Vinyl Chloride Production Senior Design Presentation

Group 10

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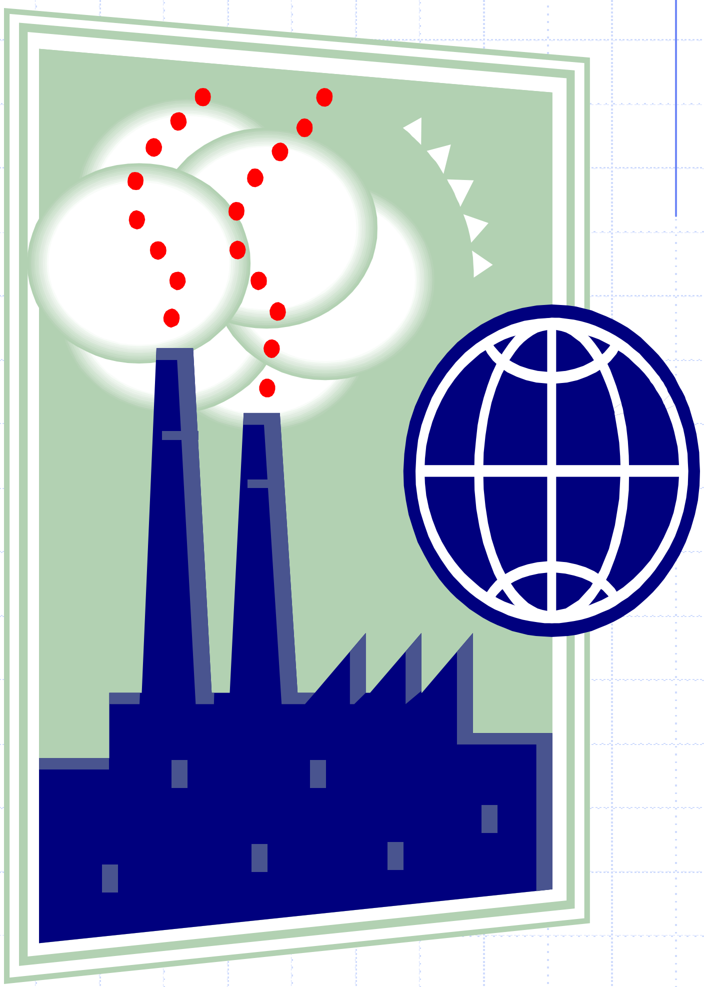
Project Purpose

- To design an environmentally safe vinyl chloride production plant.

Questions:

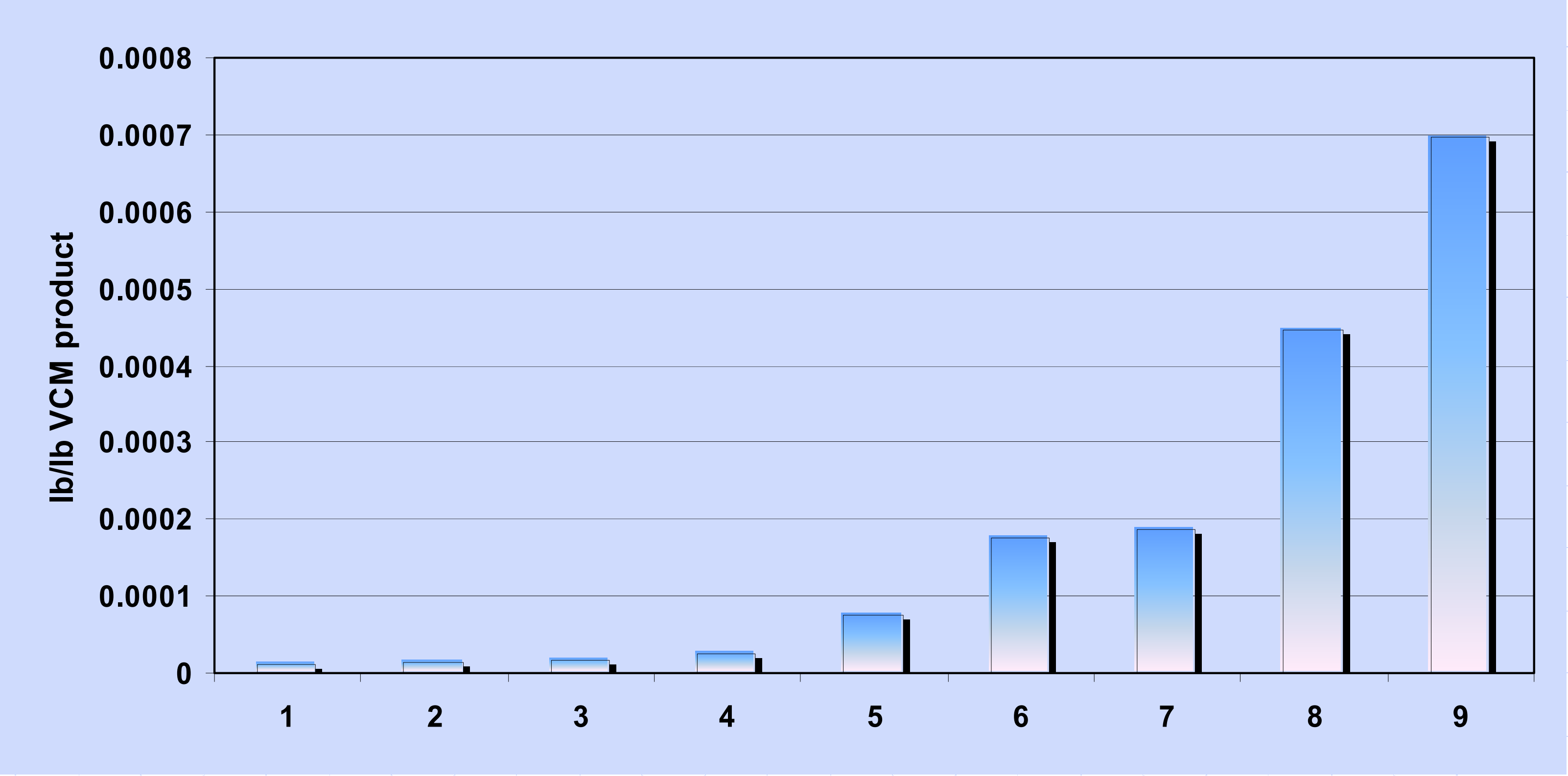
- What is Vinyl Chloride?
- How its being produced?
- How much does it cost to be environmentally friendly?



