Separation Technologies for Petrochemicals and Value Added Products from Refinery Process Streams

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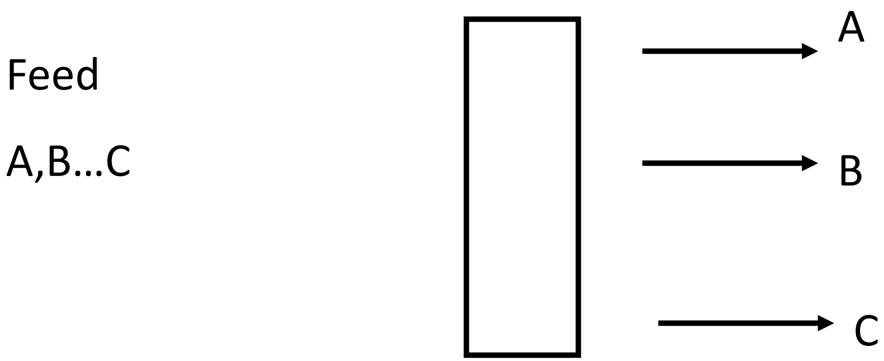
Outline of Presentation

- **Introduction of Separation Processes**
- **Recent Success Stories at CSIR IIP**
  - **Simultaneous Production of US grade Gasoline and Recovery of Benzene from FCC C6 Heart Cut by using Extractive Distillation (IIP-RIL)**
  - **Wax De-oiling Technology for Wax Production (IIP-EIL)**
- **Emerging Technologies: Commercialisation Possibilities**
  - **Production of Pure BTX from Straight Run Naphtha**
  - **Propylene Recovery from Low Propylene Bearing Streams by Adsorption**

Separation Processes

- Separ`ation Processes are the Heart of Petroleum and Chemical Industries



Indispensible in hydrocarbon industry
>40% of capex + opex

Principles of Separation

- To separate any particular component from a mixture we must make it move with respect to the mixture
- Relative motion can only be effected by exerting force on the component

Different types of forces which can be exerted on the component

- Chemical: due to chemical potential gradients
- Pressure: due to pressure gradient
- Electrostatic: due to electrostatic potential gradient

