

Paraxylene Recovery by Crystallization

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Houston, USA*

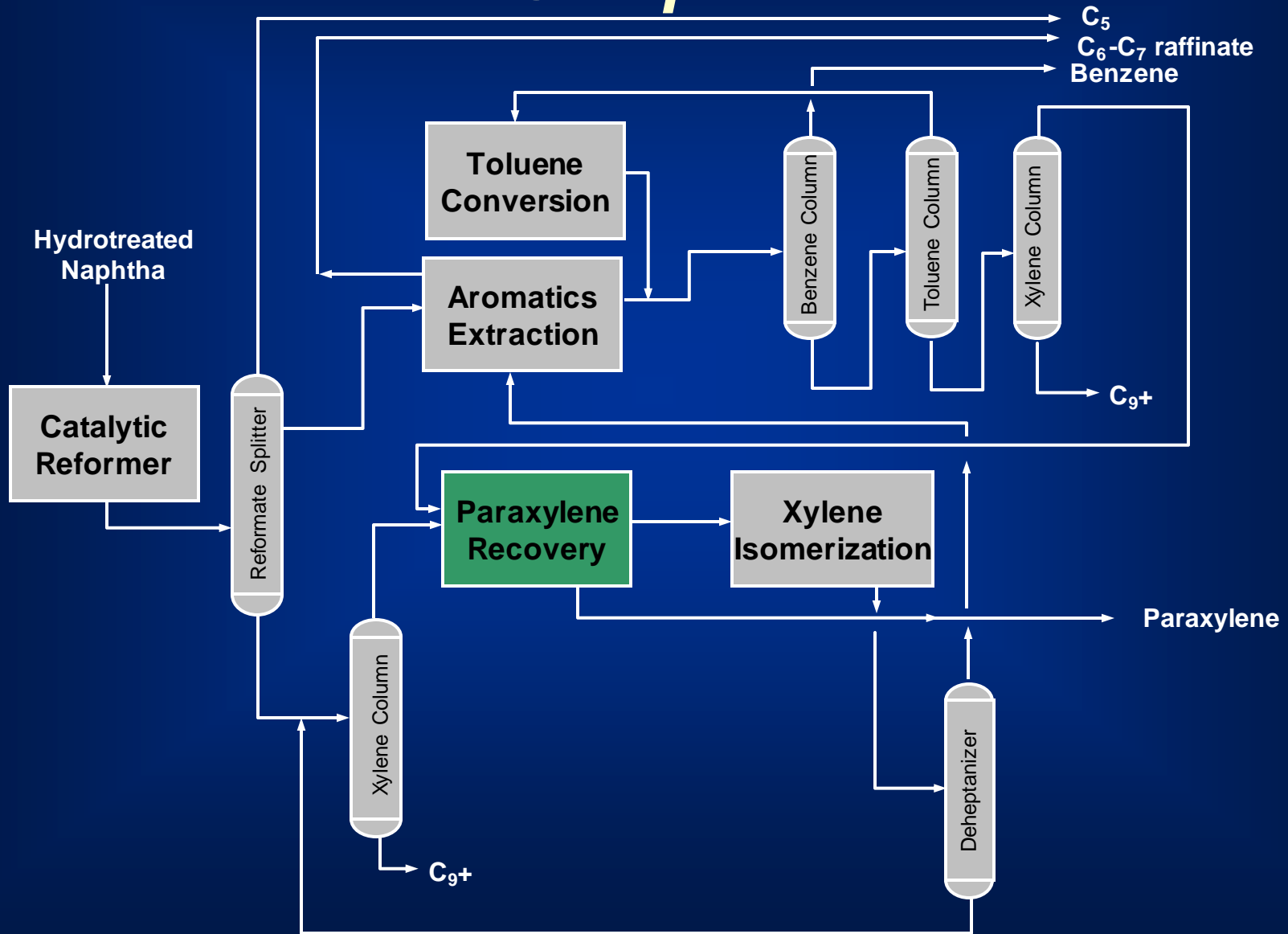
Introduction

- Paraxylene continues to be one of the highest growth petrochemical products in the world
- Attention focused on new manufacturing methods, lower production costs, and ability to match new capacity additions with market cycles
- Innovations and advances in crystallization technology provide producers with attractive options to meet processing requirements

Presentation Outline

- Relevance in Modern Aromatics Complex
- Fundamentals of Crystallization and Advances in Crystallization Technology
- Comparison with Adsorption Process
- Hybrid Concepts for Expansion
- Conclusions

Paraxylene Recovery In An Aromatics Complex



C₈ Aromatic Isomers - Separation Methods

- Boiling points of C₈ aromatic isomers are too close for distillation to be used
- Freezing points far enough apart to use crystallization
- Molecular size differences can be exploited to use adsorption

	Boiling Point, °C	Freezing Point, °C
Ethylbenzene	136.0	-95.0
Paraxylene	138.3	+13.2
Metaxylene	139.1	-47.9
Orthoxylene	144.3	-25.2

Types of PX Crystallization

- **Suspension Crystallization:**
 - PX crystallized from a solution consisting of the C₈ isomer mixture
 - Solid crystals separated from remaining liquid (mother liquor) using centrifuges
 - Continuous process
- **Static Melt Crystallization:**
 - Solutions containing C₈ isomer mixture are repeatedly cooled and heated in tubes to enrich PX to final purity
 - Batch process