Vinyl Chloride

- 99% of VCM is used to manufacture polyvinyl chloride (PVC).
- PVC consumption is second to low density polyethylene.
- VCM production results in a number of unwanted by-products.

VCM Plant Emissions in the United States



1	Formosa-LA	4	Georgia Gulf-LA	7	Borden-LA
2	Oxyvinyls-D-TX	5	Westlake Monomers-KY	8	Dow-LA
3	Oxyvinyls-L-TX	6	Formosa-TX	9	Dow-TX

Manufacturing Methods

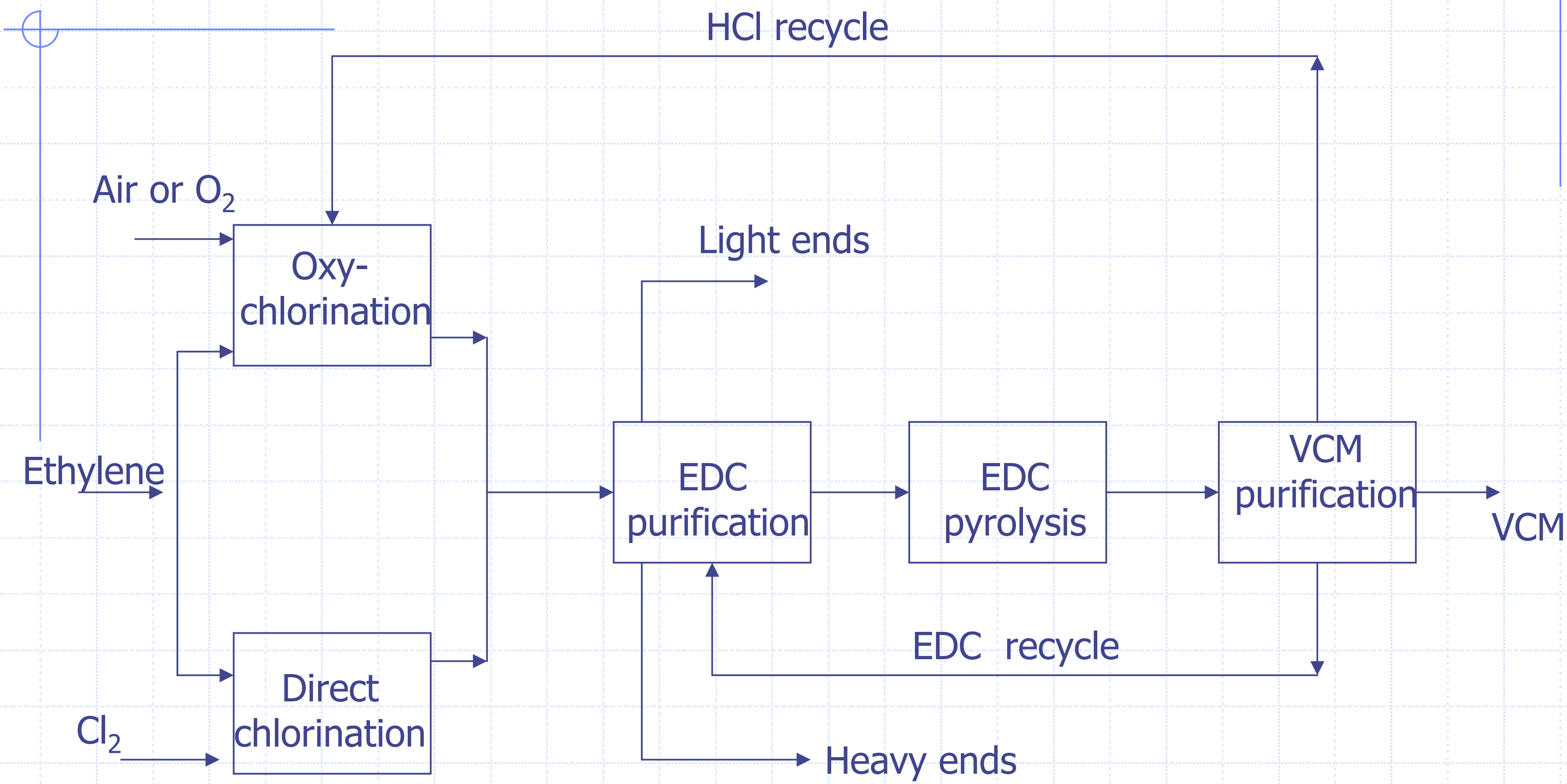
- Vinyl Chloride from Acetylene
- Vinyl Chloride from Ethane
- Vinyl Chloride from Ethylene (Direct Route)
- Vinyl Chloride from Ethylene (EDC)

