Toluene is used as raw material for toluene diisocynate (TDI) a precursor for new class of polyurethanes; also used for solvent in paints, coatings, adhesives, inks, pharmaceuticals, silicone sealants and other formulated products. Toluene is used extensively in feedstock for production of trinitrotoluene (the explosive, TNT). Thus recovery of these components from aromatic rich streams is a task of importance and profitable rather burning it along with fuel streams.

A sulfolane Extraction unit developed by CSIR-IIP and EIL jointly is usually incorporated within an aromatics complex to recover high-purity benzene and toluene products from aromatic rich streams like reformate or hydrotreated pyrolysis gasoline (HPG). The aromatics rich extract from the Sulfolane unit is clay treated to remove traces of olefins and individual benzene and toluene products are recovered by simple fractionation.

Important parameters unique to the technology

First time in the India 120,000 MTPA Aromatic Recovery Unit (ARU) based on indigenously developed technology commercialized at BPCL, Mumbai India in 1985, has the potential to fetch ~2.7 Million INR per annum from sale of high purity benzene and toluene besides saving of more than 30 crore INR for import substitution. This unit was first of its kind developed and commercialized by any CSIR laboratory in such a large scale.

- **Feedstock**
  - Reformed naphtha (boiling range 60 - 90°C)
- **Products**
  - High Purity Benzene > 99.99 % wt. with > 99.9 % Recovery and Toluene > 99.9 % wt. with > 99 % Recovery
  - Gasoline component as dearomatized product (raffinate) with Benzene < 1.0 % wt.

- Sulfolane solvent possesses a favorable combination of solvent power and selectivity resulting in recovery of aromatic hydrocarbons (like Benzene, Toluene) in high purity and yields from aromatics rich feedstocks like reformate or hydrogenated pyrolysis gasoline
- Solvent used is non-corrosive and environmentally friendly
- CSIR-IIP conducted lab experiments with actual feedstocks, developed comprehensive Technology Information Package and developed BEDP in collaboration with EIL

- Aliphatic / Non-aromatic impurities in benzene and/or toluene are as low as 300 ppm; typical design for 500 ppm.
- Low utility requirements as compared to an extractive distillation process.
- Low solvent loss
- Plant operation is flexible for future feedstocks with variations in aromatic content

Major applications/General impact, highlighting the societal impact, if any

The technology is devoted to Production of valuable petrochemicals like Benzene, Toluene, Xylene etc from refinery or petrochemical feedstocks like reformate or hydrogenated pyrolysis gasoline

- The technology has potential to reduce dependency on global player in the area of aromatic extraction e.g. UOP, Shell, Lurgi, Krupp Koppers etc.
- New units in hydrocarbon industries will employ engineers and shift operators hence will create employment
- Removal of benzene from any gasoline blending stream is mandatory hence the process is essential for recovery of benzene from any gasoline blending stream so that people involved in distribution and consumers in general will be benefited more while using dearomatized benzene lean gasoline as exposure to benzene is highly carcinogenic

Industrial partner(s) and their role in the development

CSIR-IIP completed laboratory studies and developed complete technological knowhow.
EIL, New Delhi- Completed Process package and detailed engineering
BPCL, Mumbai & KRL, Kochii-

- Provided feedstock for laboratory experimental study.
- Adopted the developed technology and put up the commercial production units

Patents obtained/licensed

Cost Economics:

Details of two licensees of the Technology are mentioned below.

Production in Tonnes per Annum

	COMPANY	BENZENE	TOLUENE	ON STREAM SINCE
1.	BPCL, MUMBAI	98,000	17,000	1985
2.	KRL, KOCHI	90,000	17,000	1987

- Estimated Cost of the Plant: ~26 Crore INR/ per plant
- First indigenously developed technology for a grass roots unit ever to be commercialised by any CSIR laboratory

Each plant has the potential to fetch ~2.7 Million INR per annum from sale of high purity benzene and toluene besides producing dearomatized product for gasoline stream.