PX Crystallization Fundamentals

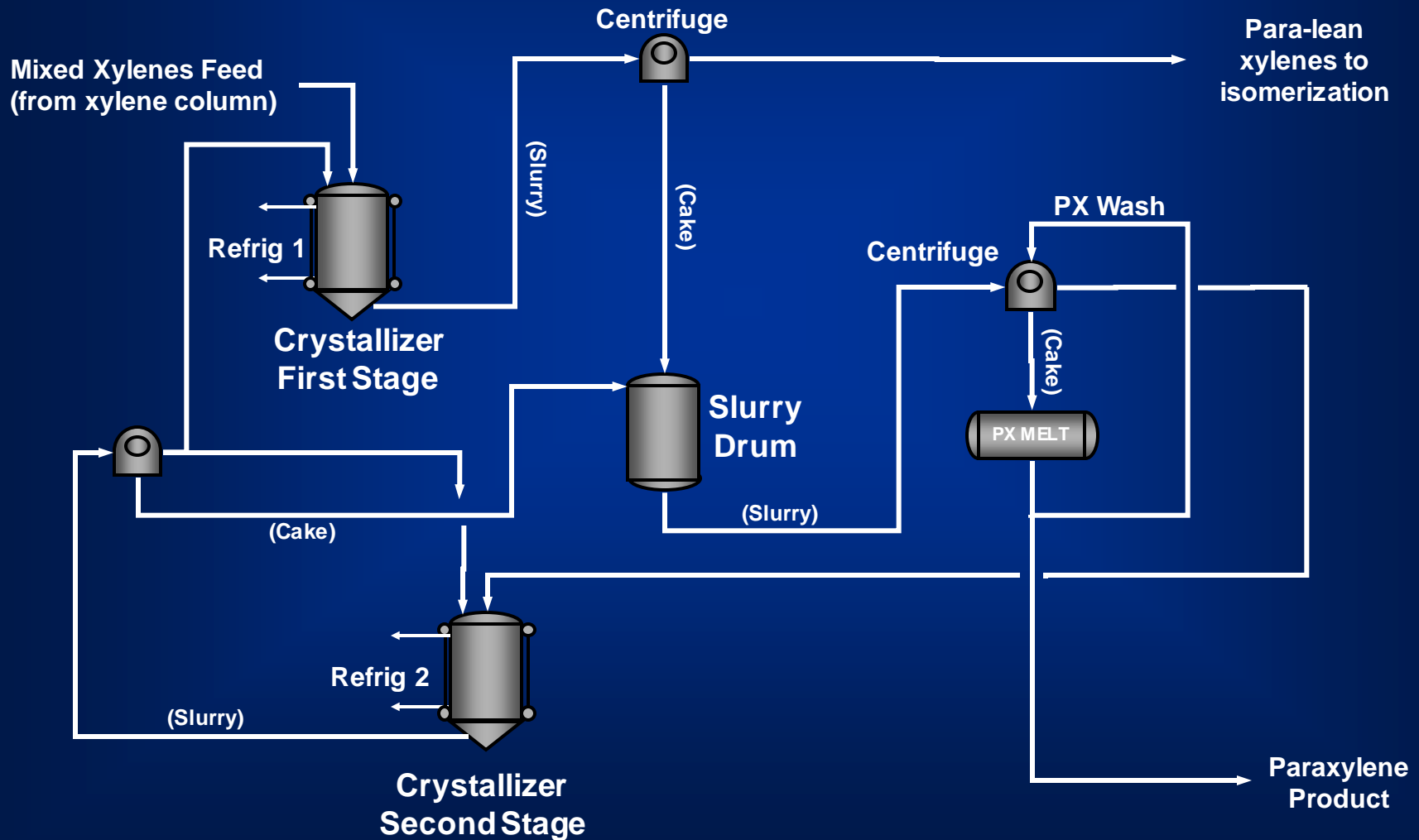
- Broad applications exist for:
 - Dilute feedstocks from reformers that contain nominally 22 wt.% PX in the C8 fraction
 - Enriched feedstocks from selective toluene conversion units that contain nominally 85 wt% PX

Component	Dilute Feedstocks	Enriched Feedstocks
Ethylbenzene	17%	4%
Paraxylene	22%	85%
Metaxylene	45%	9%
Orthoxylene	15%	1%
C9+	1%	1%