Balanced Process for Vinyl Chloride Production

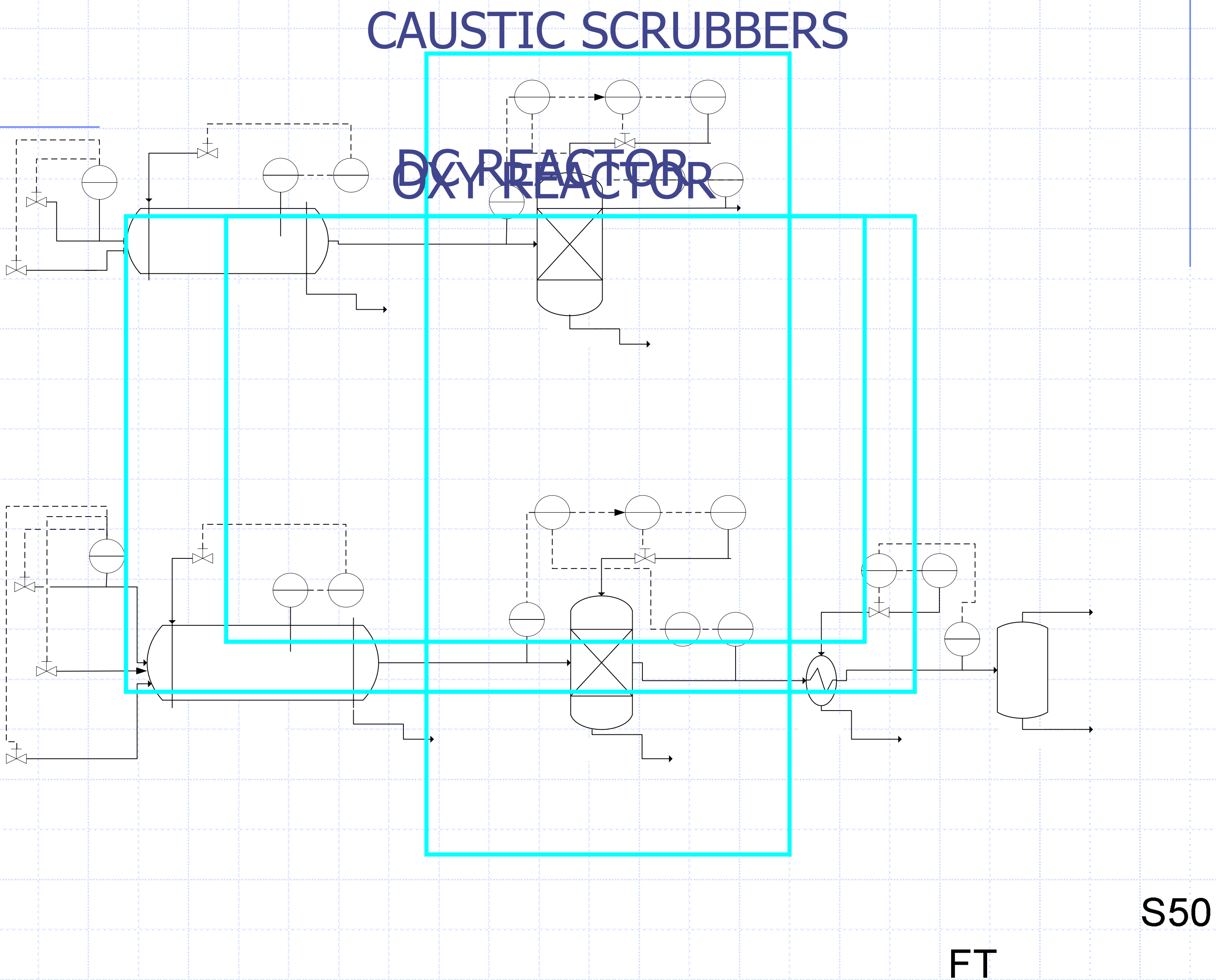
Direct chlorination	$CH_2CH_2 + Cl_2 \rightarrow ClCH_2CH_2Cl$ (EDC)
Oxychlorination	$CH_2CH_2 + 2\ HCl + ½\ O_2 \rightarrow$ EDC$+ H_2O$
EDC pyrolysis	2 EDC $\rightarrow 2\ CH_2CHCl$ (VCM) + 2 HCl
Overall reaction	$2\ CH_2CH_2 + Cl_2 + ½\ O_2 \rightarrow 2\ CH_2CHCl + H_2O$

