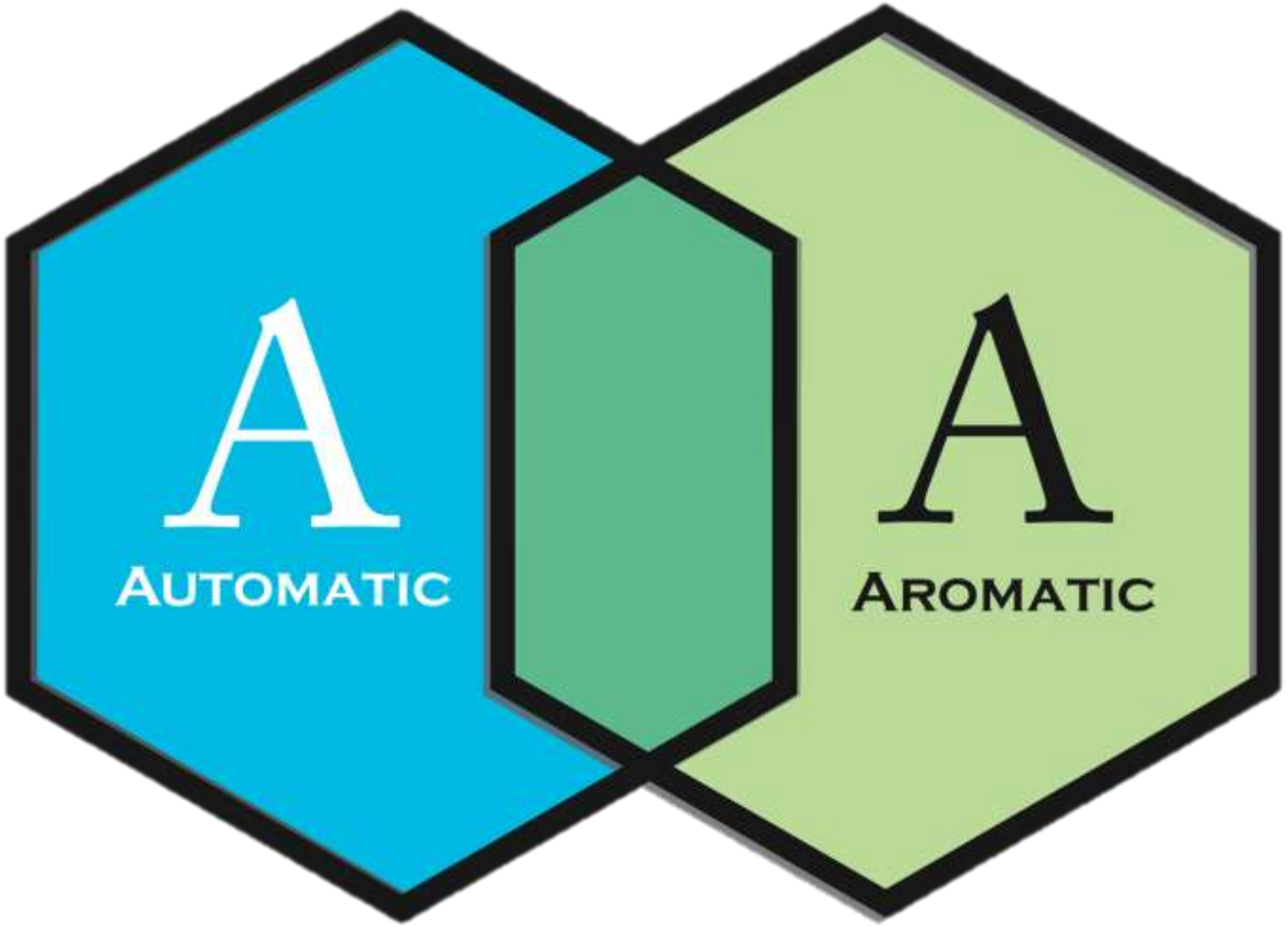

A
AUTOMATIC
A
AROMATIC

THE CONVERSION OF METHANOL TO AROMATICS

Gabrianna Ruskowsky, Tess Ward, Jonathan Weishaar, Brady Wilkison

INTRODUCTION

- **Aromatic compounds have a large variety of uses**
    - Cosmetics
    - Car dashboards
    - Aspirin
- **Para-xylene is used in the production of polyethylene terephthalate (PET)**
    - Raw material for polyester

BUSINESS OPPORTUNITY

- **Aromatics in high demand**
  - Chemistry, automotive, consumer product industries
- **Many current plants rely on oil resources**
  - Increasing shortage in oil resources = need for new techniques for producing aromatics
- **Natural gas industry provides good alternative**
  - Methanol is ideal feedstock
    - High purity
    - High profit margin
    - Readily available

POTENTIAL PROCESSES

- **2-Reactor design with DME as an intermediate**
  - Dehydration of methanol to form DME
  - DME converted to aromatics via a zeolite catalyst
- **1-Reactor design**
  - Direct conversion over ZSM5 zeolite catalyst
  - Only data available comes from lab scale experiments