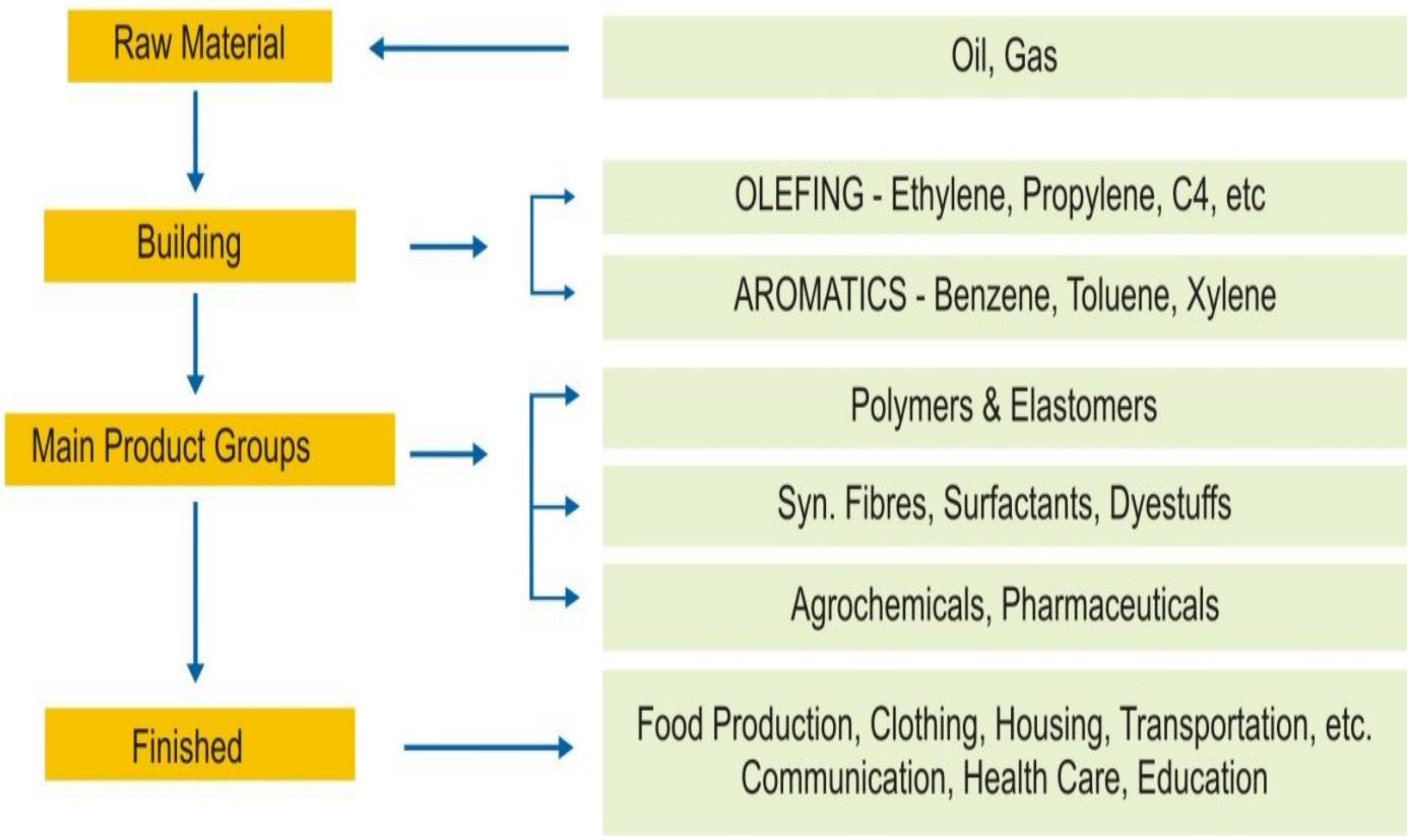
Examples of Separation Processes

Types of mass transferring agents

T Y P E of F E E D

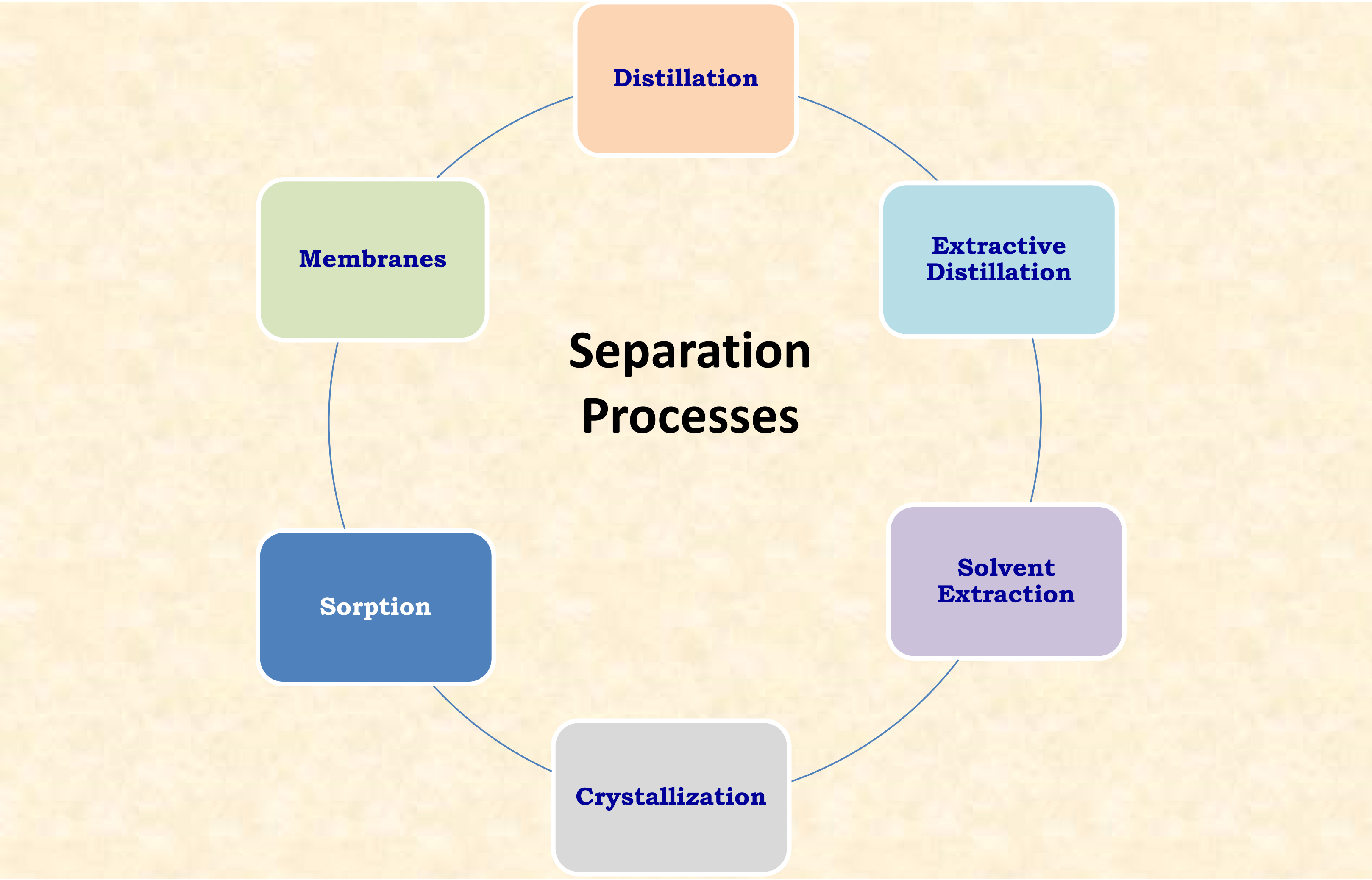
	Solid	Liquid	Gas
Solid		Leaching	Super critical separation,
Liquid	Adsorption Chromatography Ion exchange	Coagulation Solvent Extraction Extractive distill Azeotropic distill	Stripping
Gas	Adsorption Chromatography	Absorption	

Structure of the Petrochemical Industry...

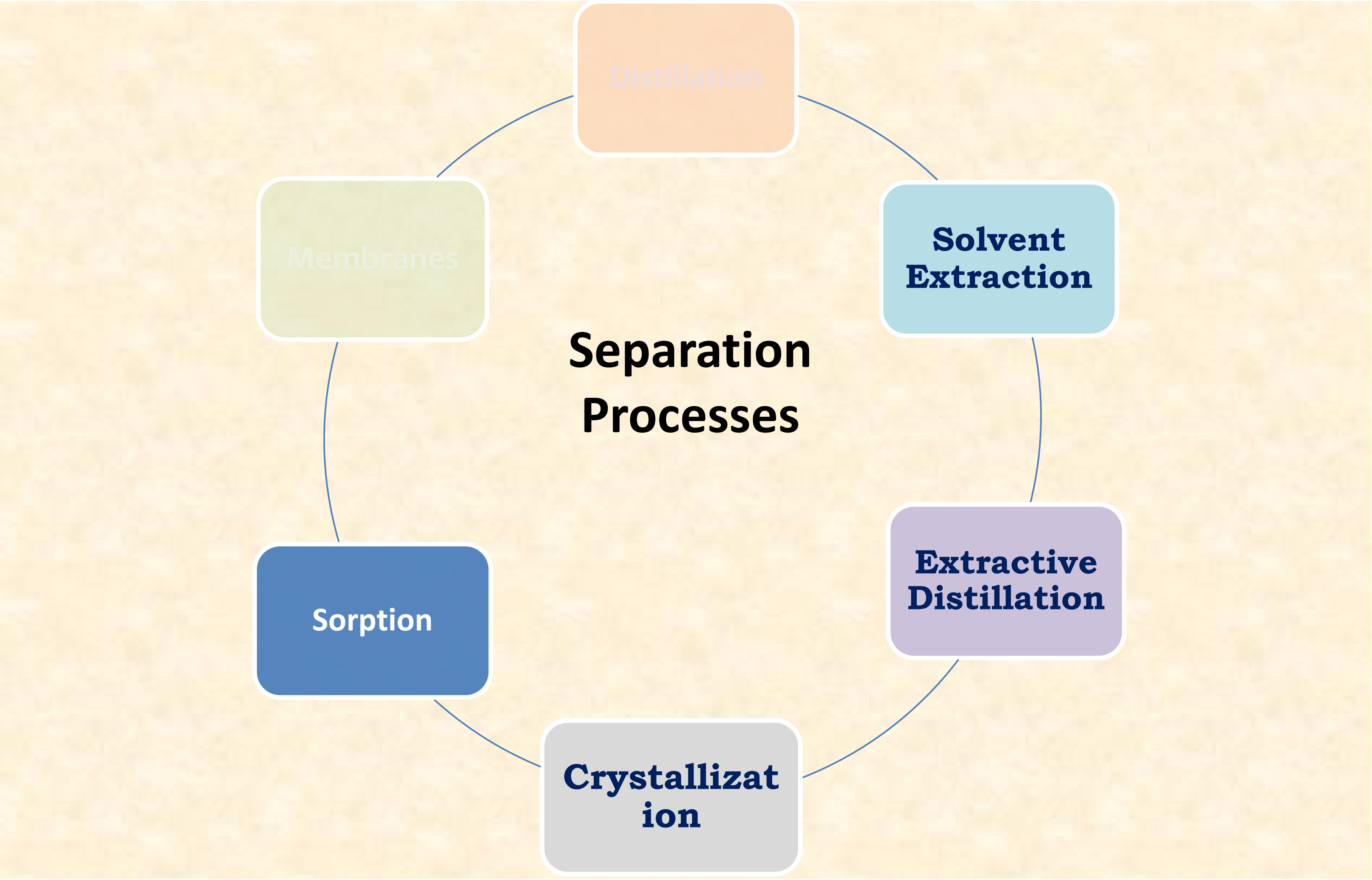


- **Petrochemical Prices ~2 to 3 times higher than transportation fuel prices**

Separation Processes Used in Hydrocarbon Industry



Separation Processes Explored at IIP Leading to Commercialization



Extraction Technologies (IIP-EIL)