- No generation of HCl
- 95% of the world's VCM is produced utilizing the balanced process

Balanced Process for Vinyl Chloride Production



Direct Chlorination and Oxychlorination P&ID



Vinyl Chloride Plant Reactor Design

- Theoretical reactor design equations
- Literature kinetic data used to calculated rate constants
- Numerical Integration used to calculated specified parameters

Reactor Design

$$\frac{dF_k}{dz} = w_k \frac{\pi d_t^2}{4}$$

F_k = molar flow rate

z = tube length

d_t = tube diameter

$w_k = \nu_i r_i$

$$r_i = k_f[C_k]-k_r[C_k]$$

Oxychlorination Chemistry

Set	Reaction	Stoichiometry
R-1	DCE formation	$C_2H_4 + 2CuCl_2 \rightarrow C_2H_4Cl_2 + 2CuCl$
R-2	TCE formation	$C_2H_4 + 3CuCl_2 \rightarrow C_2H_4Cl_3 + 3CuCl + 0.5H_2$
R-3	C_2H_4 combustion	$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$
R-4	CuCl oxidation	$2CuCl + 0.5O_2 \rightarrow CuO\text{-}CuCl_2 \rightarrow CuO + CuCl_2$
R-5	$CuCl_2$ regeneration	$CuO + 2HCl \rightarrow CuCl_2 + H_2O$

- Plus nine other main by product formation reactions
- Excel Reactor Model of Oxychlorination

Oxychlorination Reactor Results

Oxy Reactor Effluent Flow Rates (lb-mol/hr)

EDC	1341	Chloral	0.25
Water	1341	CCl_4	1.25
TEC	1.26	Methyl Chloride	0.12
CO_2	140	Chloroform	0.11
Ethylene	5.5	Chloroethane	0.11
Oxygen	2.76	Chloroprene	0.10
HCl	0.015	Vinyl Acetylene	0.09
Acetylene	0.13	Dichloromethane	0.10

Oxychlorination Reactor Parameters

Reactor Temperature (°C)	305
Reactor Pressure (psig)	58
Reactor Volume (ft^3)	461
Tube Diameter (in)	2
Tube Length (ft)	1320
Residence Time (hr)	0.05