The payback period for the Aromatic Recovery Unit (ARU) is expected not to be more than four years.

User Feedback, if any:

Commercial plants are under smooth operation with maximum throughput till date

Future Plans……:

Benzene demand growth is around 4.7% per annum hence there is still scope of more ARU plants in India. There are many refineries and petrochemical complexes in India and abroad having similar petrochemical units so they will be ready to adopt the technology.

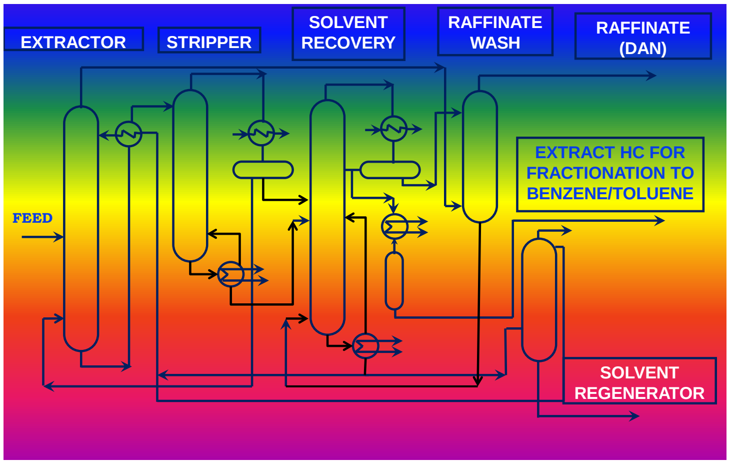
Technology may be sold to the clients abroad bringing foreign exchange to the country.

There may be scope of utility saving in new upcoming units from the experience of installed indigenous plants.

Details about availability ……:

- Commercial plants at BPCL, Mumbai and KRL, Kochii are under smooth operation with maximum throughput till date
- On spec. Benzene and Toluene are available from two running ARU units for domestic petrochemical units as well as export abroad
- Technology may be sold to the clients in India and abroad jointly by CSIR-IIP and EIL

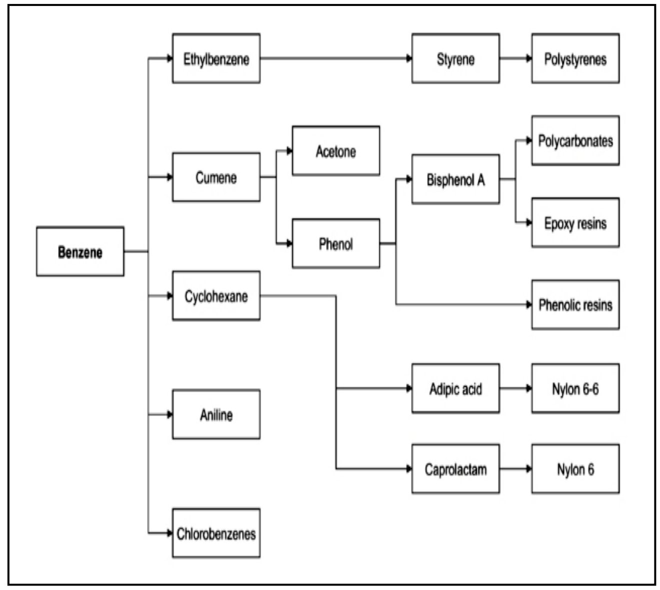
Aromatic Extraction for Production of Benzene and Toluene using Sulfolane Solvent