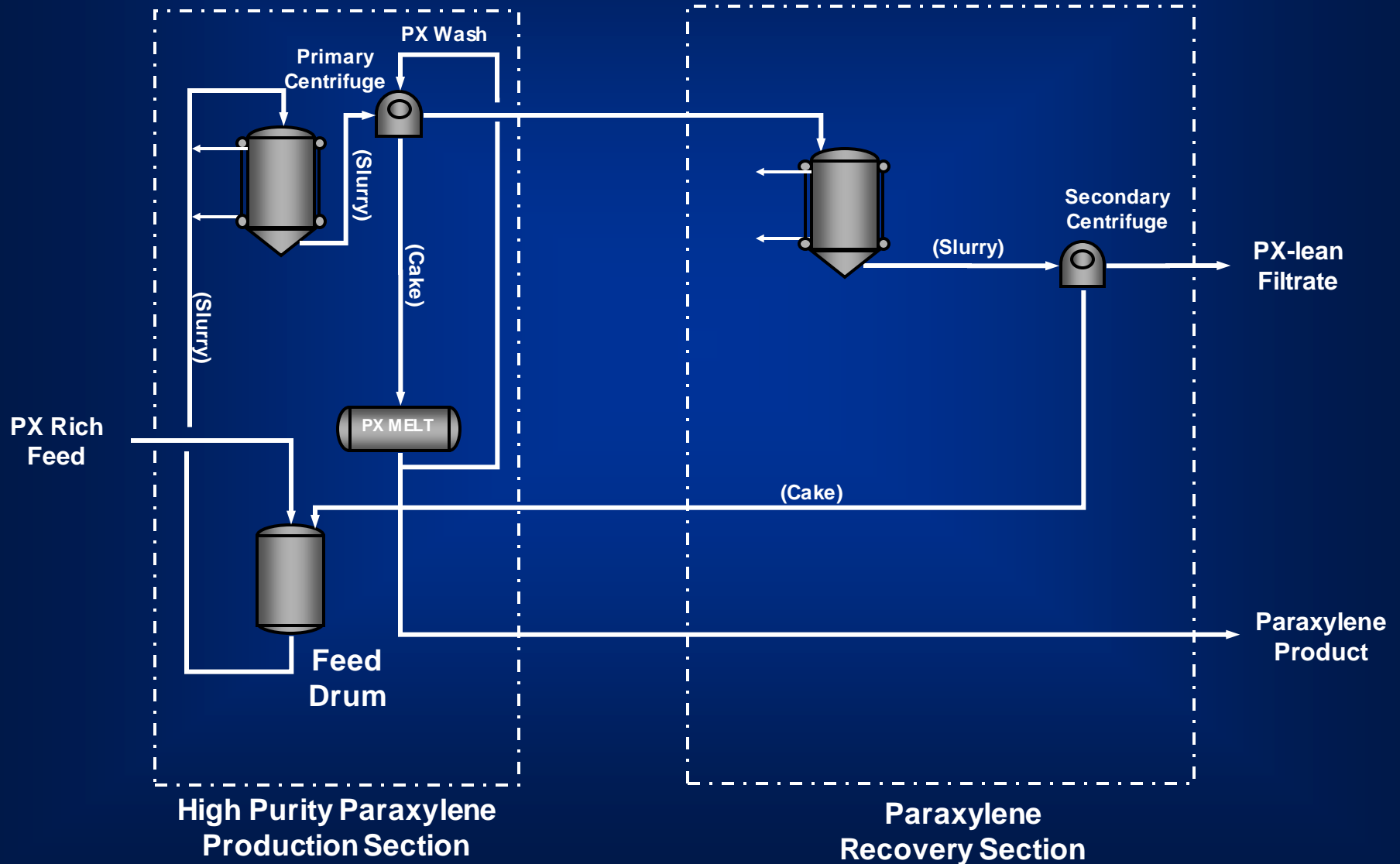
Improvements to 2-Stage Process

- Much larger and more reliable equipment;
 - First generation process produced ~3,100 MTY / crystallizer
 - Modern process produces >27,500 MTY / crystallizer
- PX product washing instead of toluene/C5 wash
- Intermediate process stages to preserve the PX concentration from the high-purity stage (gaining an additional stage) .

2-Stage CrystPX Process for PX Recovery From Dilute Feedstocks



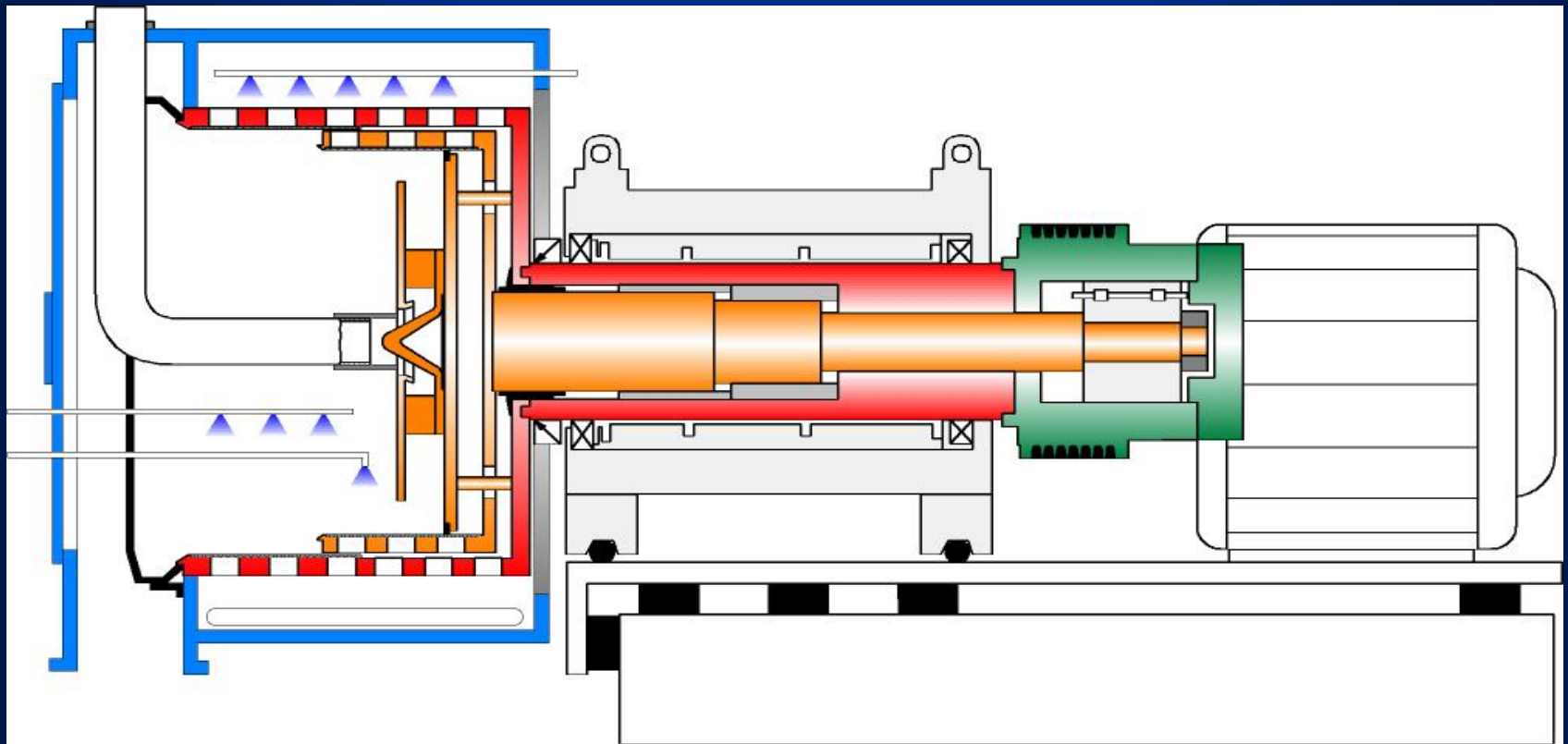
1- Stage CrystPX Process For PX Recovery From Enriched Feedstocks