S. NO	LOCATION	SOLVENT USED	CAPACITY (T/A)	STATUS OF COMMERCIALIZATION
BT				
1.	BPCL , MUMBAI	SULFOLANE	98,000 BENZENE, 17,000 TOLUENE	ON STREAM (1985)
2.	KRL, KOCHI	SULFOLANE	90,000 BENZENE, 17,000 TOLUENE	ON STREAM (1987)

Recent Success Stories at CSIR IIP

- **Simultaneous Production of US grade Gasoline and Recovery of Benzene from FCC C6 Heart Cut by using Extractive Distillation (IIP-RIL)**

- **Wax De-oiling Technology for Wax Production (IIP-EIL)**

Simultaneous Production of US Grade Gasoline and Recovery of Benzene from FCC C6 Heart Cut Using ED

Background

- EPA spec (2011) on Benzene in US gasoline : 0.62 vol.% max
- Increasing pressure on refiners worldwide to reduce benzene in gasoline pool
- RIL Jamnagar has two of the largest FCC units
- Naphtha fraction produced from these units is major contribution of benzene in the gasoline pool
  - FCC DIH side cut is rich in Benzene (11 to 19%w)
- In 2011 RIL evaluated exiting technology i.e hydrotreating for benzene removal
  - High capital and operating cost
  - Loss of Octane as well as benzene
  - Large CO_2 footprint

RIL finally approached CSIR IIP in Sept. 2011 to study the feasibility of extracting benzene from C6 Heart Cut (DIHC) FCC naphtha

Steps towards commercialization ....

- **Proof** of Concept demonstration at lab scale
- Detailed experimental studies and simulation model development
- Scale-Up, Process design and Optimization
- Development of Technology Information Package (TIP)
- Preparation of Basic Design Engineering Package
- Plant erection and commissioning

Proof of Concept Study:

Feed Characterisation

❖ Study was carried out on actual Feedstock (DIH Side cut) received from RIL in March 2011

1	Class type analysis GC, weight %	
	Mono Olefins	35.72
	C6 Di-olefins	1.18
	Paraffins (Nor + Iso)	31.54
	Naphthenes	17.47
	Benzene	14.09
2	Total Sulfur, ppm	108.1
3	Total oxygenates (EN-13132) , ppm	208
4	Total Nitrogen , ppm	6.65
5	Total Chlorides , ppm	0.1
6	Metals , ppb	40
7	Density kg/m^3 , @ 20 ^{o} C	725
8	Research Octane Number (RON)	87.0

9	Distillation, ASTM, D86, % Vol.	°C
	Initial boiling point (IBP)	48.0
	5%	67.2
	10%	67.5
	20%	67.6
	30%	68.0
	40%	68.3
	50%	68.6
	60%	69.3
	70%	69.9
	80%	70.9
	90%	72.6
	95%	74.6
	Final boiling point (FBP)	91.8
	Distillate (ml)	98.0
	Losses (ml)	0.8
	Residue (ml)	1.2

Proof of Concept Study:

Feed Characterisation

- *Heart Cut : Narrow BP range ~(60 – 90°C)*
- *High Olefin Content*
- *Presence of Naphthenes & Di-olefins which co-boil with Bz*

  - key factor for benzene purity
- *Considerable amount of high boiling C7 compounds*
- *Low benzene Content (11-19 %) as compared to conventional feeds*
- *Feed rich in Sulphur , oxygenates , also contains chlorides*

Challenging Feed Stock

Proof of Concept Study… Contd.

- **Initially Liquid-Liquid Extraction was carried with conventional solvents like Sulfolane and NMP**
  - **Product yield and purity did not meet required specifications**

- **Following which Extractive Distillation (ED) was carried out using Sulfolane**
  - **Runs could not proceed beyond 125°C – 130°C**
  - **Sulfolane started degrading above 125°C**
  - **Column choked due to polymerization**

Solvent Reactivity with Olefins

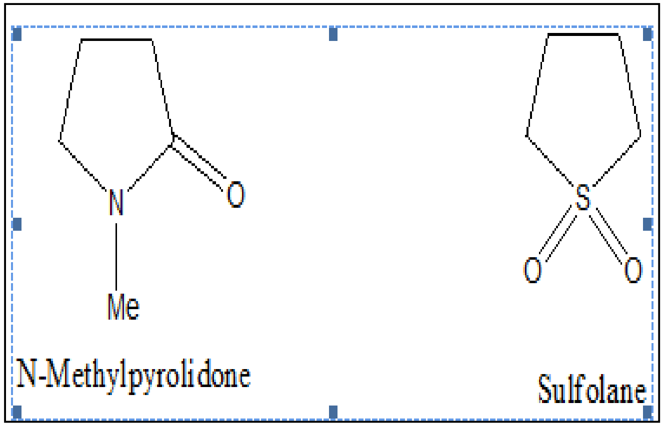
Oxidation Stability – Chemistry

- **Alkenes are well known to undergo polymerization**
  - **At high reaction temperature**
  - **In polar medium**
  - **Under acidic conditions.**
  - **Peroxide presence accelerate the polymerisation**

- **The S=O bonds of sulfolane is highly polar due to the lower bond strength in comparison to the C=O bond of the NMP**

- **Higher temperature may cause the Lewis acid initiated co-polymerization of olefins especially di-olefins and cyclic olefins**

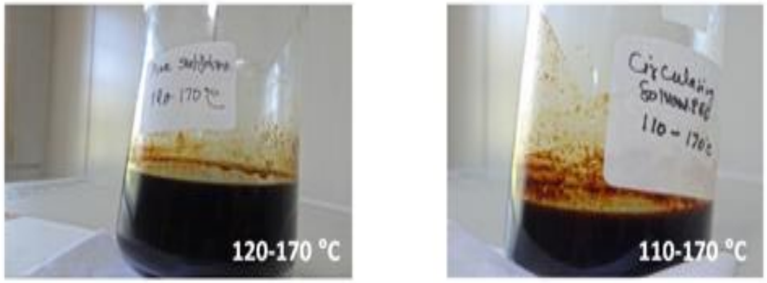
- **However, polarity as well as acidic character of C=O bond is much lower and may not initiate the polymerization of olefins in case of NMP**



PH : 7.5 – 8.0 **PH : 4.9**

Proof of Concept Study… Contd.

Thermal Stability of Solvents



Sulpholane + FCC Gasoline C6 Heart Cut

170°C

140°C

NMP+ FCC Gasoline C6 Heart Cut

	Mixture of Solvents with Feed (FCC Gasoline C6 Heart Cut)		
Solvent	**Sulfolane**	**Sulfolane + 3-Me - sulfolane (92:8 w/w)**	**NMP + Water (98 :2 w/w)**
	Observation for colour and deposits of feed solvent mixture		
Observations	**Black after 126°C**	**Black after 128°C**	**Not black (180°C)**

Thermal Stability of Solvents

Observations:

Therefore at higher temperature, olefins get polymerized in sulfolane, while in NMP polymerization does not take place

- **Feed stock re-analysed to determine peroxide content**
  - **After determining the peroxide content thermal & oxidative stability of the solvents were carried out in presence of the actual FCC heart cut feedstock**
    - **Peroxide Value, milimoles/litre ; 36.75**

Peroxides (mainly organic in nature) and Di-Olefins were attributed to solvent degradation

Why NMP?