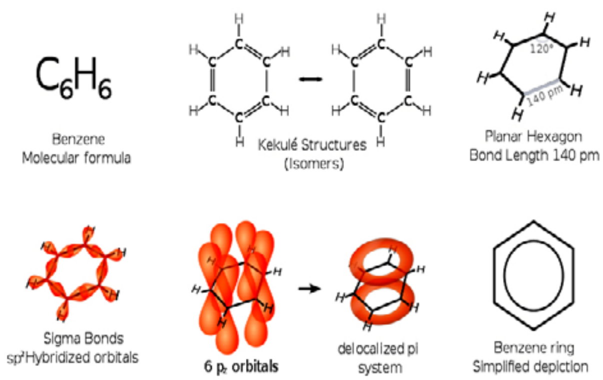


Simplified Process Diagram for ARU

Benzene

Properties	
Molecular formula	C_6H_6
Molar mass	78.11 g mol^{-1}
Appearance	Colorless liquid
Density	0.8765(20) g/cm^3
Melting point	5.5 °C, 278.7 K
Boiling point	80.1 °C, 353.3 K
Solubility in water	1.8 g/L (15 °C)
λ_{max}	255 nm
Viscosity	0.652 cP at 20 °C
Dipole moment	0 D



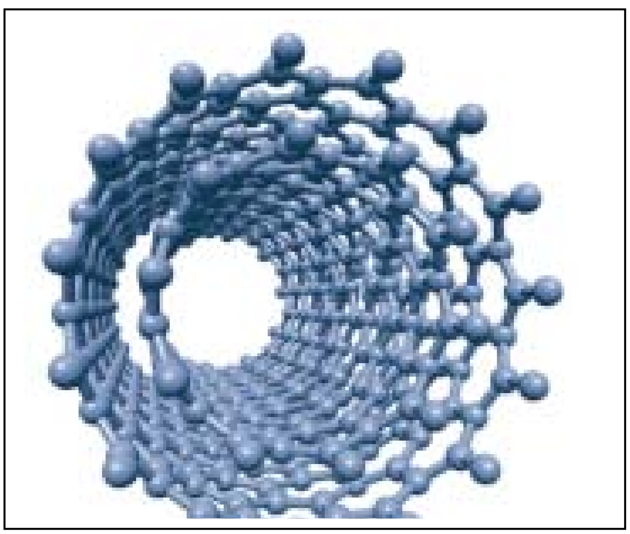


Nyl

Ny

Toluene

Properties	
Molecular formula	C_7H_8 or $C_6H_5CH_3$
Molar mass	92.14 g/mol
Appearance	colorless liquid
Density	0.8669 g/mL (20 °C)
Melting point	−93 °C, 180 K
Boiling point	110.6 °C, 383.8 K
Solubility in water	0.47 g/L (20–25 °C)
Refractive index (n_D)	1.497 (20 °C)
Viscosity	0.590 cP at 20 °C
Structure	
Dipole moment	0.36 D



Xylene Isomers				
General				
Common name	**Xylenes**	***o*-Xylene**	***m*-Xylene**	***p*-Xylene**
Systematic name	Dimethylbenzenes	1,2-Dimethylbenzene	1,3-Dimethylbenzene	1,4-Dimethylbenzene
Other names	Xylols	*o*-Xylol; Orthoxylene	*m*-Xylol; Metaxylene	*p*-Xylol; Paraxylene
Molecular formula	C_8H_{10}, $C_6H_4(CH_3)_2$ or $C_6H_4C_2H_6$			
SMILES		Cc1c(C)cccc1	Cc1cc(C)ccc1	Cc1ccc(C)cc1
Molar mass	106.16 g/mol			
Appearance	clear, colorless liquid			
CAS number	[1330-20-7]	[95-47-6]	[108-38-3]	[106-42-3]
Properties				
Density and phase	0.864 g/mL, liquid	0.88 g/mL, liquid	0.86 g/mL, liquid	0.86 g/mL, liquid
Solubility in water	practically insoluble			
Soluble in non-polar solvents such as aromatic hydrocarbons				
Melting point	−47.4 °C (−53.3 °F; 226 K)	−25 °C (−13 °F; 248 K)	−48 °C (−54.4 °F; 225 K)	13 °C (55.4 °F; 286 K)
Boiling point	138.5 °C (281.3 °F; 412 K)	144 °C (291.2 °F; 417 K)	139 °C (282.2 °F; 412 K)	138 °C (280.4 °F; 411 K)
Viscosity		0.812 cP at 20 °C (68 °F)	0.62 cP at 20 °C (68 °F)	0.34 cP at 30 °C (86 °F)