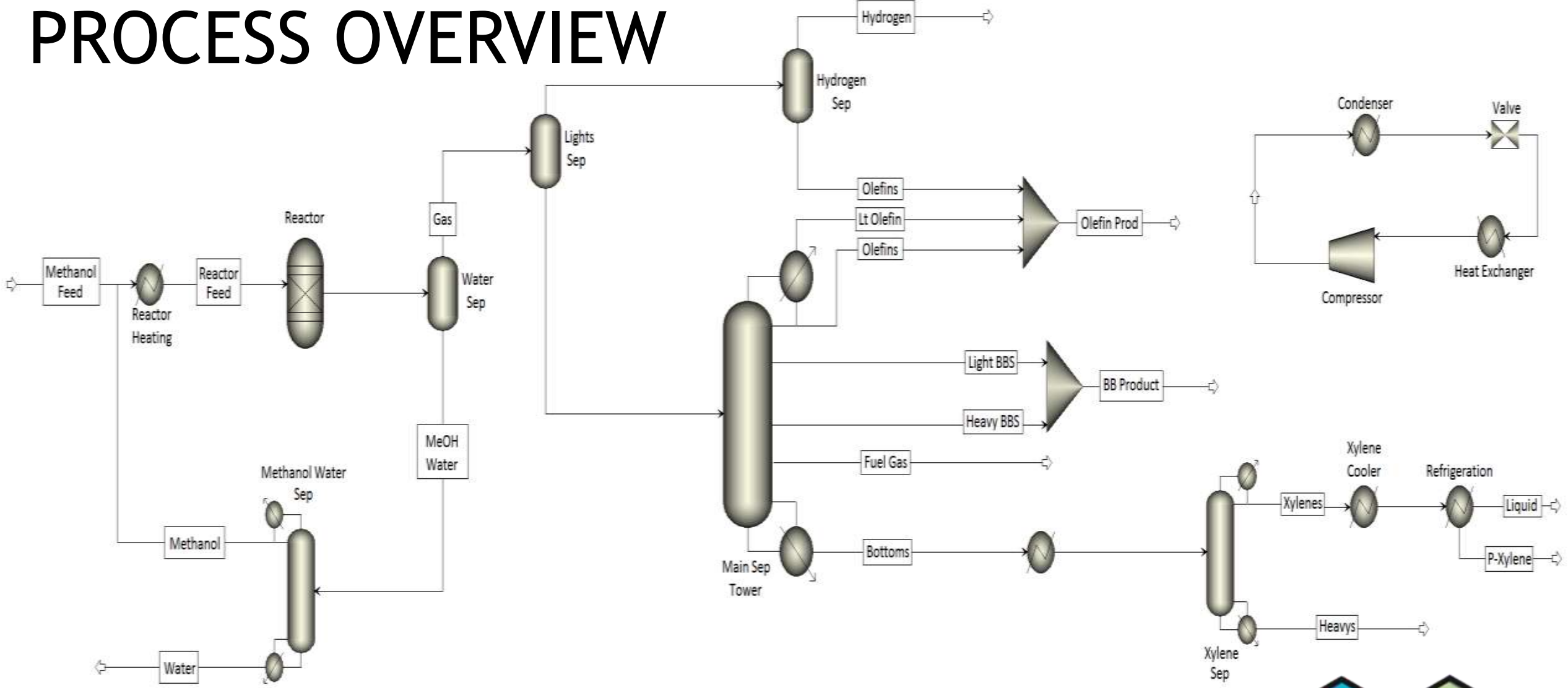
SCOPE OF WORK

- **Developed a 1 MMMlb/yr aromatic plant**
  - ZSM5 zeolite catalyst impregnated with silver ions
  - Paraxylene as major product
- **Simulation of the plant**
- **Economic Analysis**
- **Sensitivity analysis**
- **Environmental Analyses**
- **Safety Analyses**
- **Design Alternatives**

KEY PROJECT CONSTRAINTS

1. Must not exceed 10% products/byproduct/feedstock markets
2. Methanol feedstock can not be purer than 99%
3. Towers and reactors must not exceed 200 feet tall
4. All equipment must be of a size that is commercially available and feasible
5. Hazardous and carcinogenic materials must be adequately contained
6. Permits for all gas emissions and disposal of products
7. The IRR of the plant must exceed 20%