Stable to Heat and Oxidation

- **NMP used in base oil extraction (285-290 °C)**

- **Used in Butadiene Extraction (45-55% Di-olefins – Butadiene)**
  Clear indication of Thermal & Oxidation Stability of the solvent

- **Stability at high temperatures enables ED bottom and SRC operation at positive pressure vis a vis vacuum in Sulfolane case, which avoids air ingress into the system**

Proof of Concept Study… Contd.

Experimental Work

- **Series of ED runs were carried out at different operating conditions**
  - **3 different ranges of water content were studied (< 1.0 wt. %, 2.0 – 2.5 wt. %, > 4.0 wt. %)**
  - **Reboiler temperature varied from 160 to 190 °C**
  - **Solvent to feed ratio 2 to 5**
- **A basic simulation model was developed to compare with the experimental results**
- **Interaction parameters were fine tuned to match the experimental results**

ED Run Results compared with Simulation Values

- **Feedstock: FCC C6 Heart Cut stream**
- **Column Operating Pressure – 1 atm abs.**
- **Stages in Oldershaw Column : 30**

Conclusive Findings

- **Benzene impurity in Raffinate < 0.2 wt. % in all runs with varying water content**
- **Benzene purity in Extract > 97 wt. % in all runs with varying water content**
- **Solvent system remains stable even up to temperatures of 180°C**

Components	Raffinate (Solvent Free)		Extract (Solvent Free)	
	Lab.	Simu.	Lab.	Simu.
	Mass %	Mass %	Mass %	Mass %
Mono Olefins	41.20	41.19	0.40	0.33
C6 Di-Olefins	0.42	0.39	1.43	1.60
Paraffins (N+I)	38.07	38.11	0.24	0.32
Naphthenes	20.3	20.3	0.01	0.08
Benzene	0.02	0.01	97.92	97.67
Total	100.0	100.0	100.0	100.0
Sulfur (ppm)	3.1		628.6	
	Lab.	Simu.		
EDC Reboiler Temperature °C	160.0	159.6		

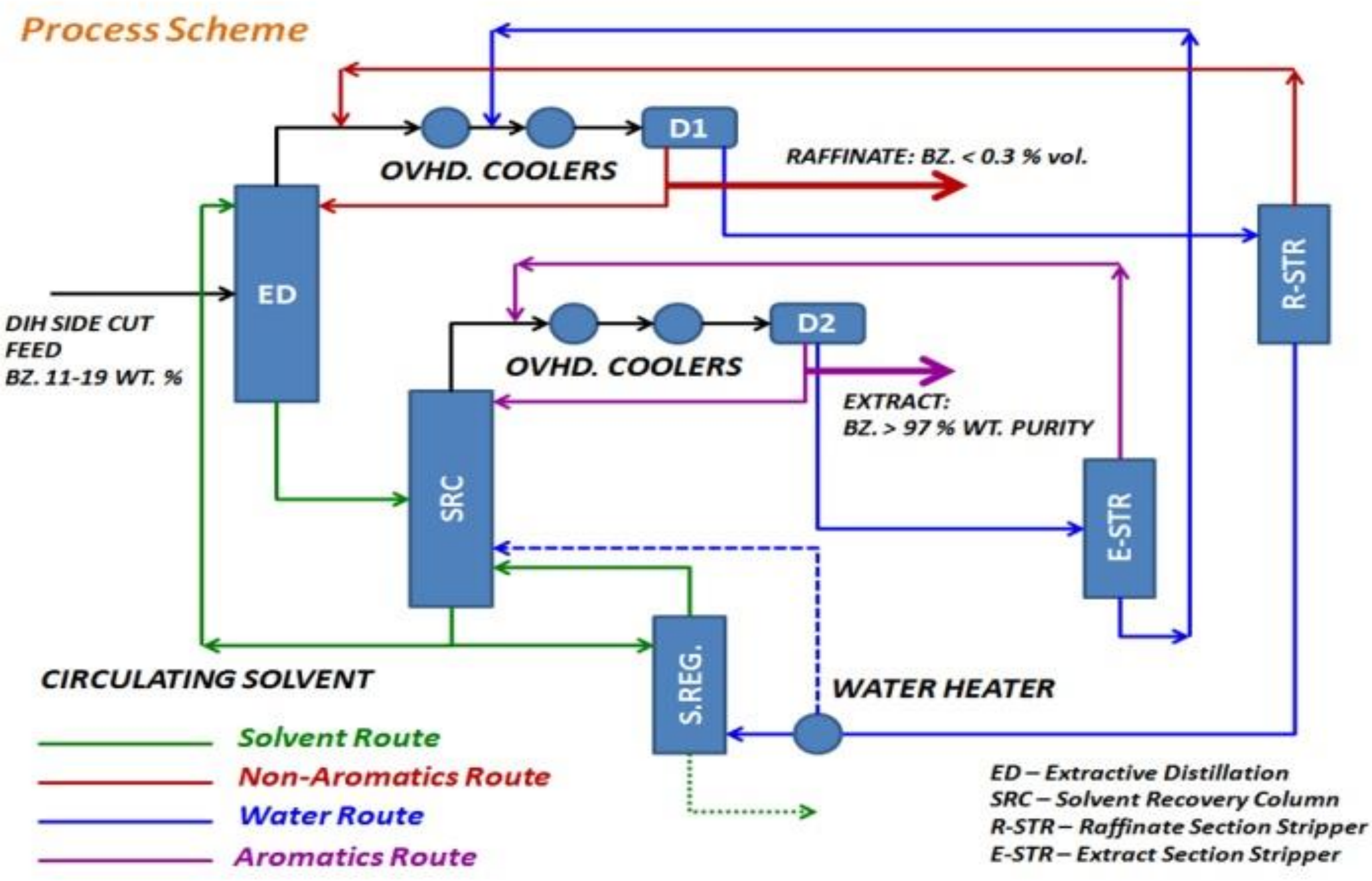
Technology Information Package

- **Process engineers from Reliance and CSIR–IIP developed TIP jointly**
- Unit is designed for feed flow rate of 70 TPH with 20 % overdesign
- **Technology Information Package (TIP)** consists of the following

- **Finalized design basis**
- **Process description**
- **Process flow diagram**
- **Process stream summary**
- **Heat and material balance**
- **Equipment data sheets**
- **Utility summary sheets**
- **Column Process data sheets,**

- **Process Data Sheets for Heat Exchangers & Air coolers**
- **Preliminary control loops**
- **Sampling Schedule, Test methods & Lab equipment**
- **Waste and Effluent summary,**
- **Chemical & additives summary and consumption**
- **Material Safety Data Sheets (MSDS)**

Simplified Process Flow Diagram



Salient Features of Technology

- **Process conceived is totally new in the Refining Industry - First time in the world**
- **Designed with an out-of-the box process configuration which minimizes solvent loss, utility requirements, and maximizes yield & purity of products.**
- **The process does not require any prior hydrogenation step (Naphtha SHU) to saturate di-olefins which makes it simple, energy efficient, and low cost.**
- **Highly thermal stable solvent system**
- **Both columns (EDC & SRC) run at positive pressure (no requirement of vacuum)-No air ingress**
- **Recovery of benzene is very high i.e. more than 99%**
- **This process provides a high recovery of de-aromatized gasoline fraction, with almost nil benzene and minimal loss of octane value**

Plant Commissioning at RIL Jamnagar

The unit was commissioned successfully on 23rd May 2016.