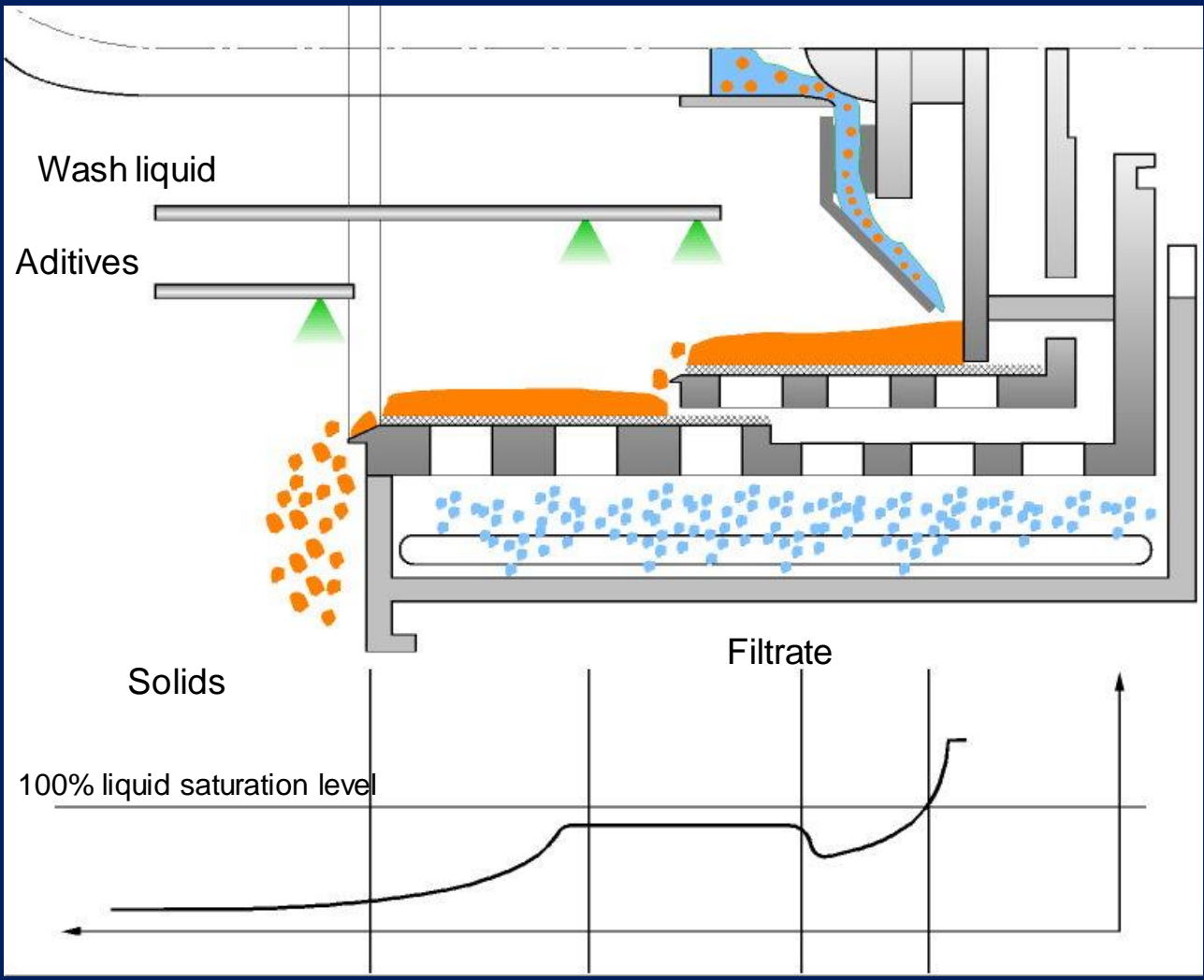


Major Equipment

- Crystallizers
 - Scraped Surface Jacketed
- Centrifuges
 - Screen Bowl
 - Pusher
- Refrigeration Unit