PROCESS OVERVIEW



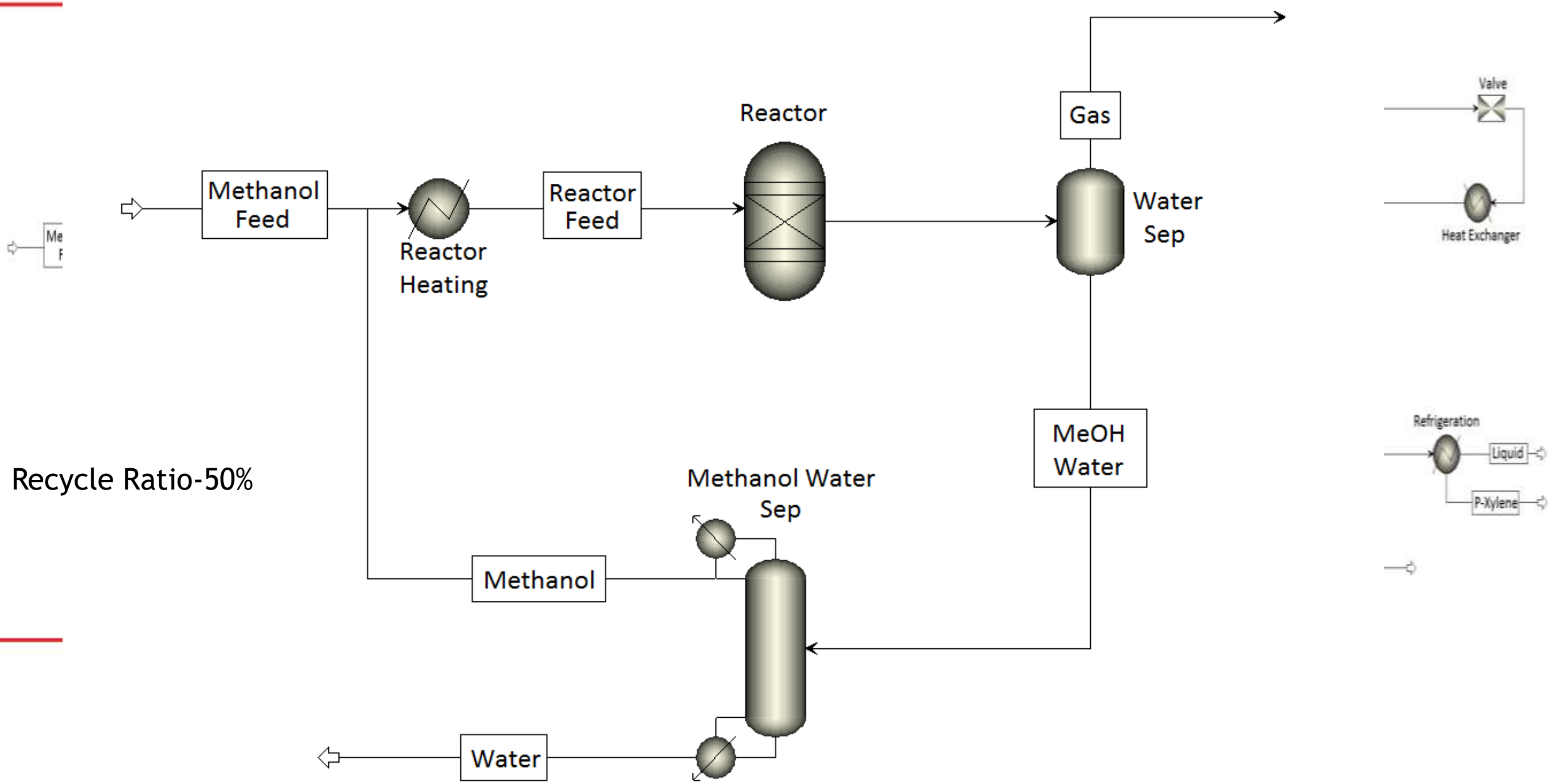
AUTOMATIC AROMATIC

Key Assumptions

- Separation of the aqueous and organic phases->Wilson-Redlich-Kwong EOS
- All other processes->Peng-Robinson EOS
- No CO_2 production
- 100% conversion of methanol with recycle