- **Flawless commissioning**
- **No incident/accident**
- **On spec Product out in 48 Hrs.**
- **100% throughput within a week**

- **Benzene content in raffinate : nil to 0.01% (against the spec of 0.2%.)**
- **Benzene recovery >99.9% against >99% in design.**
- **Entire gasoline pool with Bz <1% v achieved at RIL and Sulphur < 5 ppm**
- **Producing extract containing more than 98% aromatics.**

Performance Guarantee Test Run

- **Performance guarantee test run (PGTR) conducted from September 21-24, 2016 using design spec through puts (Feed and solvent)**

With the commissioning of this unit it has been proved to the world that this difficult stream can be used to produce not only low benzene gasoline but also rich aromatics

Formal Recognition and Awards Conferred for the Innovation

- ❖CSIR Technology Award for Innovation in 2014
- ❖ Best Innovation Award for Technology Development 2015

By Ministry of Petroleum & Natural Gas (MoPNG)/ CHT, New Delhi

- ❖ICC Award for Excellence in Process design 2016

Patents

Process for production of benzene lean gasoline by recovery of high purity benzene from unprocessed catalytically cracked gasoline containing organic peroxides

US	May 13, 2014 Feb 13, 2013	8722952 B2
JP	12-5-2017 13-3-2015	6138938 2015-526010
SU	12-5-2017 13-3-2013	973016 2015108049
CN	25-08-2017 13-3-2013	ZL201380049094.5 Chinese Patent Gazette, Issue No. CN 104718276 B

Wax De-oiling Technology for Wax Production
(IIP-EIL)

Production of Paraffin & Microcrystalline Waxes at NRL (IIP_EIL)

Wax production unit , NRL, Assam

Numaligarh Refinery has installed a Wax Deoiling Unit with investment of Rs.~753.72 crore

Production Capacity

- **45,000/50,000 TPA Paraffin Wax**
- **5000 TPA Microcrystalline Wax**

Dewaxing-Deoiling Pilot Plant at CSIR-IIP

- **Basic Design data generated at CSIR-IIP**
- **BEDP by EIL along with IIP's Technical Support**

Plant commissioned in April 2015

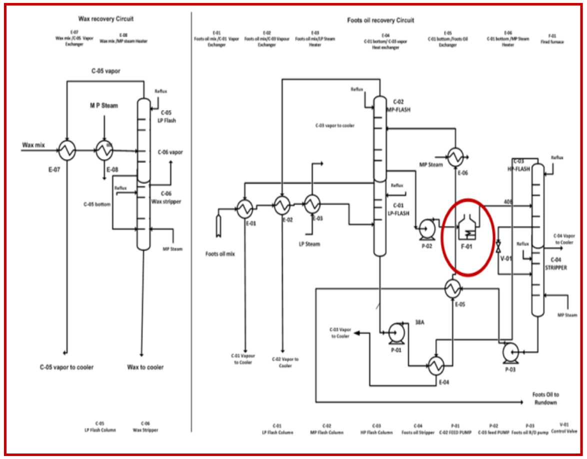
Chronology of Commissioning of Wax Plant

- The construction activity of NRL Wax Plant was started in January, 2011.
- The mechanical work of wax plant was completed in October, 2014.
- Commissioning of wax plant was completed in March, 2015
- Numaligarh Refinery Limited (NRL) has initially started commercial production of Bureau of Indian Standard (BIS) Type-2A & 3 Paraffin Wax from June, 2015
- First Paraffin wax sample produced at NRL

Numaligarh Refinery Limited (NRL) has started commercial production of BIS Type - 1 & 2 Paraffin Wax from February, 2016.

Innovative Component

- Wax production process uses large quantity of solvent for crystallization of wax. The solvent is recovered for its reuse in the process.
- In initial licensed technology proposed to NRL has fired furnace in the solvent recovery section which was very expensive, needs huge foot print in the plant and require significant operational and maintenance cost.



Our Approach:

- 'Pinch Analysis' on Solvent Recovery Section of Foots Oil in Primary design.
- The entire hot utility requirement can be met by using MP steam.
- **No requirement of 'Fired Furnace' (4.0 MMkcal/hr)**

Elimination of the Furnace results in significant savings on fixed capital investment.

Salient Features of Wax De-oiling Technology

- Use of single solvent (MIBK)
- Lower solvent-to-feed ratio
- The novelty of IIP's De-oiling Process is unique multi-stage dilution pattern employing combination of delayed dilution, cold dilution and incremental pattern for maximum gains.
- High filtration rate
- Lower chiller/filtration area & refrigeration requirements
- Controlled crystallization for producing larger wax crystals with narrow crystal size distribution
- Lower Cost in comparison to foreign technology
- Energy efficient process with built in operational flexibility
- In this process, furnace was eliminated from solvent recovery system - by applying pinch analysis - which helped NRL to reduce carbon foot print

Dedication of Wax Plant to the Nation

- This Numaligarh Wax plant was dedicated to the nation by Honorable Prime Minister, Shri Narendra Modi Ji on 5th February, 2016.

- The commercialization of indigenous Wax De-oiling Technology is in line with ***'Make in India'*** initiative taken by the Government of India (GoI).

Economic Benefits of Commercialization of Wax Technology at NRL

- First wax plant set-up by any petroleum refinery in the country based on indigenously developed technology with the largest investment (Rs 676 Crores).
- The wax plant is designed to produce 50,000 TPA of Paraffin Wax and 4500 TPA of Microcrystalline Wax
- This technology helped to increase refinery profitability.
- With the addition of the new product slate of paraffin Wax into the refinery product range, there is an increase in the GRM to the tune of USD 0.53/bbl equivalent to Rs 77.0 Crore.
- This technology cut down the wax import by 50%
- It saved foreign exchange of the order of Rs. 300 crore/annum
- **NRL captured 52% of market share in India; Started wax export to 13 countries**

Societal Benefits of Wax Plant at NRL

- The wax plant generated direct employment for local people

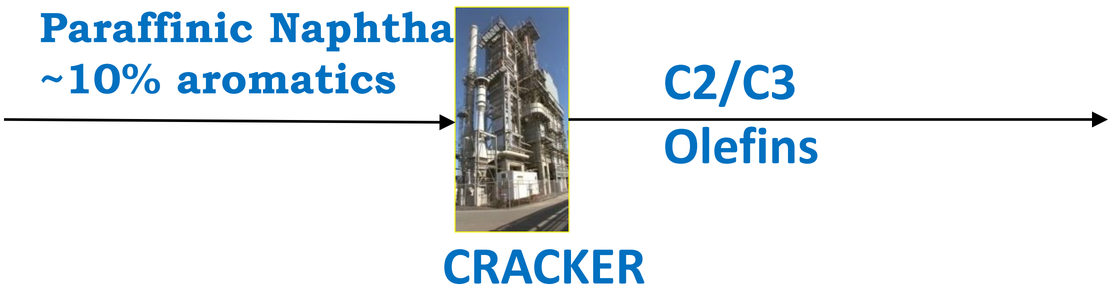
- Setting–up of ancillary medium and small sized plants will also create avenues for generating large scale indirect employment in neighboring areas in **North-East region of India**.