DC Reactor Modeling Results

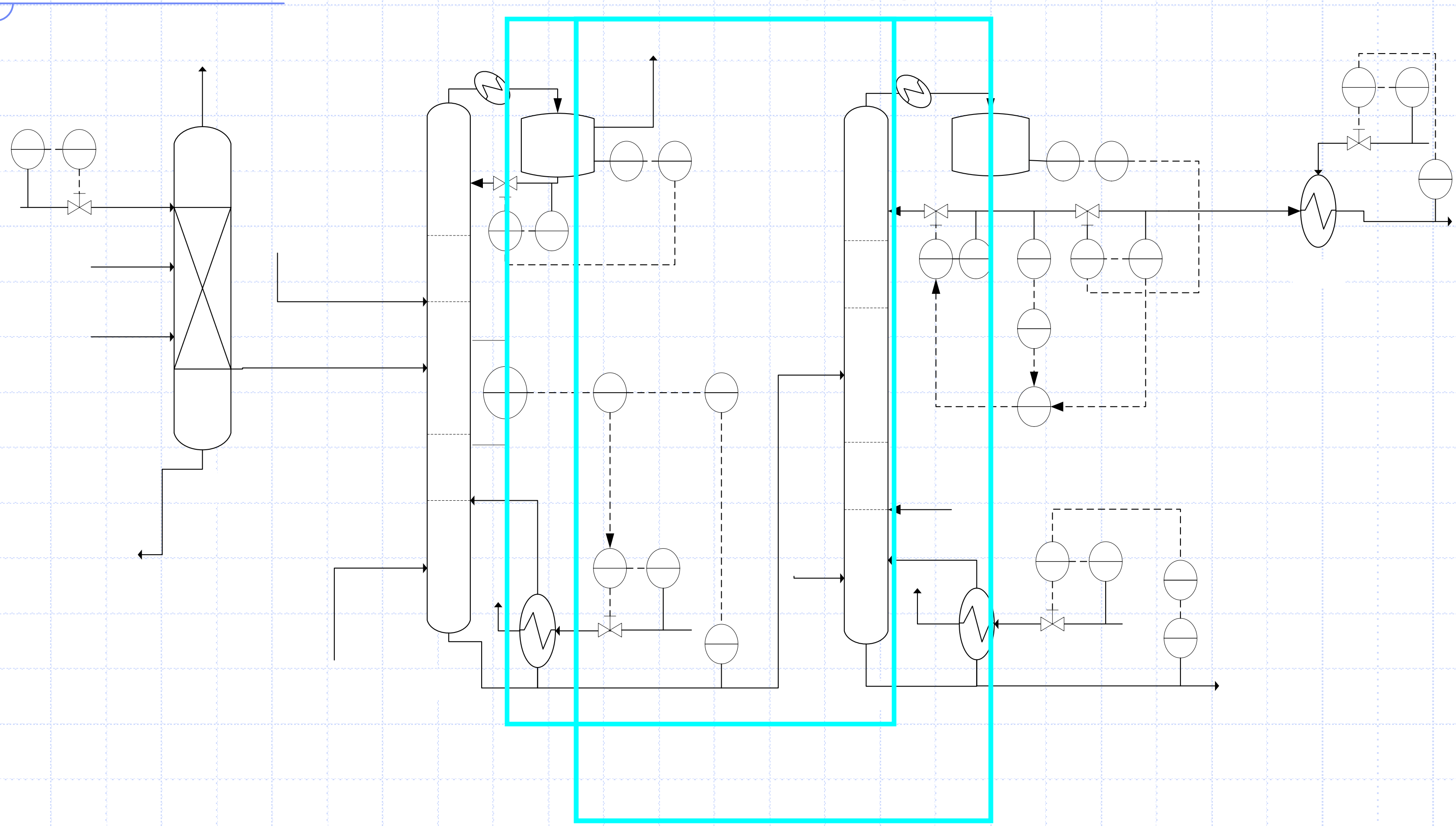
DC Reactor Kinetic Results

	Modeling Results	Literature Values
Conversion of ethylene	99.93%	99.94%
Selectivity to EDC	99.8%	99.4%

DC Reactor Parameters

Reactor Temperature (^{o}C)	120
Reactor Pressure (psig)	15
Reactor Volume (ft^3)	90
Tube Diameter (in)	2
Tube Length (ft)	115
Residence Time (hr)	0.018