Pusher Centrifuge Cross Section





Wash liquid

Additives

Solids

Filtrate

100% liquid saturation level

Discharge

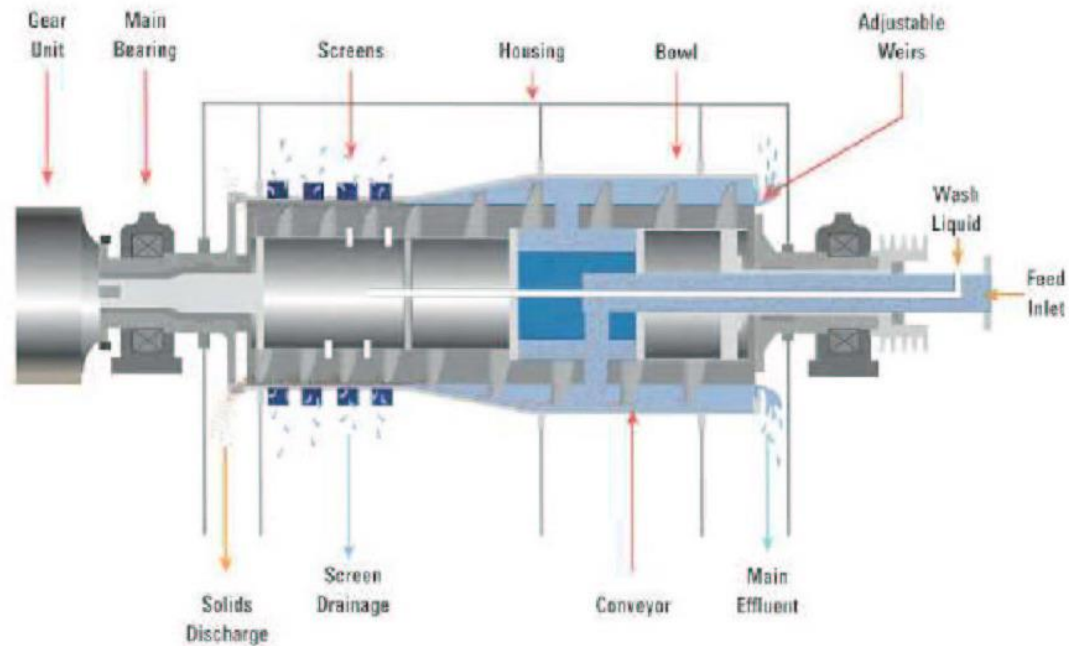
Final dewatering

washing

intermediate dewatering

Feeding, distribution & main dewatering

Screen Bowl Centrifuge



Design Parameters

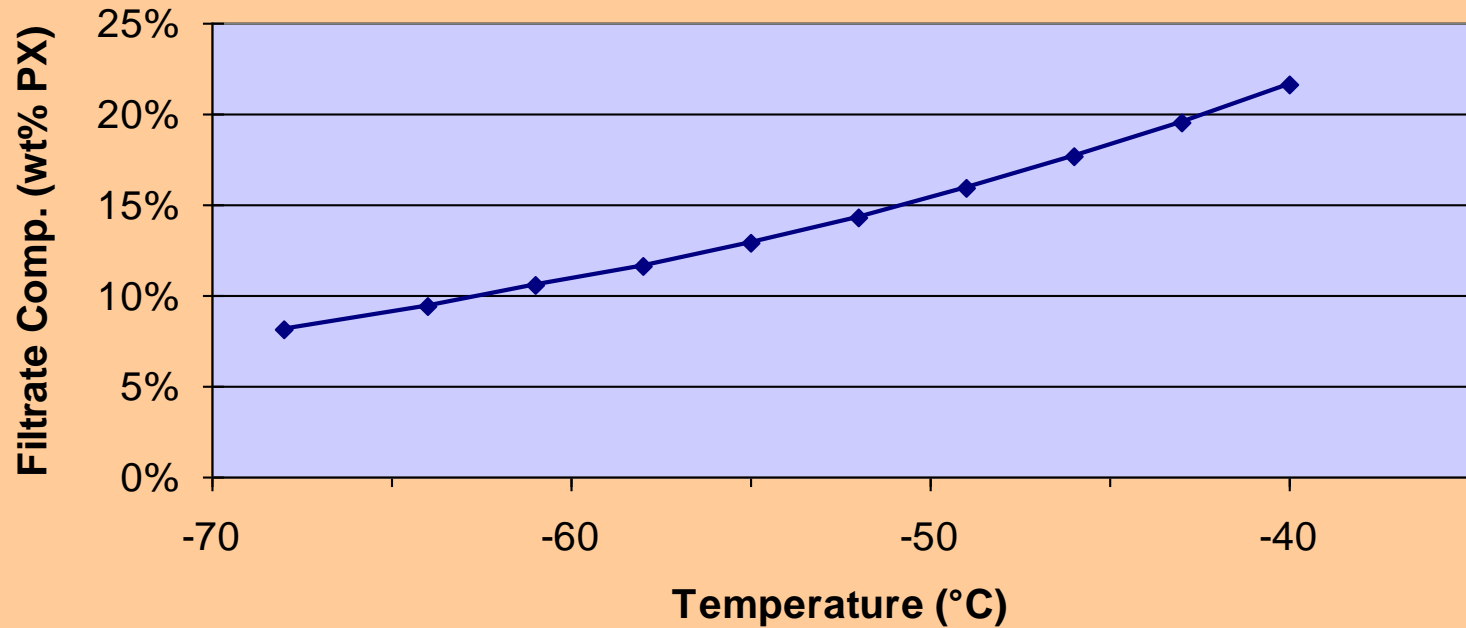