Category – II : Brochure on Major Technology Development

Title

Dearomatization of light naphtha fraction for the Production of food grade hexane and special boiling point (SBP) solvents extraction technology using Sulfolane solvent

Slogan: Make in India

General Introduction:

Food Grade Hexane (FGH) and SBP solvents may be produced either hydrotreating light naphtha or by dearomatization of light naphtha (50 – 120 °C) fraction, using solvent extraction. Hydro saturation of benzene involves use of hydrogen at high temperature and pressure and becomes costly (Capital intensive as well operational cost) besides generating green house gases (GHG).

Food Grade Hexane (FGH) is a hexane rich heart cut naphtha having a boiling range of 63 – 69 °C. It is extensively used in the agro-industry for extraction of vegetable oils (used for cooking) from seeds. Special Boiling Point (SBP) solvents are a class of benzene lean narrow or wide boiling range solvents. They are used extensively in the Tyre, Rubber and Paint Industry. The sulfolane based extraction technology for simultaneous production of FGH and SBP has been commercialized in BPCL, Mumbai. The technology has been developed in collaboration with EIL, India. In this technology, the feedstock used is hydrotreated naphtha with boiling range of 50 - 120°C. The dearomatized raffinate obtained is fractionated to yield 3 cuts; top (50 - 63°C), middle (63 - 69°C) and bottom (69°C+). The middle light fraction is FGH whereas the top and bottom fractions are mixed to produce SBP.

Important parameters unique to the technology

- Sulfolane has good selectivity and capacity
- Solvent based dearomatization is more cost effective than hydrogenation
- Hydrogenation route is unattractive for feeds with high aromatic content, as it requires higher capital investment
- Sulfolane extraction technology developed at IIP can accept feed with any benzene content
- Solvent used is no-corrosive and environmentally friendly
- CSIR-IIP developed the Technology Information Package, Basic Engineering Design Package (BEDP) developed in collaboration with EIL. Detailed Engineering done by EIL
- Unit in BPCL, Mumbai has a capacity to produce 25000 TPA of FGH and 80000 TPA of SBP
- The unit is on-stream since 1989

Major applications/General impact, highlighting the societal impact, if any
Production of FGH (for refining/extraction of edible oils) and SBP for use in Tyre, Rubber and Paint Industries

- ➢ First Indigenous development commercial plant for production of FGH and SBP solvents

- First commercial plant at BPCL, Mumbai in 1989 for FGH and SBP and then in CPCL, Chennai in 1992 for FGH only
- Improved economy by putting almost complete brake to import thus saving enormous foreign exchange
- Creating jobs by putting new vegetable oil extraction /refining units due to easy availability of FGH in the country
- Peoples' health will be less harmed by using improved FGH (< 100 ppm benzene) for refining vegetable oils
- New FGH unit will create more jobs for engineers and shift operators

Industrial partner(s) and their role in the development

CSIR-IIP completed laboratory studies and developed complete technological knowhow.
EIL, New Delhi- Completed Process package and detailed engineering
BPCL, Mumbai & CPCL, Chennai-

- Provided feedstock for laboratory experimental study.
- Adopted the developed technology and put up the commercial production units.

Patents obtained/licensed

Cost Economics: Marginal cost of around INR 21 Crore for each unit

	COMPANY	FGH	SBP	ON STREAM SINCE
1.	BPCL, MUMBAI	25000	80000	1989
2	CPCL, Chennai	25000	-	1992

- First indigenously developed technology for FGH and SBP, a grass roots unit ever to be commercialized in India at BPCL, Mumbai and later on at CPCL, Chennai.
- Each Plant has the potential to fetch more than ~INR 2.5 Crore per annum as sales realized by selling the FGH product besides INR 3.8 Crore per annum for sales of SBP solvent by BPCL
- Each Plant has the potential to fetch more than ~INR 30 Crore per annum as import substitution
- The payback period for the FGH/SBP units had been less than three years.