Key Issues

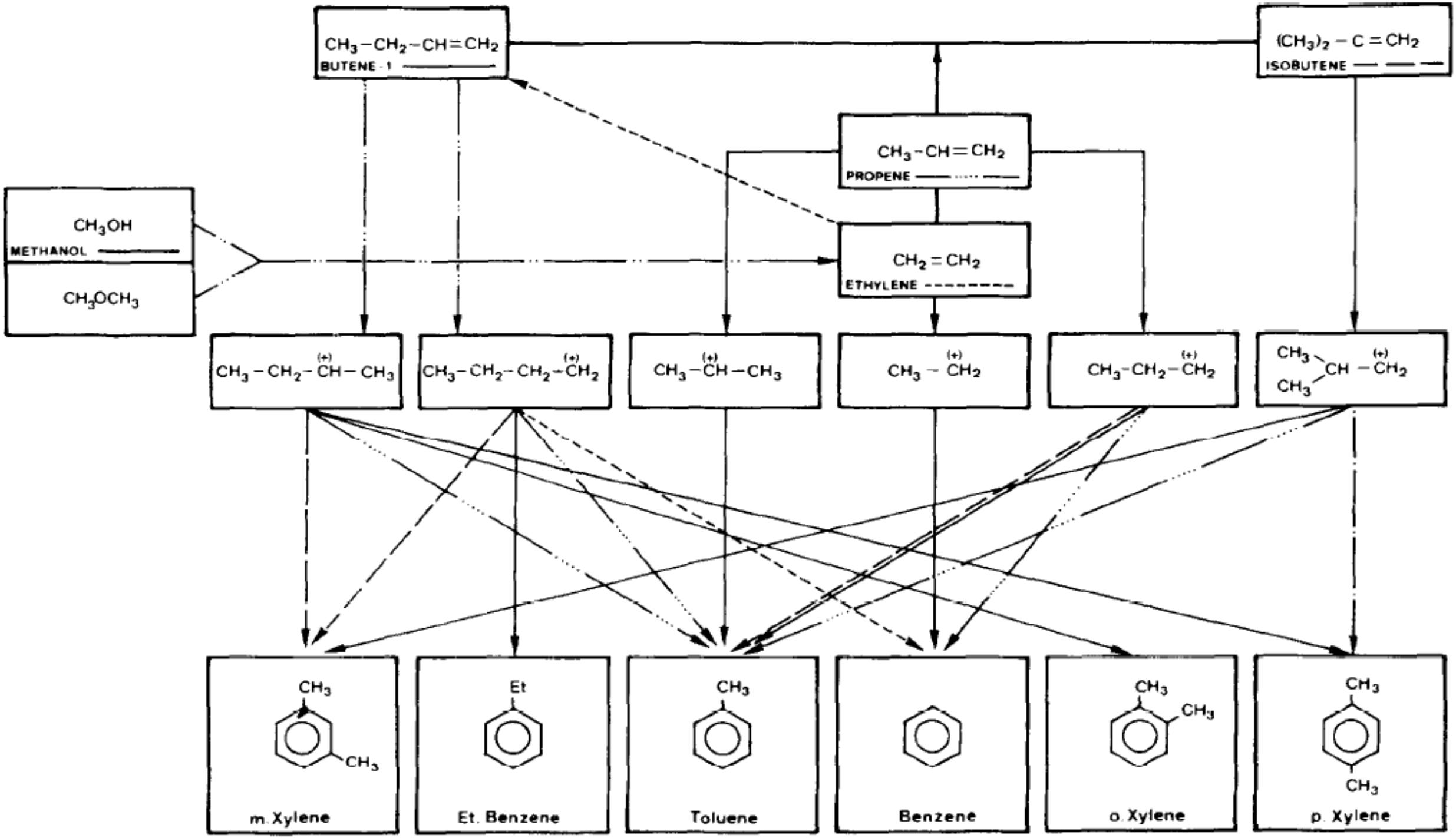
- Life span of catalyst – Assumed 1 year replacement



Recycle Ratio-50%

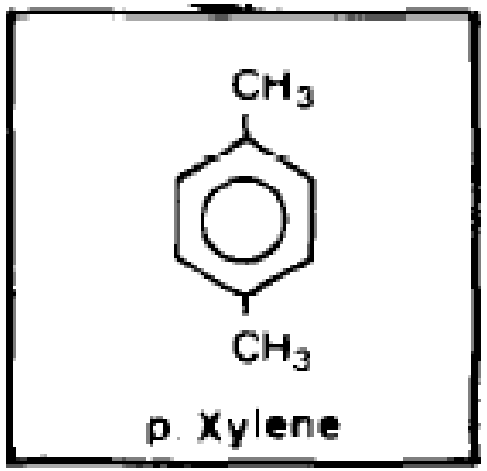
REACTOR DESIGN

- **ZSM5 zeolite impregnated with Ag+**
  - ZSM5 commercially available
  - Processing required to impregnate with Ag+
- **Fixed Bed**
  - ~100% conversion with methanol recycle
  - 2 parallel reactors allow for maintenance


$CH_3-CH_2-CH=CH_2$
BUTENE-1
$(CH_3)_2-C=CH_2$
ISOBUTENE
$CH_3-CH=CH_2$
PROPENE
CH_3OH
METHANOL
CH_3OCH_3
$CH_2=CH_2$
ETHYLENE
$CH_3-CH_2-\overset{(+)}{C}H-CH_3$
$CH_3-CH_2-CH_2-\overset{(+)}{C}H_2$
$CH_3-\overset{(+)}{C}H-CH_3$
$CH_3-\overset{(+)}{C}H_2$
$CH_3-CH_2-\overset{(+)}{C}H_2$
$CH_3-CH(CH_3)-\overset{(+)}{C}H_2$
m.Xylene
Et. Benzene
Toluene
Benzene
o.Xylene
p.Xylene

OVERALL REACTION

$$8CH_3OH \longrightarrow C_6H_4(CH_3)_2 + 8H_2O + 3H_2$$



REACTOR MATERIAL BALANCE

		Mass Flow (lb/hr)				
Feed Streams	METHANOL	114077				
	Reactor Products				TOLUENE	4778.708
	METHANE	955.7189			P-XYLENE	6690.26
	ETHYLENE	5734.427			O-XYLENE	1911.438
	ETHANE	477.8594			METHYL-ETHYLBENZENE	3345.243
	PROPENE	8123.839			N-OCTANE	1911.438
	PROPANE	955.7189			TRI-METHYLBENZENE	954.806
	ISOBUTANE	3822.99			TETRA-METHYLBENZENE	95.72
	1-BUTENE	2389.411			N-UNDECANE	1433.578
	N-BUTANE	1911.438			WATER	64141.99
	N-PENTANE	2150.082			HYDROGEN	620.2248
	N-HEXANE	238.6445				
	BENZENE	1433.578			SUM	114077

LIQUID-LIQUID SEPARATOR

- Separates water and methanol from hydrocarbons
- Aqueous mixture is sent to a distillation tower to recycle methanol and dispose of water
- Organic goes to further processing