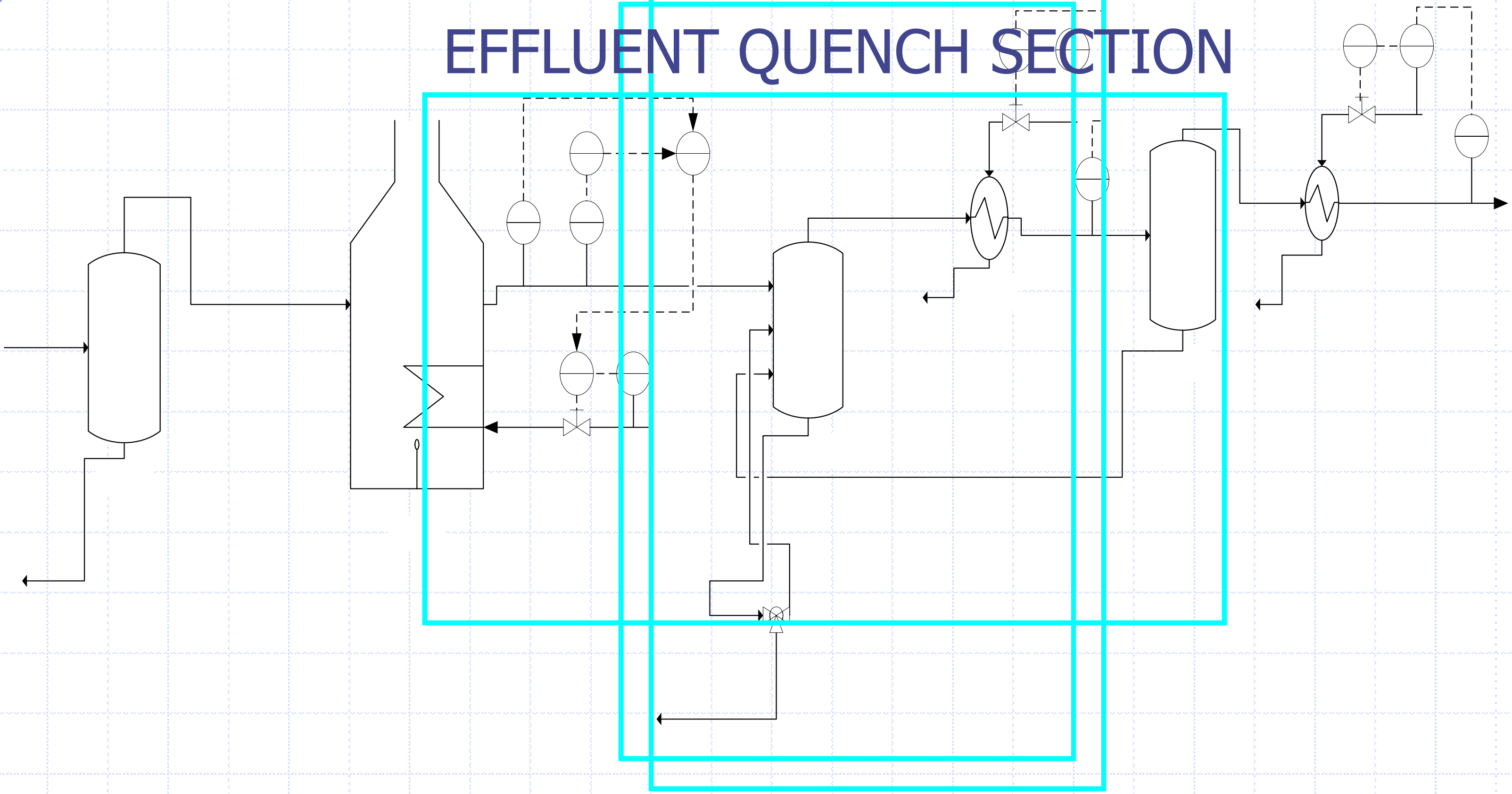
EDC Purification P&ID



EDC Pyrolysis P&ID

CRACKING FURNACE
FURNACE FEED FLASH

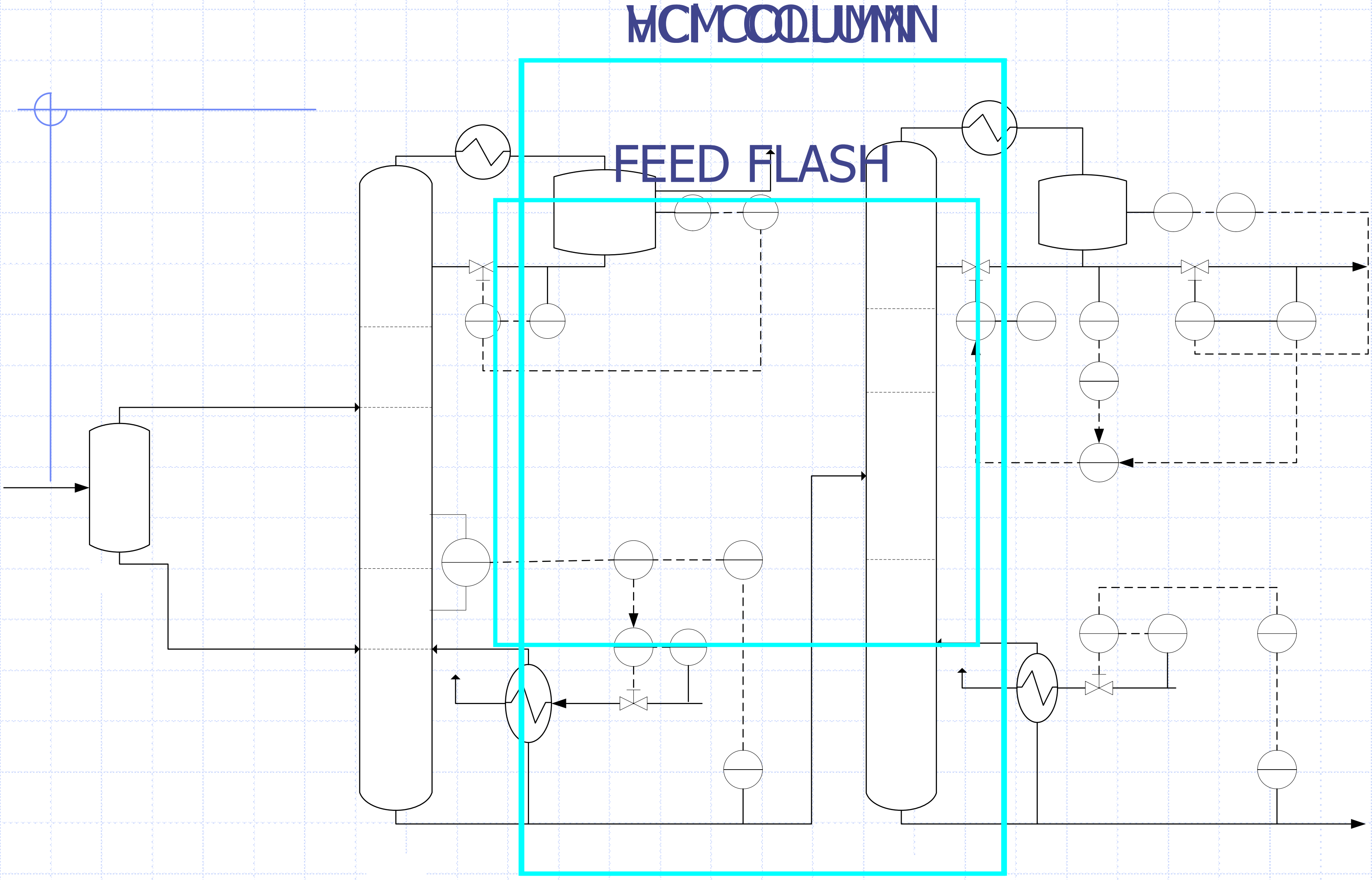
EFFLUENT QUENCH SECTION



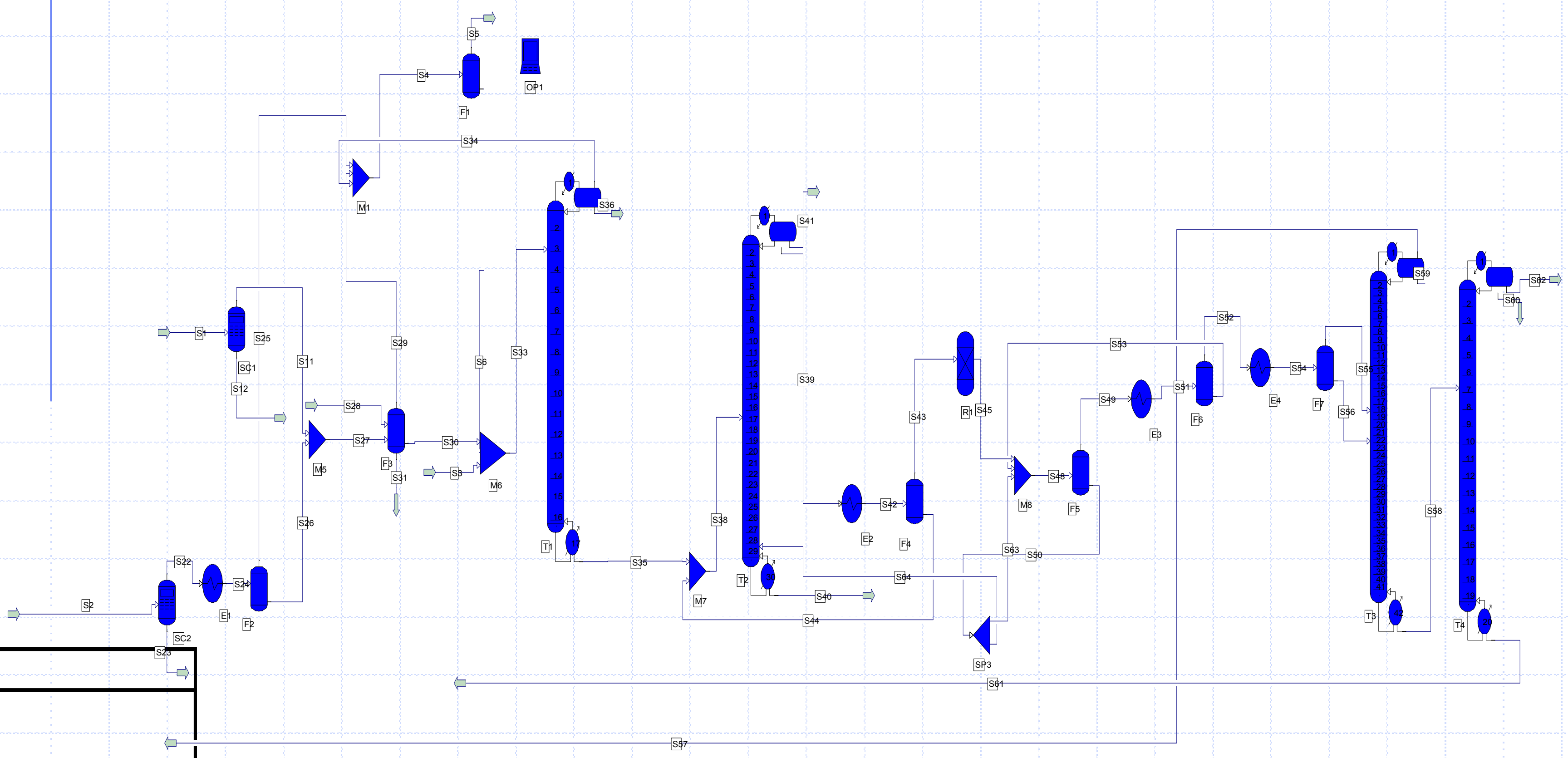
EDC Pyrolysis Reactor Modeling Results

- Conversion of EDC per pass is maintained at 50-55%
- Increasing cracking severity beyond this level results in insignificant increase in conversion and a decrease in selectivity to VCM.
- Conversion can be increased by the addition of CCl_4
- Modeling results produced conversion equal to 60%
- Major by products of EDC pyrolysis: Acetylene, benzene, 1-3 butadiene, vinyl acetylene, chloroprene.