Emerging Technologies:
Commercialisation Possibilities

- **Production of Pure BTX from Straight Run Naphtha**
- **Propylene Recovery from Low Propylene Bearing Streams**

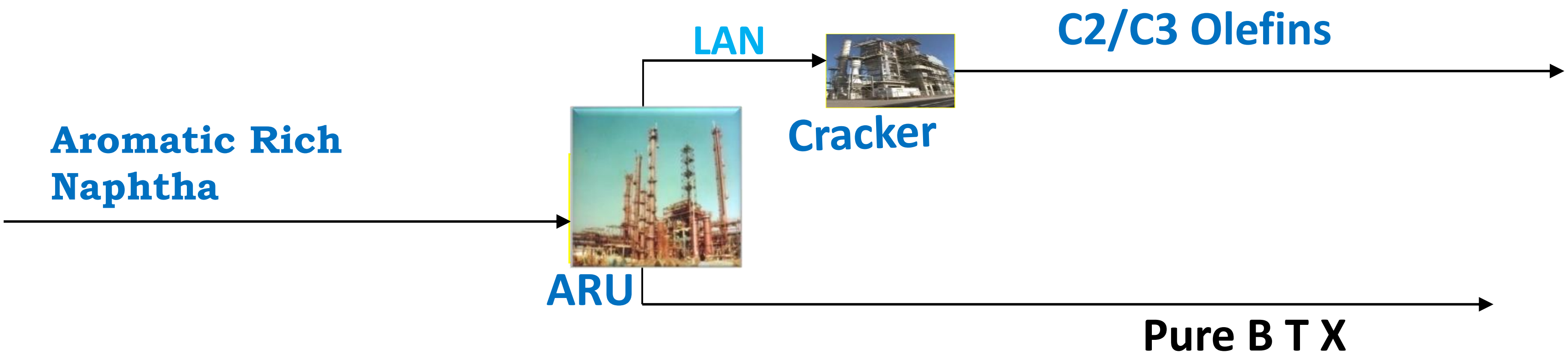
Pure BTX from Straight Run Naphtha

- Conventional Naphtha Cracking



- Aromatics Difficult to Crack
- LAN costly feedstock

- Proposed Approach

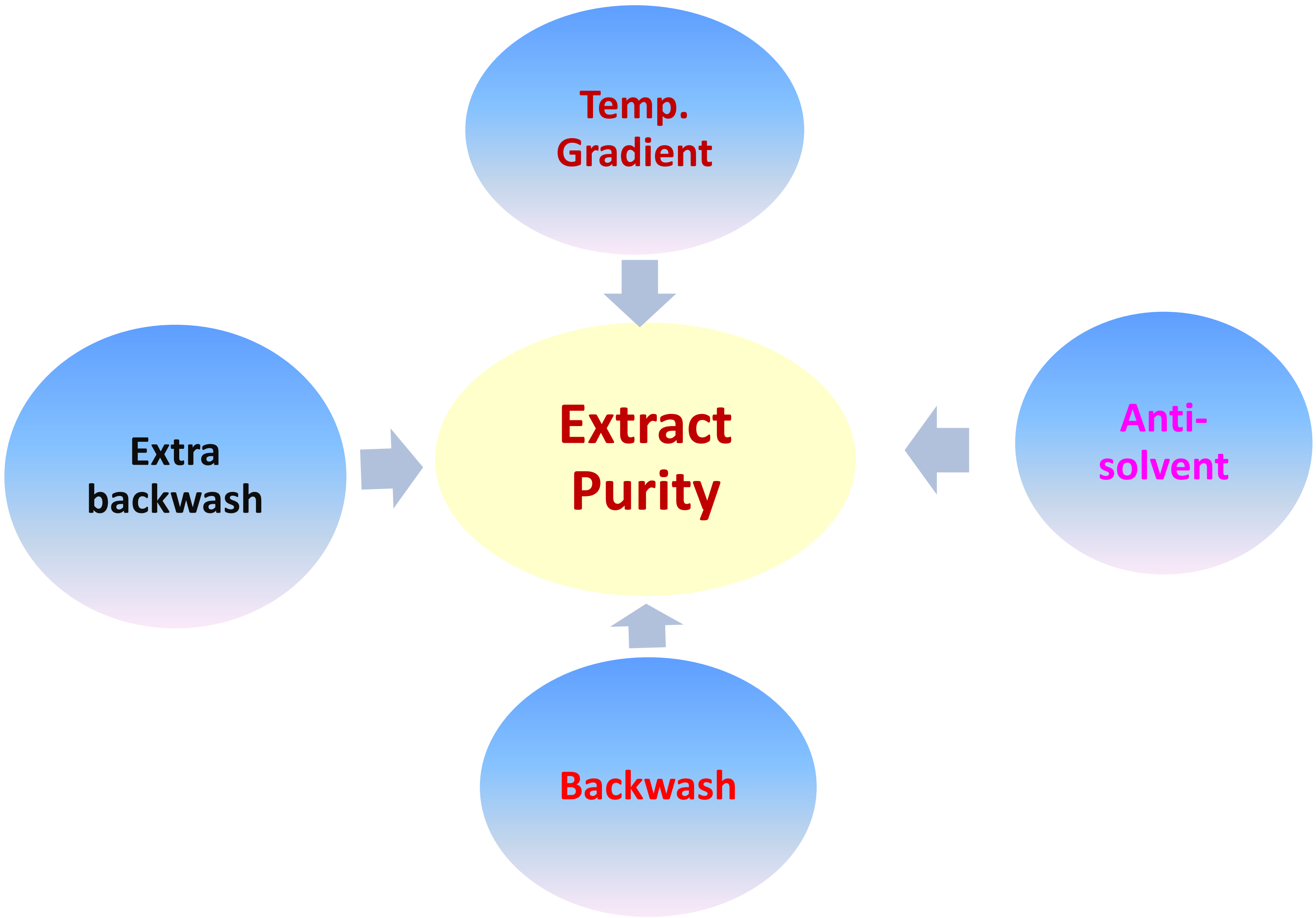


- **Additional capacity of the Cracker due to LAN processing**
- **Off spec cracker naphtha feeds can be used**
- **Improvement in economic due to production of pure BTX**