METHANOL/WATER SEPARATOR

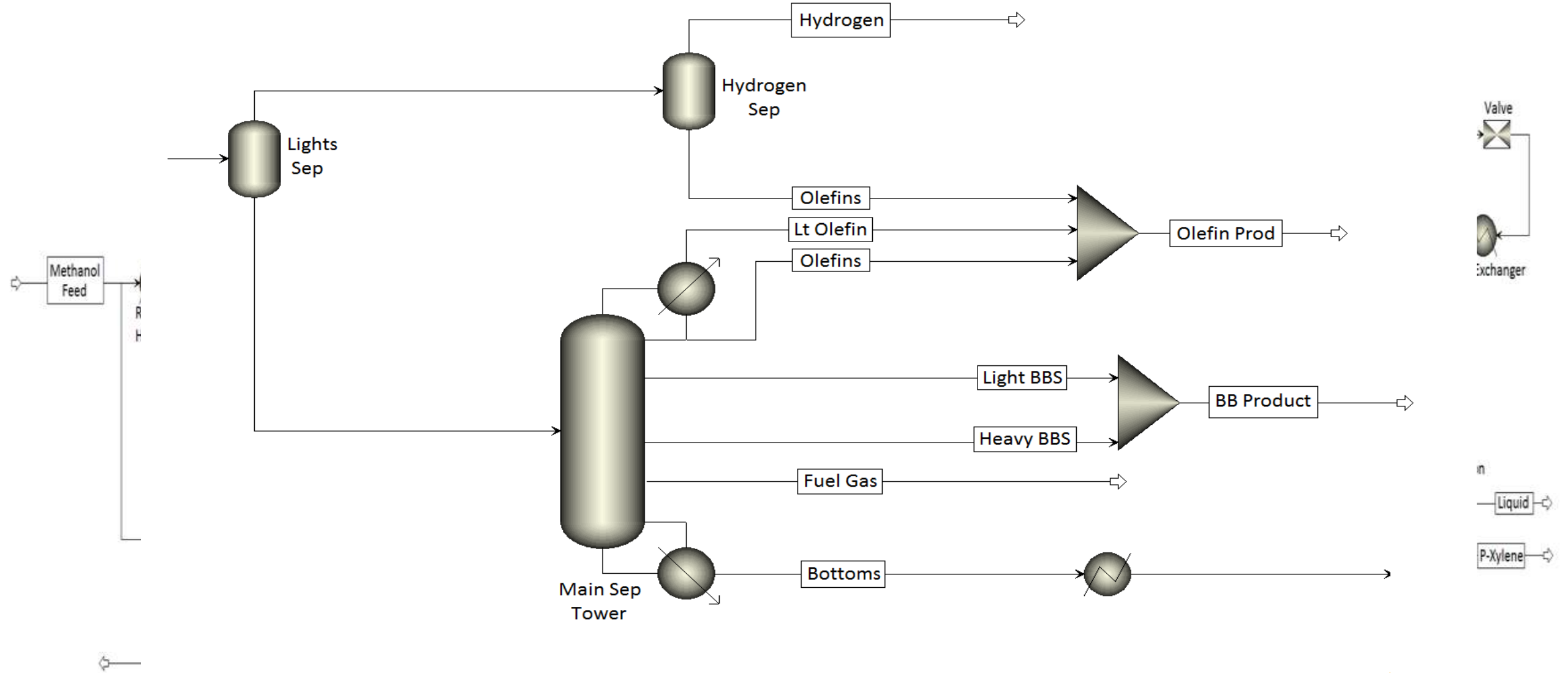
- **Separates methanol and water via distillation**
- **Two design specifications for mole purity and mole recovery**

LIGHT HYDROCARBON SEPARATOR

- **Flash drum separates hydrogen and C1's to C3's from liquid hydrocarbon stream**
- **Main goal: separate all hydrogen and non-condensables before sending to distillation**