User Feedback, if any:

Commercial plant is under smooth operation with maximum throughput till date

Future Plans……:

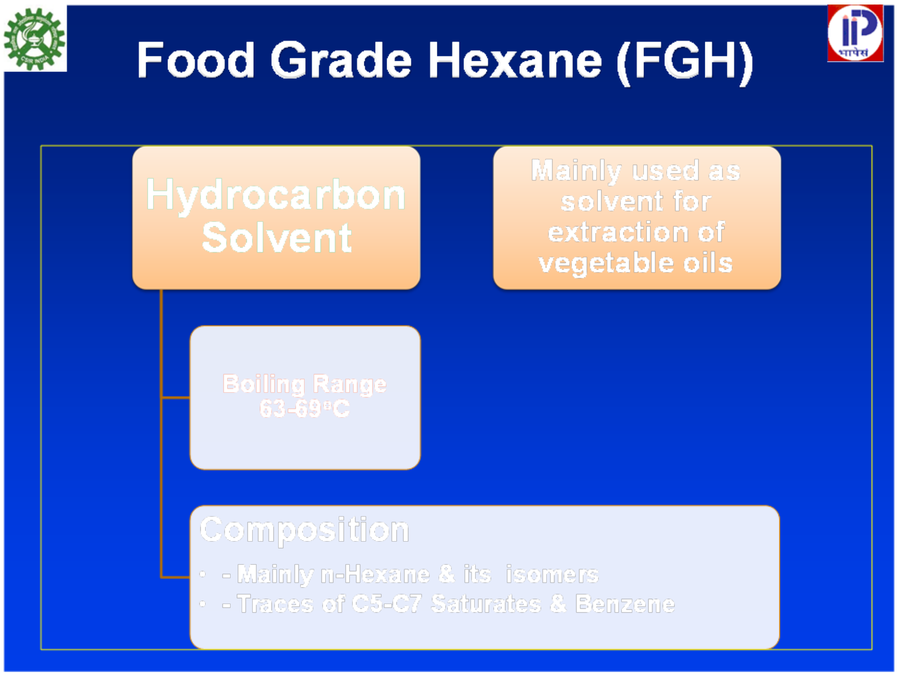
There are many refineries in India and abroad having similar feedstock streams and with the requirement of more and more FGH refiners will be ready to adopt the technology.

Technology may be sold to the clients abroad bringing foreign exchange to the country.

There may be scope of utility saving in new upcoming units from the experience of indigenous plants.

Details about availability ……:

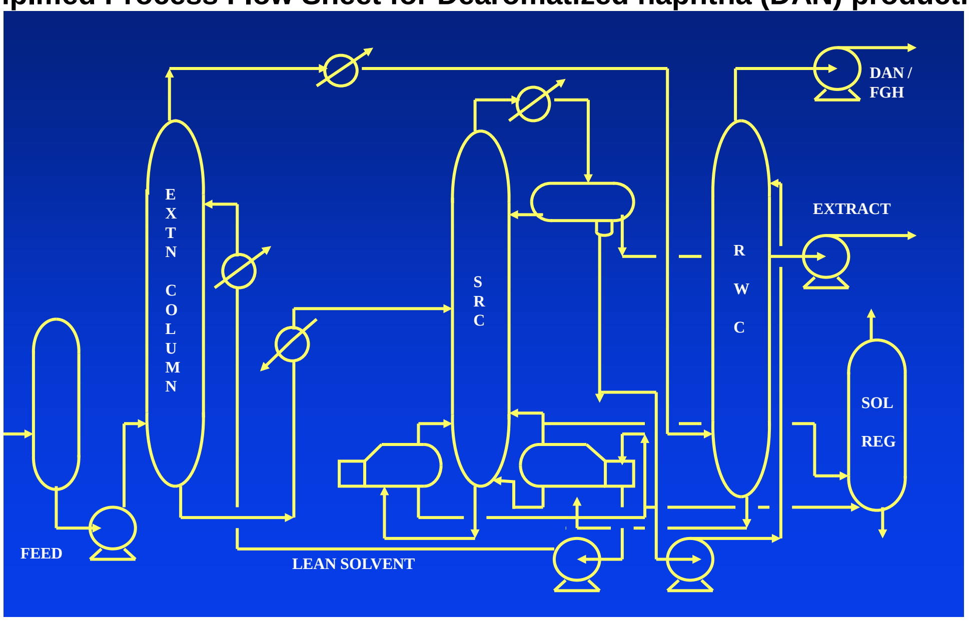
- A FGH/SBP production unit based on this technology is successfully running in one of the refineries of India since more than 25 years, and is under smooth operation with maximum throughput
- Benzene < 500 ppm in FGH is available from BPCL Mumbai for refining of vegetable oils for domestic consumption as well as export and SBP solvent containing < 5% aromatics being supplied to tyre/ rubber industry
- Technology may be sold to the clients in India and abroad by CSIR-IIP and EIL.