Recovery

1. Coldest crystallizer temperature (limited by eutectic)
2. Feed composition
3. Solids losses in centrifuges

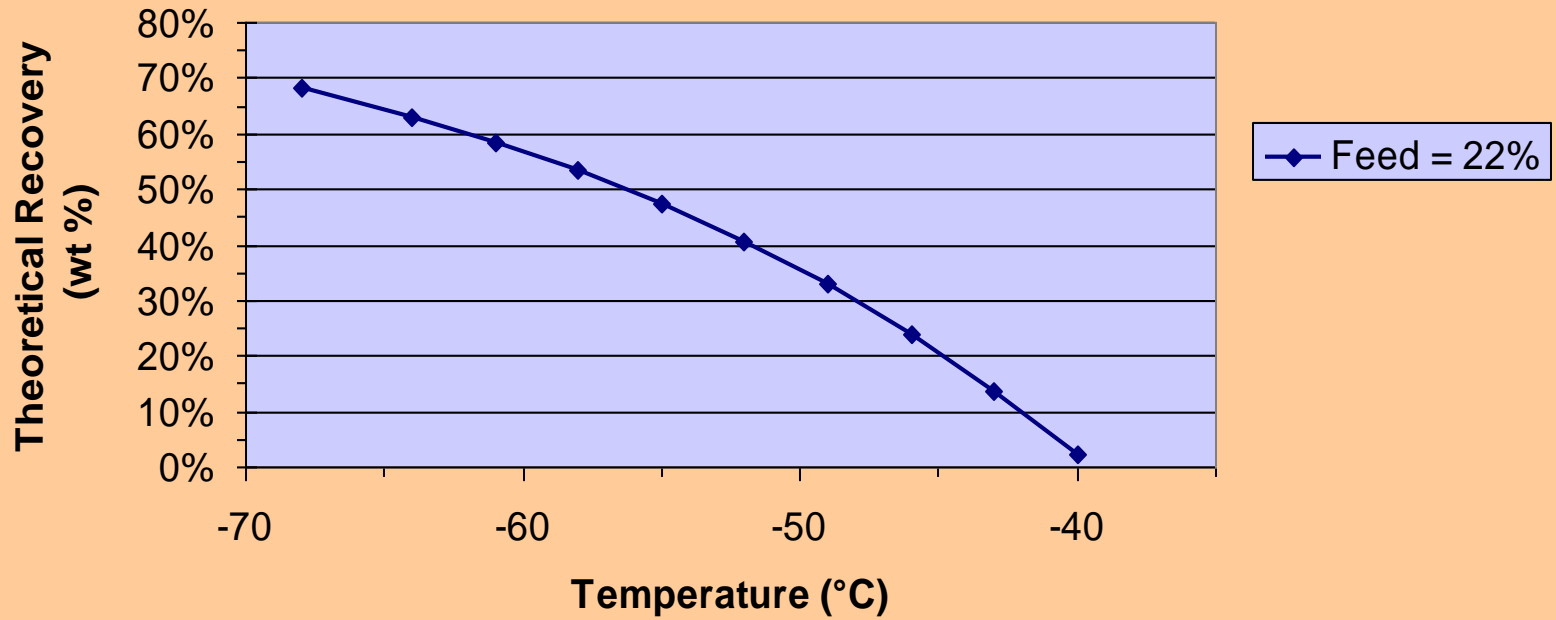
Purity

1. Product crystallizer temperature
2. Cake wetness
3. Wash efficiency

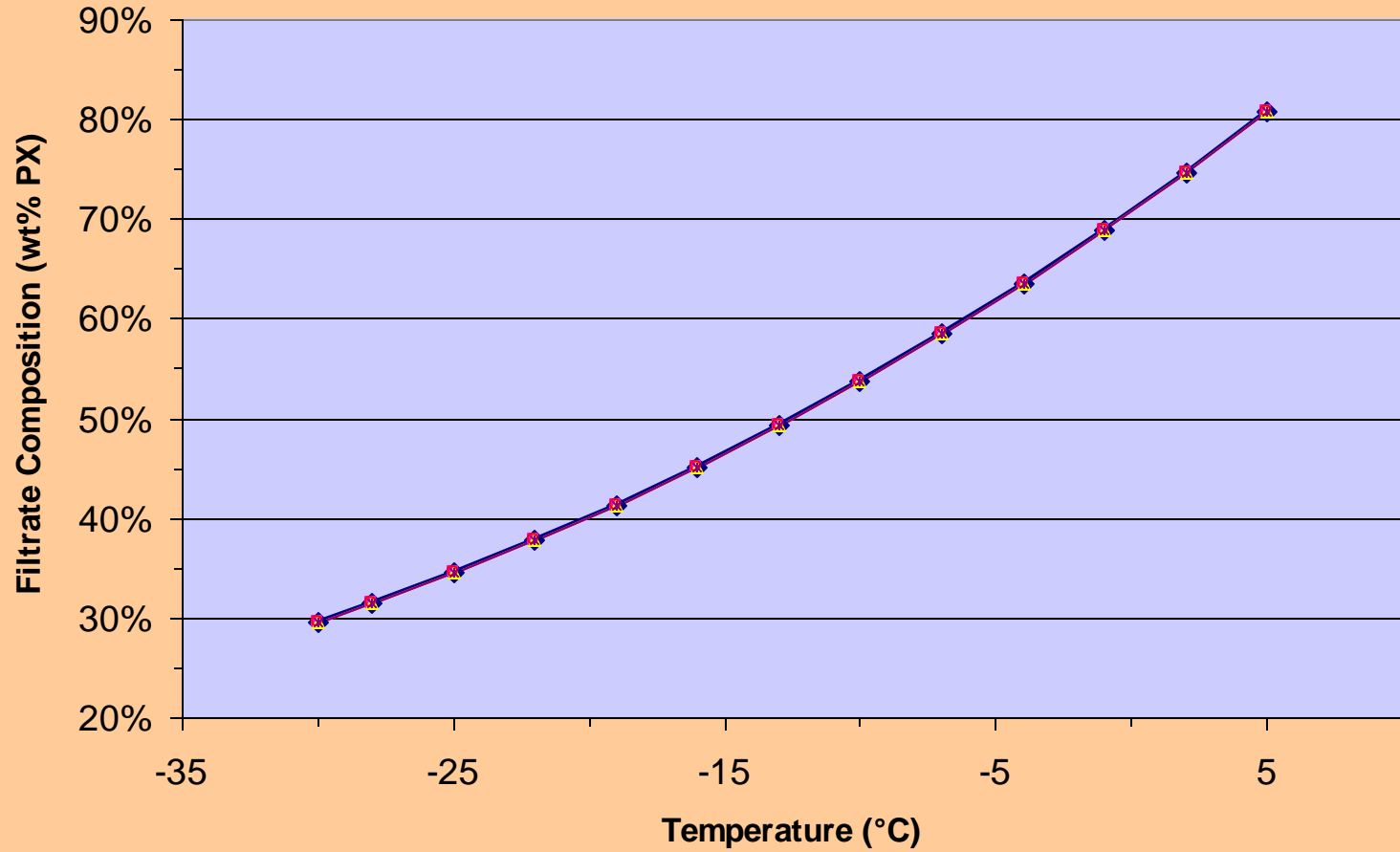
Filtrate Composition vs. Temperature (2-stage)