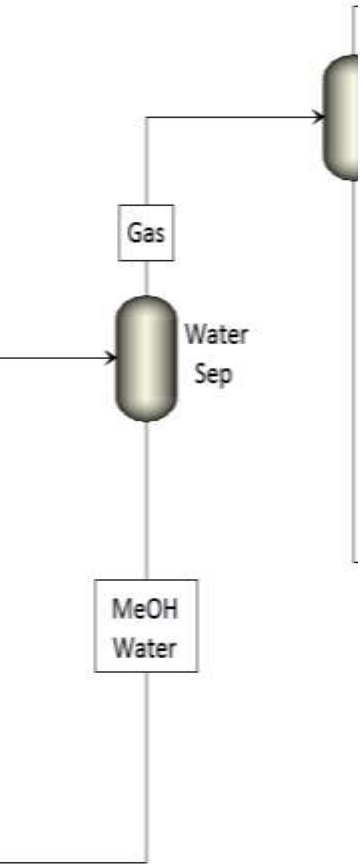
HYDROGEN PURIFICATION

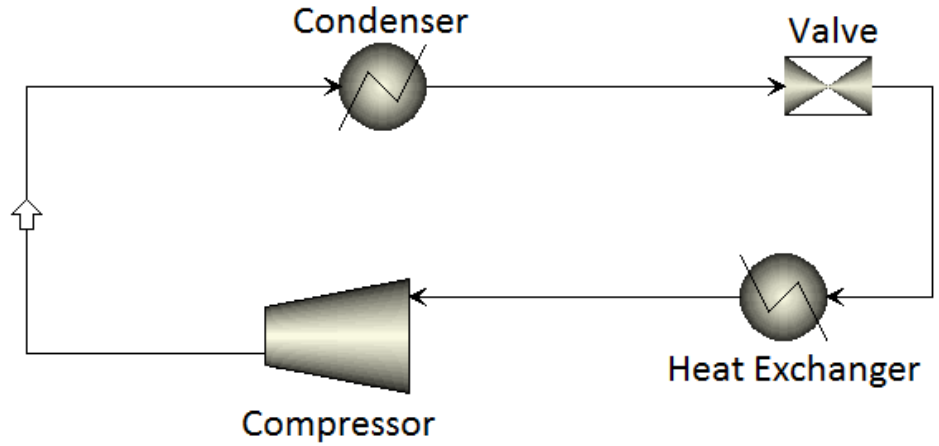
- **A variety of means of purification**
  - Pressure Swing Adsorption
  - Dense Thin Metal Membrane Purifier
  - Palladium Exchange Membrane
- **Economics assumed are variable**

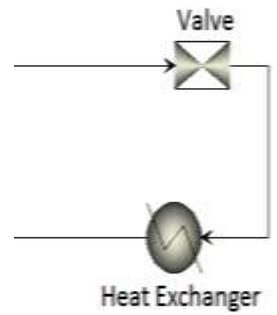

Hydrogen
Hydrogen Sep
Lights Sep
Olefins
Lt Olefin
Olefins
Olefin Prod
Methanol Feed
Light BBS
Heavy BBS
BB Product
Fuel Gas
Bottoms
Main Sep Tower
Valve
Exchanger
Liquid
P-Xylene

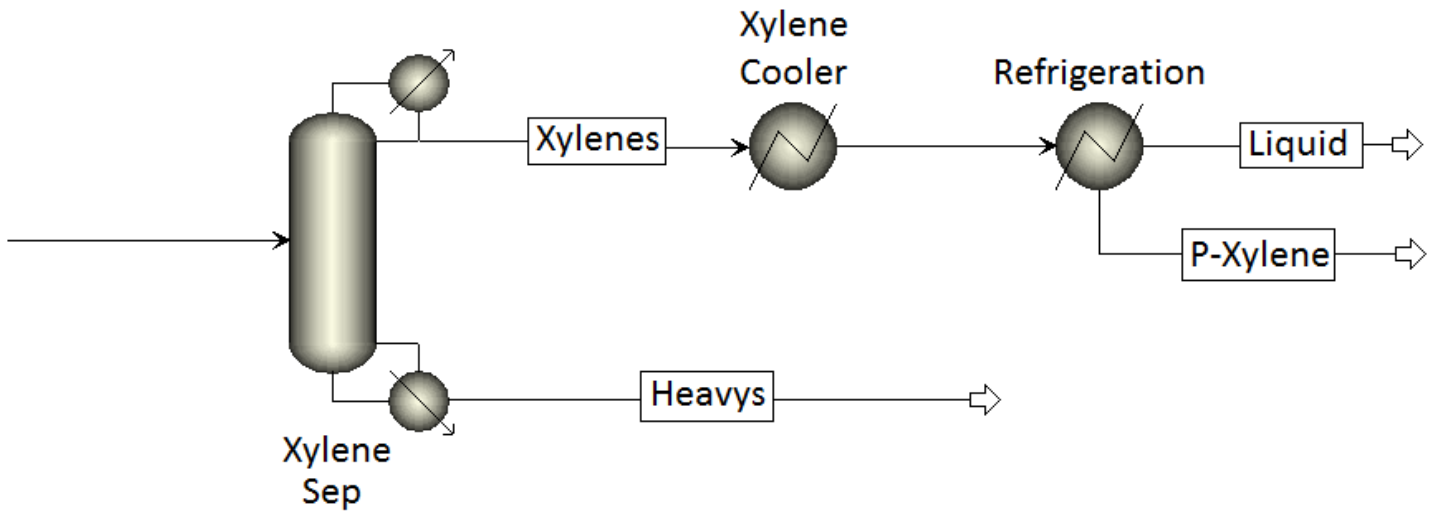
MAIN SEPARATOR

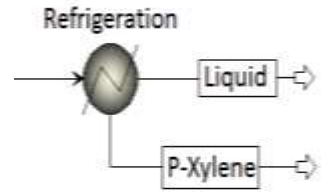
- **Separates hydrocarbon stream into several streams with side draws**
- **Draws include propane and propylene stream, butane and butylene stream, C6's and light aromatics stream, and xylenes and heavier aromatics stream**