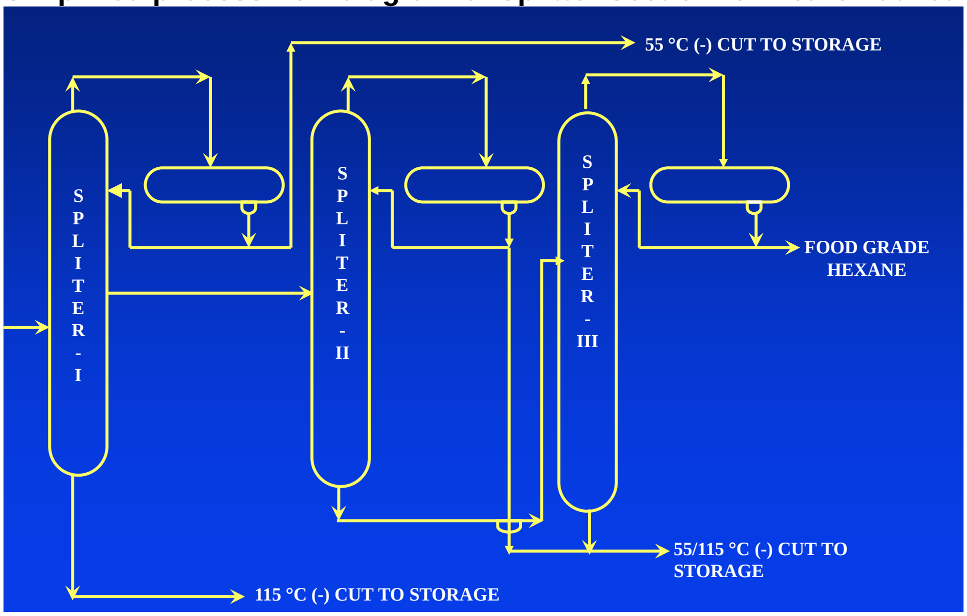
Dearomatization Technology for Production of Food Grade Hexane/ SBP using sulfolane solvent