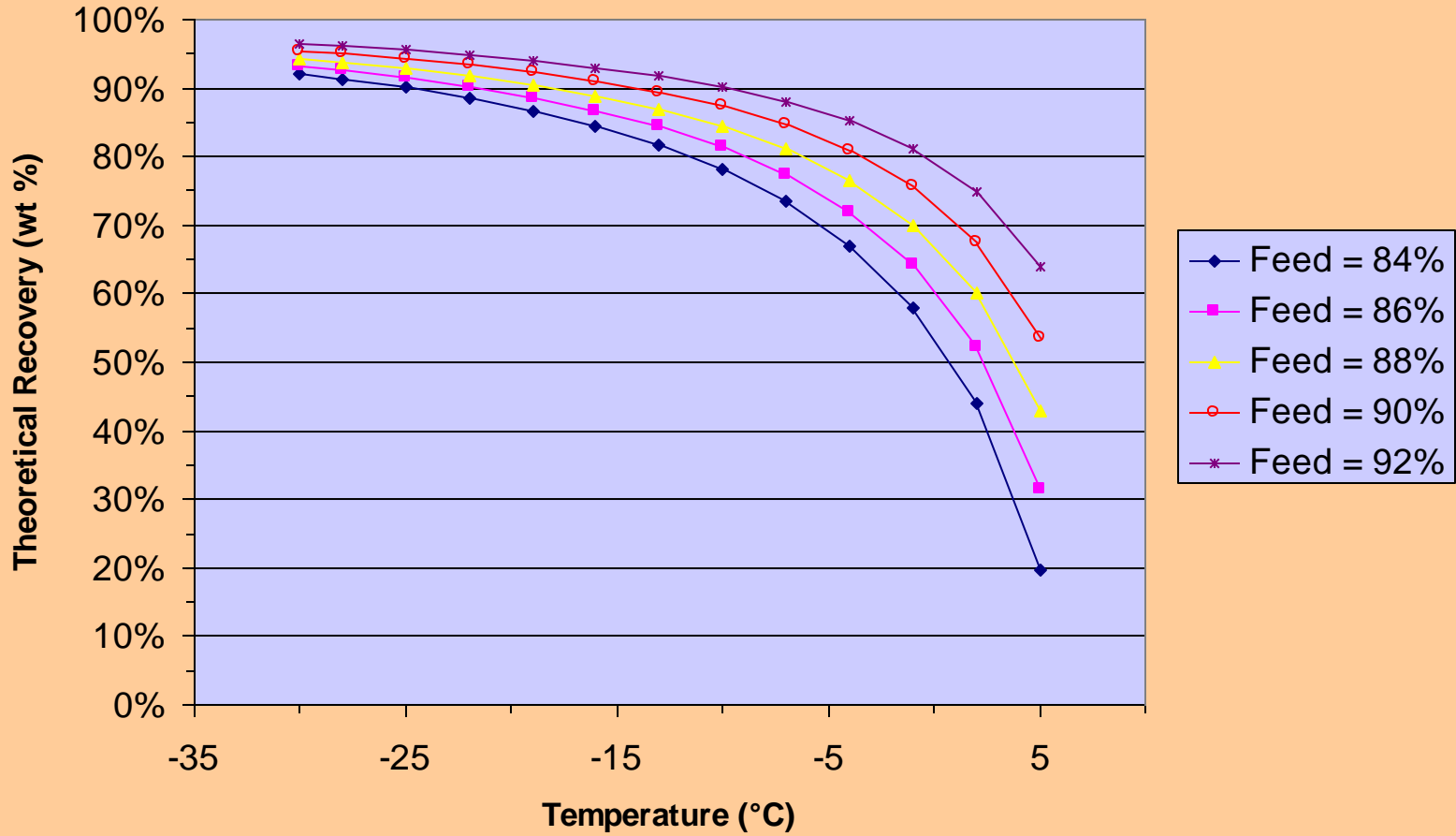
Theoretical Recovery vs. Temperature (2-stage)



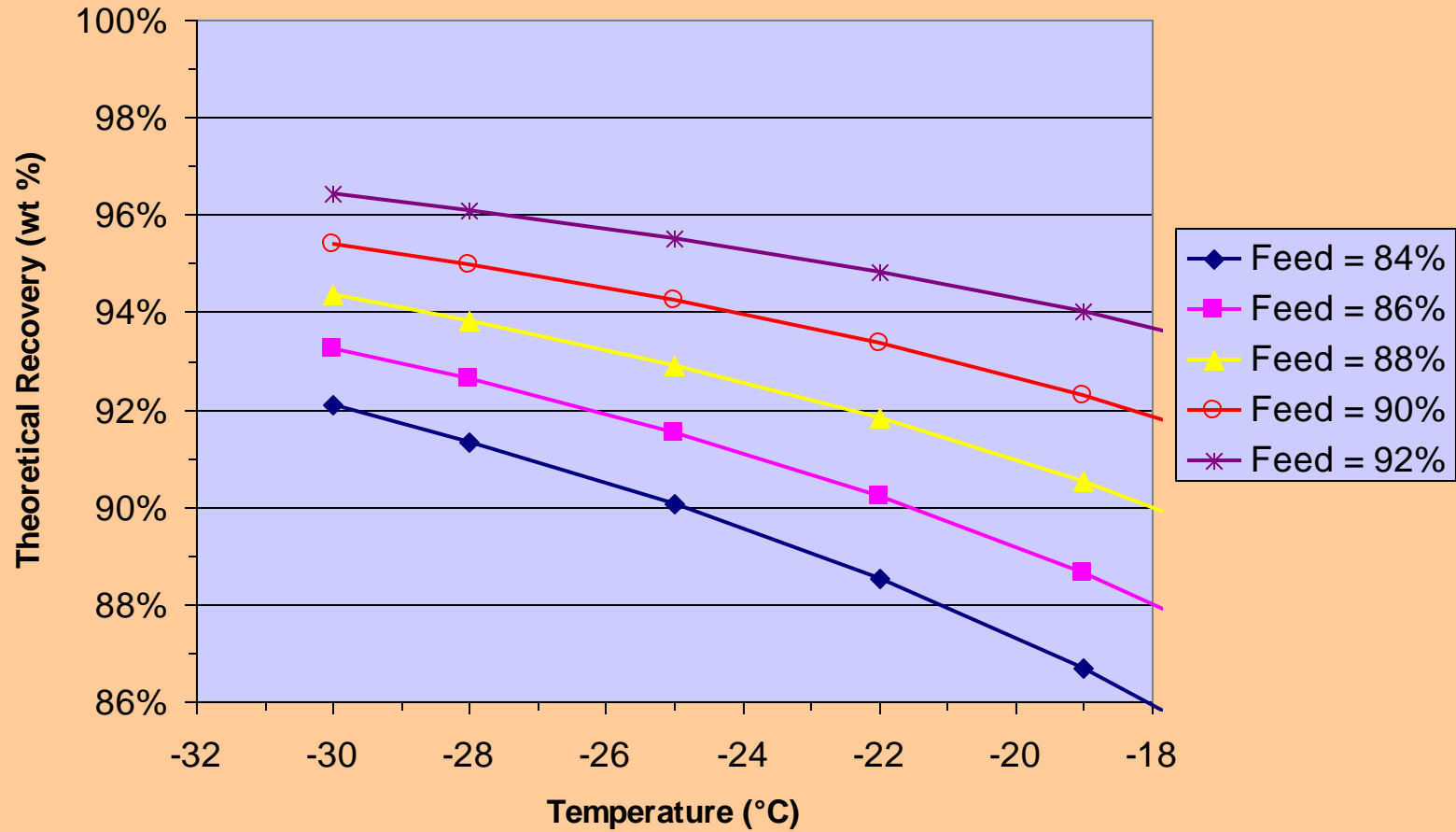
Filtrate Composition vs. Temperature (1-stage)



Theoretical Recovery vs. Temperature (1-stage)



Theoretical Recovery vs. Temperature (1-stage)



Advantages of 2-Stage Crystallization Compared to Adsorption Processes

Advantages

- Lower installed cost
- Equipment easily procured
- Feed preparation requirements are relaxed, and insensitive to most common feed impurities
- Highest product purity
- Convenient to add incremental capacity
- No expensive adsorbent and desorbent required
- Simple concept for easy operation

Disadvantages

- Lower per-pass recovery results in increased recycle to Isomerization Unit.
 - This is offset by making a short circuit of the recycle flow scheme, because of the tolerance that the crystallization technology has for C9+ components in the recovery section feed.