Gas
Water
Sep
MeOH
Water


Condenser
Valve
Heat Exchanger
Compressor


Valve
Heat Exchanger


Xylene
Cooler
Refrigeration
Xylenes
Liquid
P-Xylene
Heavys
Xylene
Sep


Refrigeration
Liquid
P-Xylene

XYLENE/HEAVY AROMATIC SEPARATOR

- **Separates xylenes, toluene, and benzene from heavy aromatics**
- **Mixed xylene stream is sent to a crystallizer to separate para-xylene from ortho-xylene, toluene, and benzene**

CRYSTALLIZER

- **Uses a propane refrigeration system to crystallize para-xylene from toluene, benzene, and ortho-xylene**
- **Para-xylene slurry is sent to a centrifuge to recover crystalized para-xylene**

DESIGN ALTERNATIVES- CATALYST

- **Can use unaltered catalyst**
  - Does not have high selectivity for aromatic compounds
- **Can impregnate catalyst with different ions**
  - Hydrogen
  - Zinc
    - Comparable performance

Catalyst	Ag-ZSM-5		H-ZSM-5	Zn-ZSM-5[a]
	700 K	750 K	700 K	700 K
Products (in C%)				
CH_4	1.3	5.0	2.1	2.4
C_2H_6	0.4	1.0	0.7	1.0
C_3H_8	3.5	2.2	11.8	6.3
C_4H_{10}	4.0	1.2	8.6	3.4
C_2H_4	8.1	7.0	7.9	8.1
C_3H_6	6.2	2.6	10.6	4.7
C_4H_8	2.5	0.4	5.3	3.4
C_5+aliphatics	1.5	0.3	4.6	1.9
Aromatics	72.5	80.3	48.4	68.8
Moles of H_2 formed per 100 moles of CH_3OH reacted	22	22	1.6	22

$W/F = 9.0$ g h mol^{-1}; CH_3OH pressure = 20 kPa.
[a] 22 kPa.

DESIGN ALTERNATIVES- SEPARATIONS

- **Currently have only 2 high purity streams**
  - Hydrogen
  - Paraxylene
- **Separate valuable products into purer streams**
  - Toluene and benzene
    - Currently sold as mixed streams to refinery
  - Not economically valuable at this time

OVERALL MATERIAL BALANCE & PRICING

Stream Name	Mass Flow (lb/hr)	Pricing (USD/lb)	MMUSD/yr
Methanol Feed	114,077	0.94	129.39
Hydrogen	615	2.00	30.65
Olefin Product	21,526	1.76	82.09
BB Product	5,330	0.31	2.70
Benzene	598	2.60	1.81
PX	6,587	3.60	26.31
Crystallizer Liquid	9,552	2.43	26.62
Heavy Aromatics	5,792	0.20	1.33