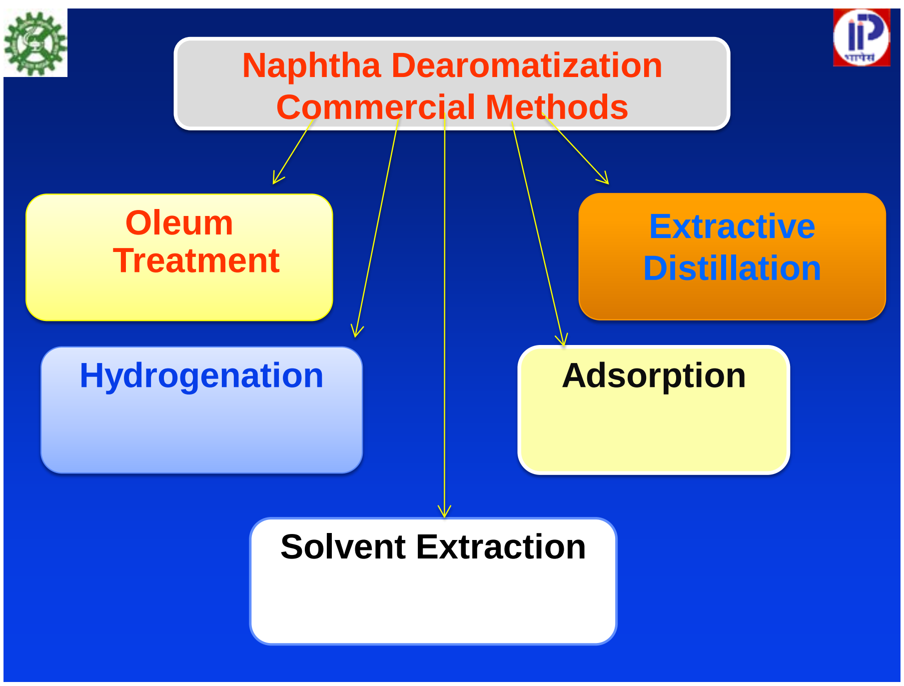
Technology Developers	CSIR-IIP- EIL
Feed	Light naphtha Fraction(50-120°C)
Solvent	Sulfolane
Product	FGH/ SBP
Continuous phase	Feed stock
Dispersed Phase	Sulfolane
Commercial unit location	BPCL , Mumbai (1989)
Capacity	25,000 TPA FGH, 80,000 TPA SBP

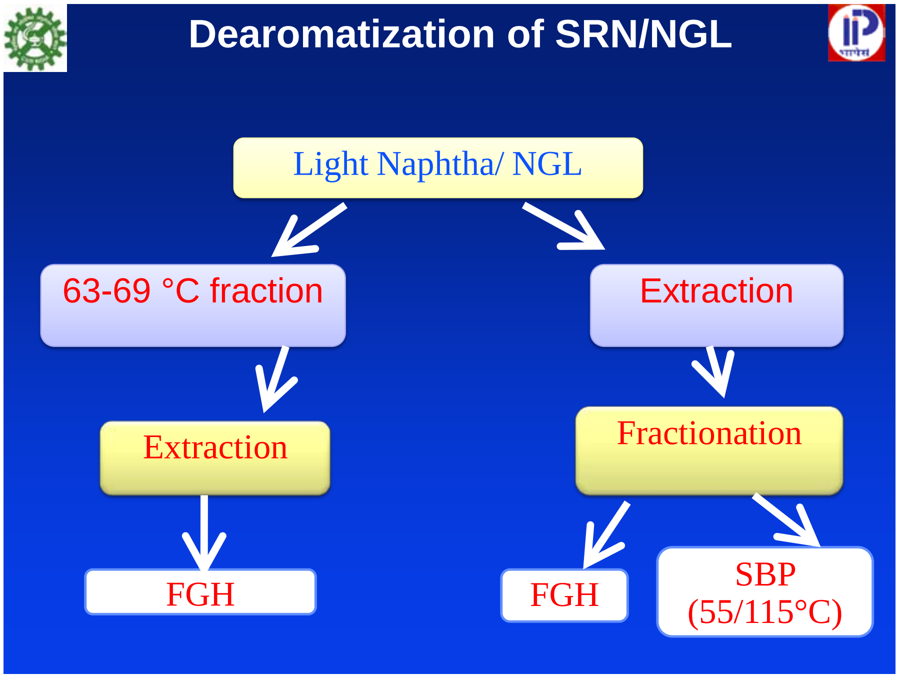
Simplified Process Flow Sheet for Dearomatized naphtha (DAN) production



Simplified process flow diagram of Splitter Section for Dearomatized naphtha






Dearomatization of SRN/NGL
Light Naphtha/ NGL
63-69 °C fraction
Extraction
Extraction
Fractionation
FGH
FGH
SBP
(55/115°C)

Jambu Oil

Gauva oil