Comparison of Feed-stocks for BTX Production

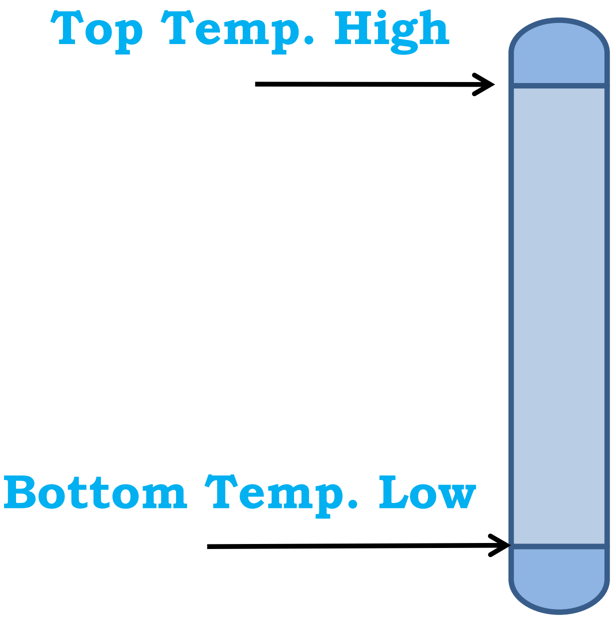
	Conventional		Challenging
Characteristics	Reformate	PG	S R Naphtha
Total Paraffins, wt.%	24.4	7.38	65.42
Total Naphthenes, wt.%	2.42	8.78	25.14 (high)
Total Aromatics , wt.%	73.18	83.84	9.44 (low)
AR/ Naphthenes Ratio	30.2	9.5	0.37

Innovations for Removal of Naphthenes



Techniques for Improving Extract Purity

Temperature Gradient



Top Temp. High

- More Capacity
- More Recovery of Aromatics
- Extract Purity Low

Bottom Temp. Low

- Low Capacity
- Non-Aromatics easily expelled from Extract Phase
- Purity of Aromatics High

Techniques for Improving Extract Purity

Use of Anti-solvent

Effect of Introducing Anti-solvent in Bottom

Top :

Pure Solvent (e.g NMP)

- **increases capacity**
- **more aromatics recovered**

Bottom :

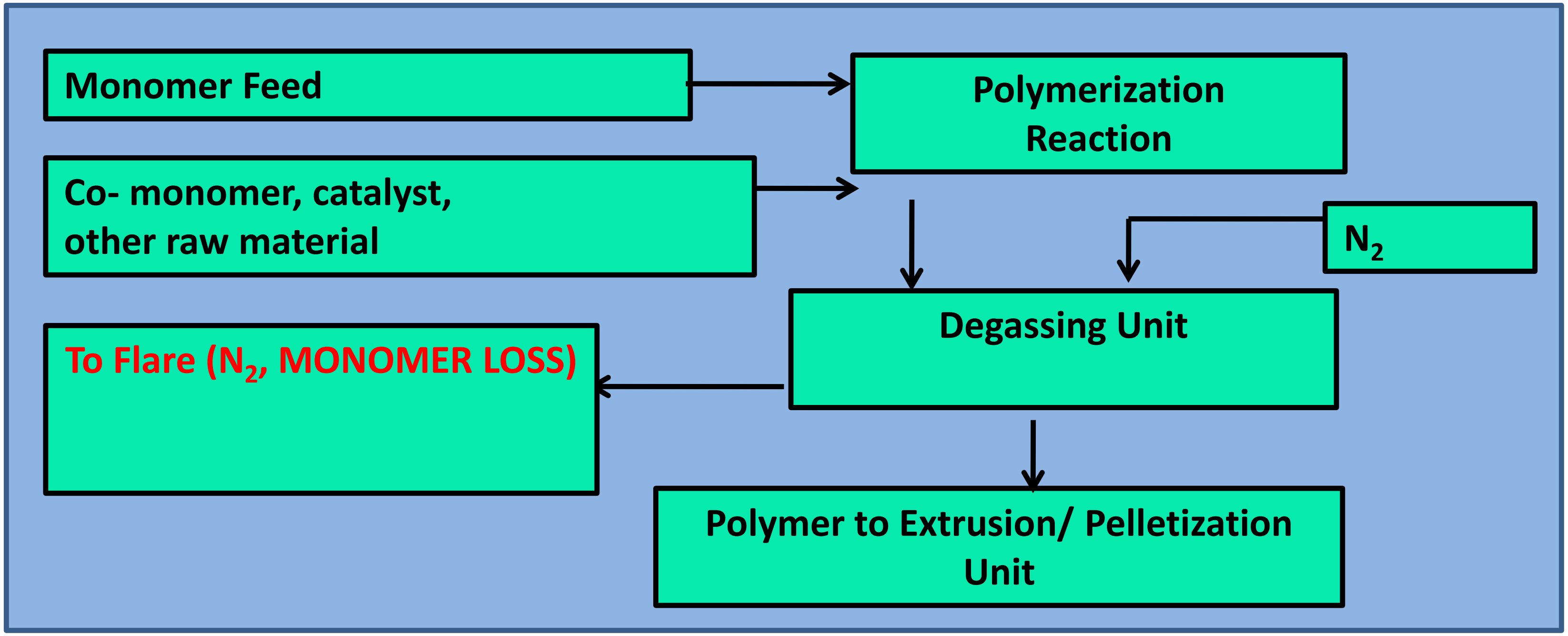
- **Anti-solvent (e.g WATER)**
- **reduces capacity**
- **non-aromatics expelled easily**

IIP Technology for pure BTX from S R Naphtha

Outcome

- Technology successfully developed and demonstrated on lab scale

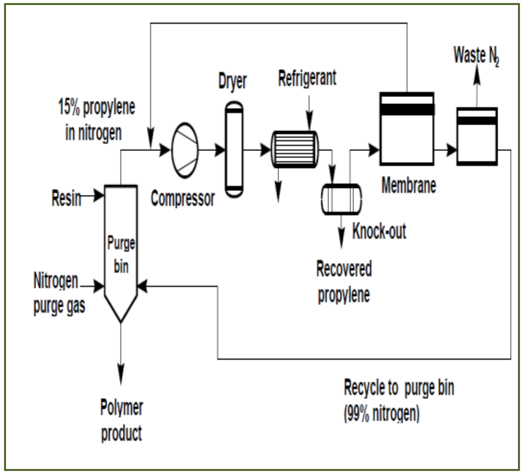
Propylene Recovery from Low Propylene Bearing Streams



- **Loss of monomers in a polyolefin plant: Up to 2 % of the feed amounting to 2000 to 4000 tons/year**
- **Recovery of propylene and Nitrogen both becomes crucial for enhancing margin of operation**