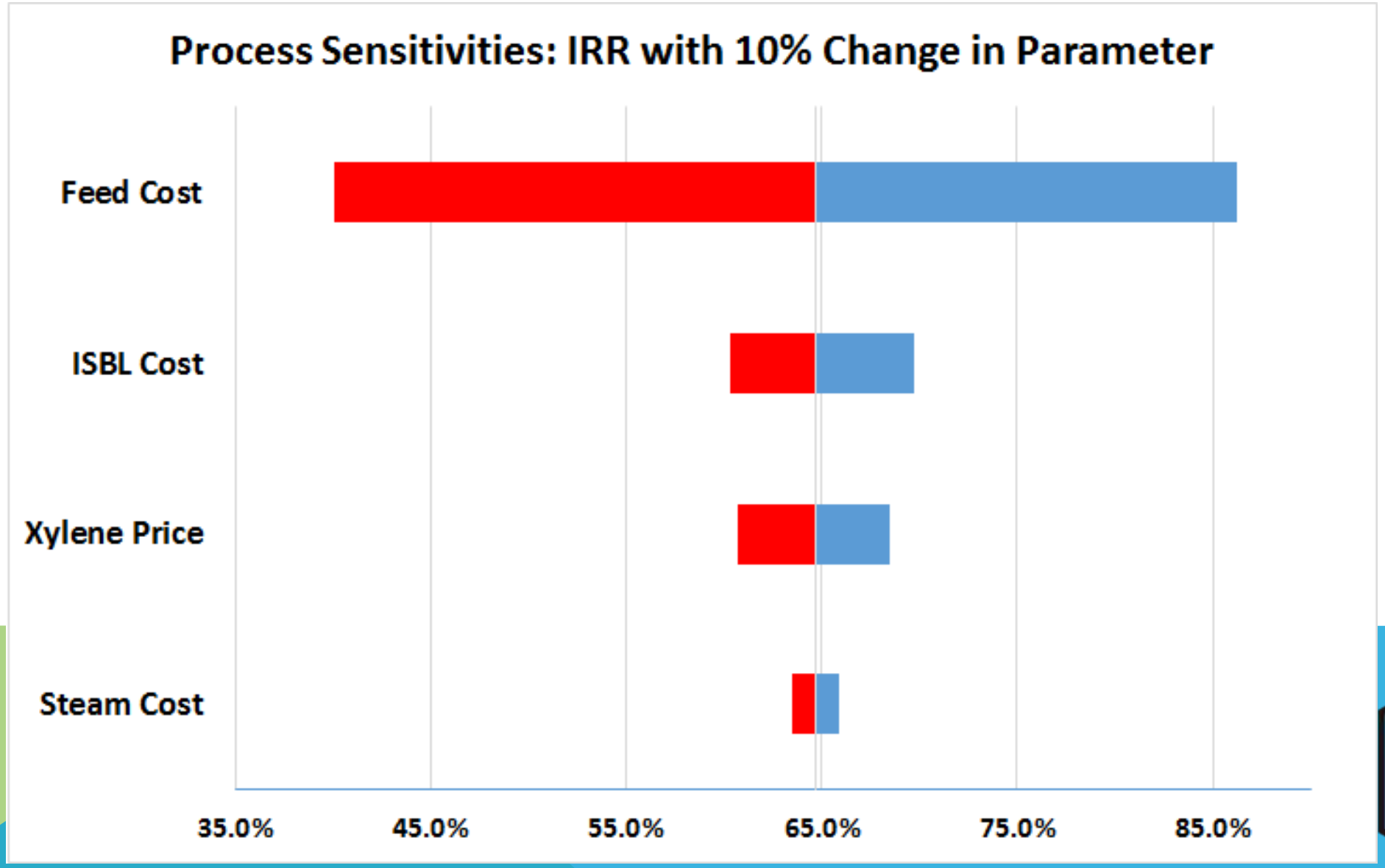
EQUIPMENT COST SUMMARY

Equipment	Aspen Name	L or H (ft)	D (ft)	Area (ft^2)	Heat Duty (BTU/min)	Purchased Cost (USD)
Reactor	R101	158	53	-	-	$160,000.00
Aqueous Sep	TK101	17	6	-	-	$61,600.00
2-Phase Organic	TK102	15	6	-	-	$57,200.00
2-Phase H_2 Sep	TK103	8	3	-	-	$22,000.00
Main Sep	T101	137	17	-	-	$1,067,457.00
Aromatic Sep	T102	49	9	-	-	$186,677.00
MeOH Sep	T103	49	13	-	-	$262,765.00
Crystallizer	E104	60	10	-	-	$724,800.00
Centrifuge	Not Modeled	-	-	-	-	$579,840.00
Pre-Reactor Heat Exchnagers	F101	-	-	2,731	-	$180,000.00
Xylene Stream Cooling	F101	-	-	117	-	$3,500.00
Propane Condenser	F101	-	-	111	-	$3,500.00
Furnace	F101	-	-		198833	$250,000.00

ECONOMICS

Summary	
Capital MM$	19.7
Revenue MM$/yr	26.3
Var Costs MM$/yr	8.7
IRR, %	65%
NPV10, $MM	140.6

ECONOMICS


Process Sensitivities: IRR with 10% Change in Parameter
Feed Cost
ISBL Cost
Xylene Price
Steam Cost
35.0%
45.0%
55.0%
65.0%
75.0%
85.0%

LOCATION

- The nature of our products make it necessary to locate near chemical plants using our products as feed stocks
- We need to be somewhere near natural gas sources supplying syngas
- Proximity to ports, rail, other transportation
- All of these are present on the gulf coast.

ENVIRONMENTAL CONCERNS

- **Water Emissions from Methanol/Water Separator**
- **Air Emissions from Furnace**

Contaminant	MCLG (mg/L)	MCL or TT (mg/L)	Potential Health Effects from Long-Term Exposure Above the MCL
Benzene	zero	0.005	Anemia; decrease in blood platelets; increased risk of cancer
Ethylbenzene	0.7	0.7	Liver or kidneys problems
Toluene	1	1	Nervous system, kidney, or liver problems
Xylenes (total)	10	10	Nervous system damage

CAS Number	Chemical Name
71432	Benzene (including benzene from gasoline)
100414	Ethyl benzene
110543	Hexane
67561	Methanol
91203	Naphthalene
108883	Toluene
1330207	Xylenes (isomers and mixture)
95476	o-Xylenes
108383	m-Xylenes
106423	p-Xylenes

COMBUSTION EMISSIONS

- **Natural Gas Feedstock**
  - NOx and SOx
  - CO and CO_2
  - N_2O
  - Particulate Matter

GLOBAL AWARENESS

- **Price Comparisons**
  - Methanol
  - Natural Gas
- **Emissions Requirements**
- **Xylene Demand**

PROJECT RECOMMENDATIONS

- **Price Lock-Ins**
- **Natural Gas Plant Attachment**
  - Day to Day Variations

FUTURE GOALS

- Pilot Plant
- Catalyst Life Span
- Other Economic Sensitivities
- Recycle Toluene and Benzene
- Friedel-Crafts Alkylation

DIVISION OF LABOR

- **Brady**
  - Modeled T101, refrigeration cycle, LL separator, and reactor
  - Material Balances
  - Product pricing
  - Equipment costs on reactor and LL separator
- **Gigi**
  - Modeled T102
  - Product pricing
  - Equipment costs for heat exchangers and crystallizer
  - Environmental and Permitting
  - Global Awareness
- **Tess**
  - Modeled T102
  - Equipment costs for separation towers
  - Production cost estimate
  - Design Alternatives
  - Design Constraints
  - Business opportunity and product market
- **Jon**
  - Modeled T103
  - Variable costs
  - Economics analysis
  - Project definition

QUESTIONS?