C₈ Aromatic Isomers - Separation Methods

- Crystallization units often mischaracterized as outdated; however, modern designs offer:
 - Higher equipment reliability and reduced maintenance requirements
 - Larger-scale equipment and reduced equipment count
 - Higher efficiency based on newer configurations and processing schemes

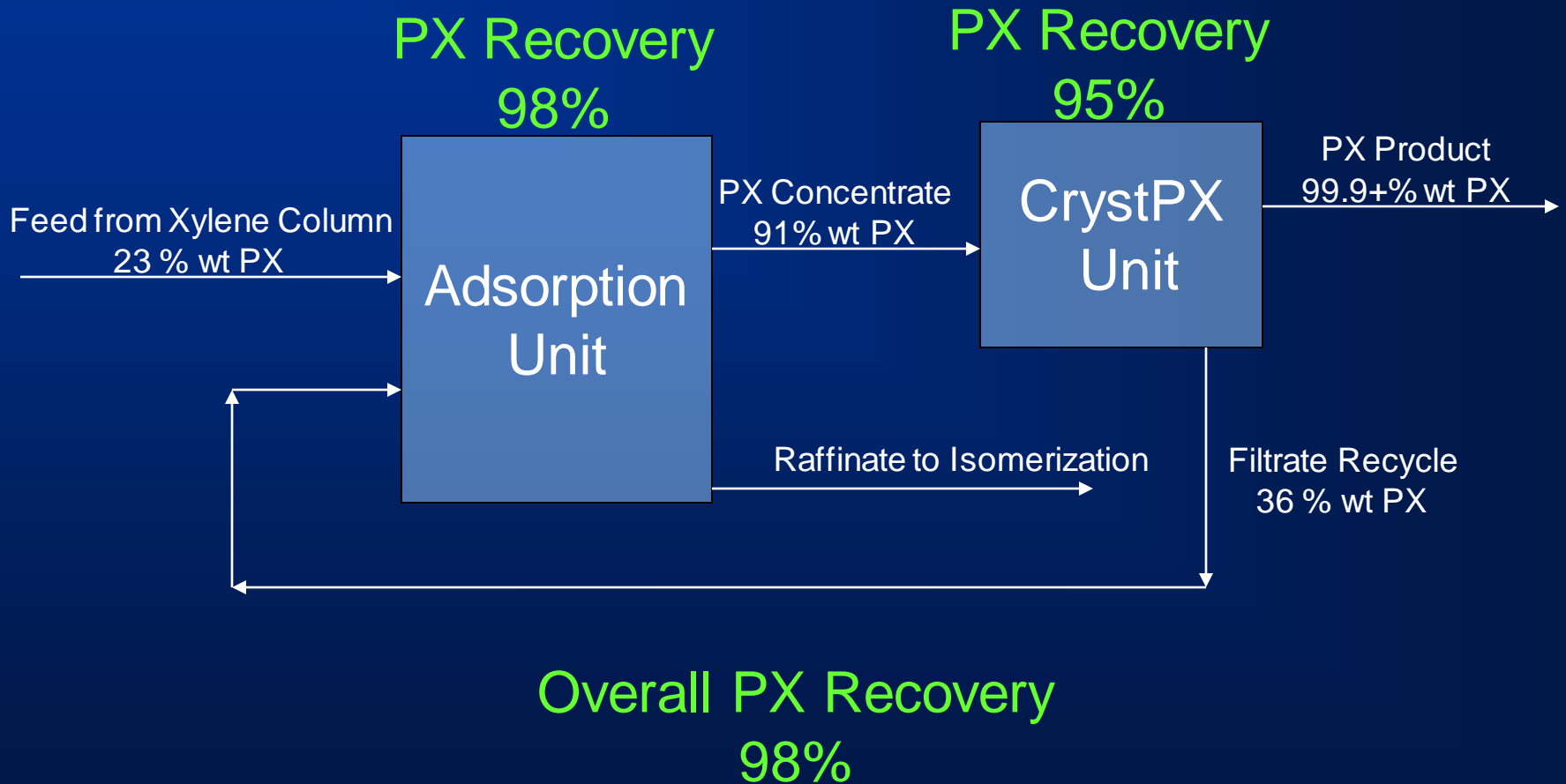
Advantages of 1- Stage Crystallization Process For PX Recovery From Enriched Feedstocks

- Fewer equipment pieces result in the lowest investment cost
- Less equipment leads to lower maintenance and production costs
- Stable operation with simple process controls; product quality maintained by paraxylene wash rate
- Highly efficient refrigeration system requires minimum cooling water consumption
- Turndown operation permissible; operating flexibility and simplicity
- Enriched feedstock results in high recovery

Hybrid Concepts Using CrystPX Process For Expansion Of Existing Paraxylene Units

- Combination of crystallization with adsorption
- Crystallization used to make final product at high-purity
- Adsorption recovers PX from low-purity streams
- Expansion of existing adsorption unit possible by relaxing output PX purity to 90%, and using crystallization to upgrade stream to 99.8 wt.% purity.

Hybrid Concepts Using CrystPX Process For Expansion Of Existing Paraxylene Units



Conclusions

- Historical traditional method for PX production has been crystallization
- Adsorption processes have enjoyed popularity due to advantages over first-generation crystallization technologies
- Updated design features, improved equipment, and world-scale designs are making crystallization once again desirable
- In the future, hybrid crystallization/adsorption may be the best solution as they exploit inherent advantages of each process