Current Recovery Practices

Membrane Based Recovery



Process: VAPORSEP

Hydrocarbon permeating membrane

Polymer Used: Silicone Rubber, Pebax, PTMSP

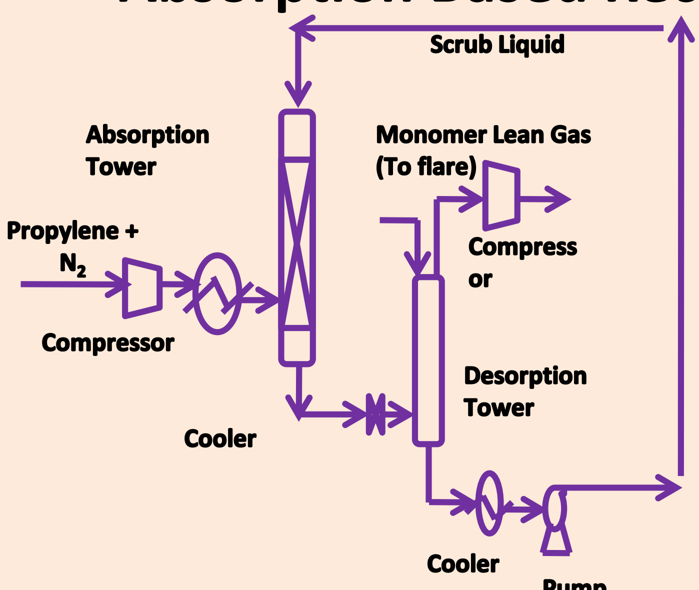
Feed pressure: 19 bar

Permeate Pressure: 1.5 bar

Temperature: - 40 ^{0}C

COMMERCIAL Licensor Membrane Technology Research, USA

Absorption Based Recovery



Absorbent: N-Hexane
Pressure: 23 Bar
Temperature: -20 To - 10 ^{0}C
Composition: 51 Wt % N2, 43 Wt % Propylene, 6 Wt % 1-hexene
Hexane Flow Rate Equals 2 Times The Gas Flow Rate
Temperature (Scrub Unit): 20 ^{0}c and + 10 ^{0}C
Recovery: 30 % (At 10 ^{0}C) And 40 % (At -20 ^{0}C)

Limitations of Such Approaches

- Sub zero temperatures operation
- High pressures compression of feed
- High cost of compression and refrigeration
- Issues with membrane fouling

Preliminary Results:

- **A single column VSA process tested for recovery of Propylene and nitrogen using commercial adsorbent**
- **Nitrogen can be recycled for polymer purge**
- **Propylene can be sent to existing C_3 recovery / Alkylation unit / FCC etc**
- **There is scope in improvement of process performance by using two/ three column VSA process**

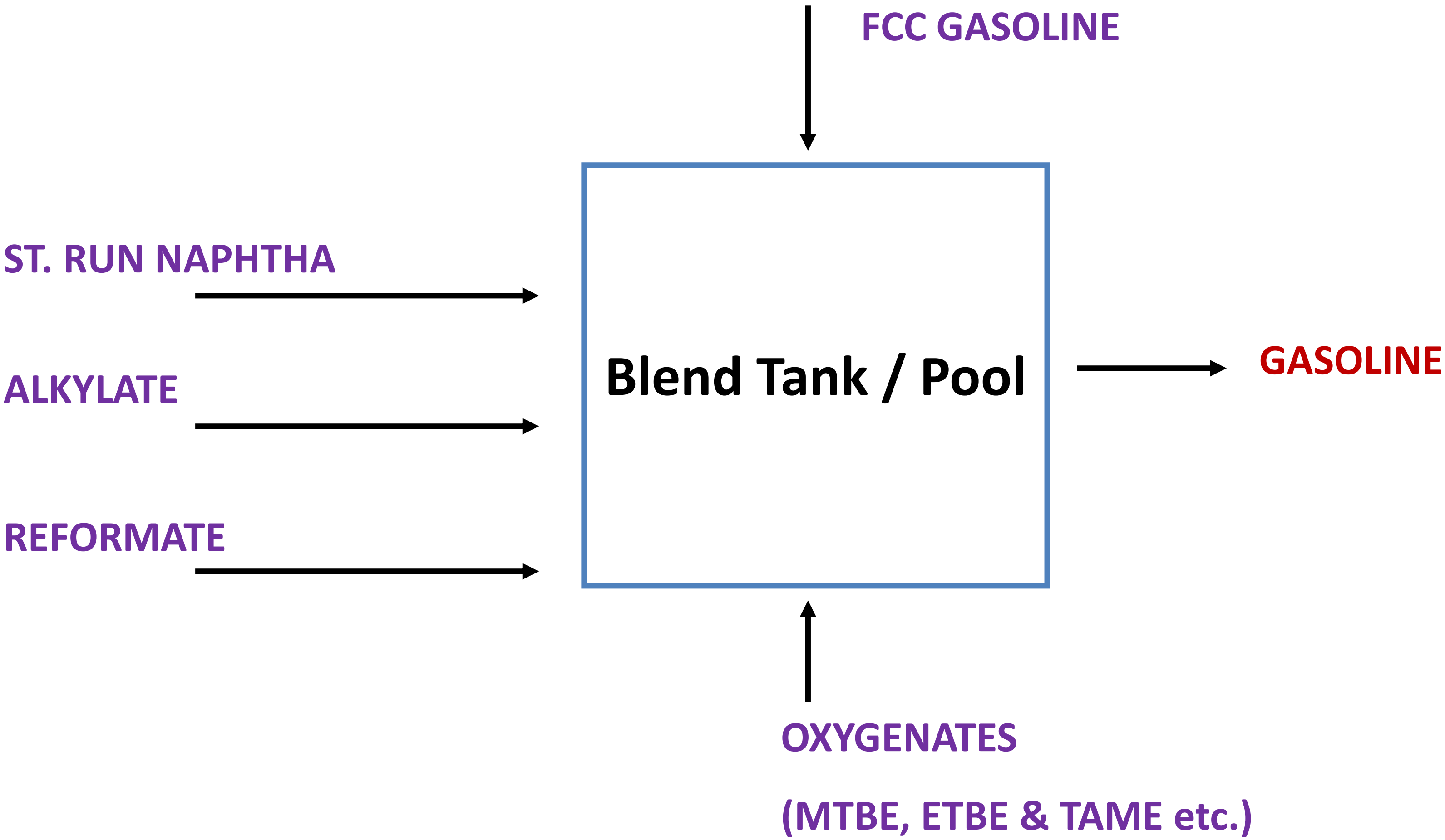
	Purity (Mol%)	Recovery (mol%)
Propylene	> 65	~ 90
Nitrogen	>99	~70

Scope for Improvement

- **Screening for better adsorbent**
- **Simple Pressure/ Vacuum Swing Adsorption Cycle to reduce power usage**
- **Development of two/ three column cycle**
- **Effect of operating conditions**
- **Simulation of Process for accurate prediction of performance**

THANK YOU

Gasoline Production







BTX Quality Specifications

- Solvent contamination : 1ppm

- Non-aromatic content (based on normal boiling point)

  - bp<110 °C : 700 ppm wt/wt in benzene fraction
  - 110 °C<bp<136 °C : 2000 ppm wt/wt in toluene fraction
  - 136 °C<bp<138 °C : 3000 ppm wt/wt in ethyl benzene fraction
  - 145 °C<bp : 5000 ppm wt/wt in remaining fraction