VCM Purification P&ID



Pro II Simulation PFD



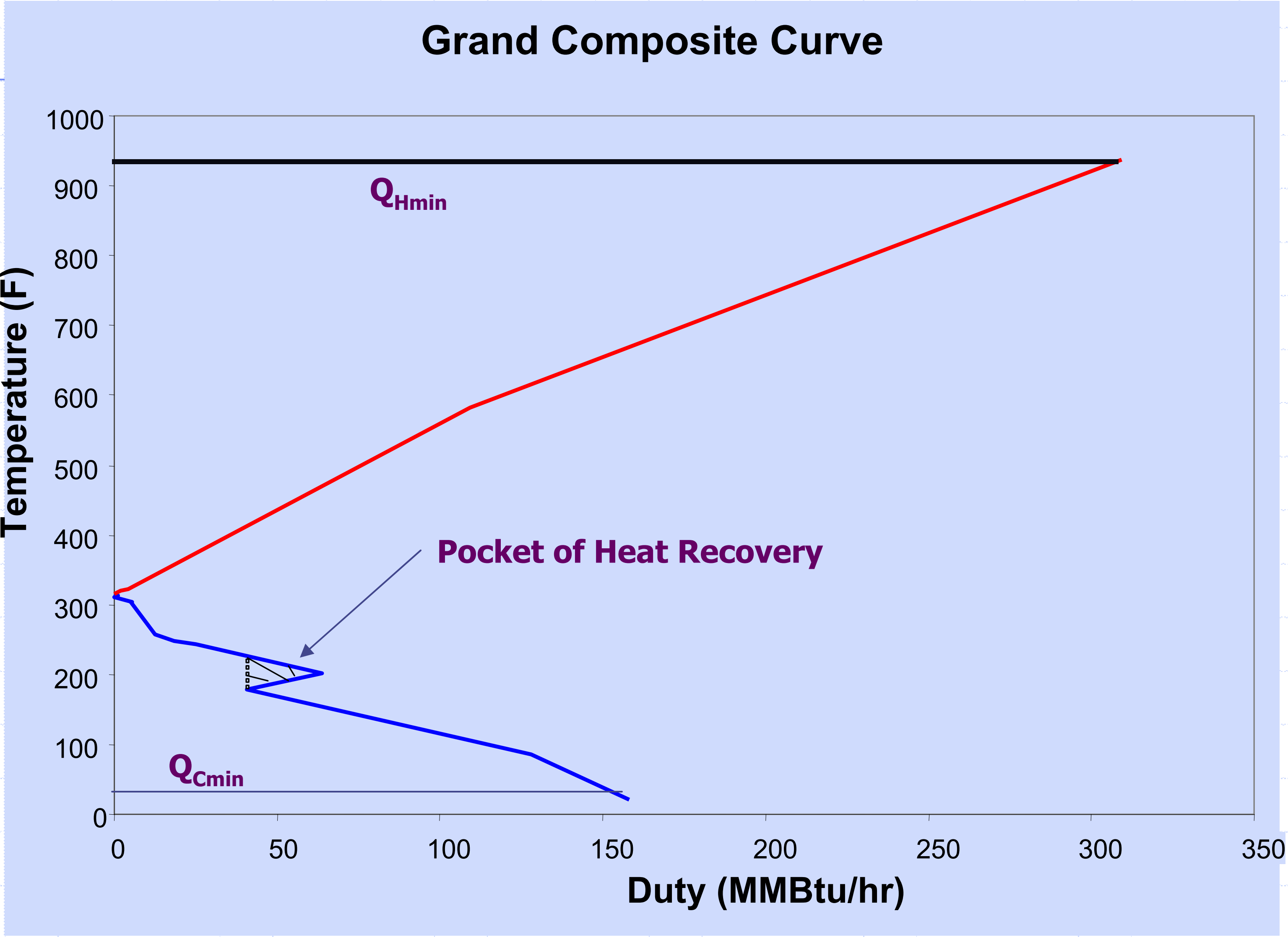
Liquid
Liquid

Heat Integration

Pinch Design Method

- Optimization method that reduces energy cost
- Utilizes process to process heat transfer
- Optimal pinch temperature→ 316^{o}F

Heat Integration



Heat Integration Results

- Hot Utility 401 → 308 MM Btu/hr
- Cold Utility 251 → 158 MM Btu/hr

Energy Reduction Results in a savings of $2.4 Million/year!

Waste Stream Treatment

Location of Waste Streams

- EDC Purification/Pyrolysis
- Oxychlorination Reaction Section
- Direct Chloriantion Caustic Scrubber

Contents of Waste

Liquid Waste

- Ethylene
- EDC
- C_2HCl_3
- VCM

Vapor Waste

- Ethylene
- EDC
- Carbon Tetrachloride
- $CHCl_3$
- Dichloromethane
- C_2HCl_3
- C_2H_2
- VCM
- C_2HCl_3O
- Vinyl Acetylene
- Chloroethane

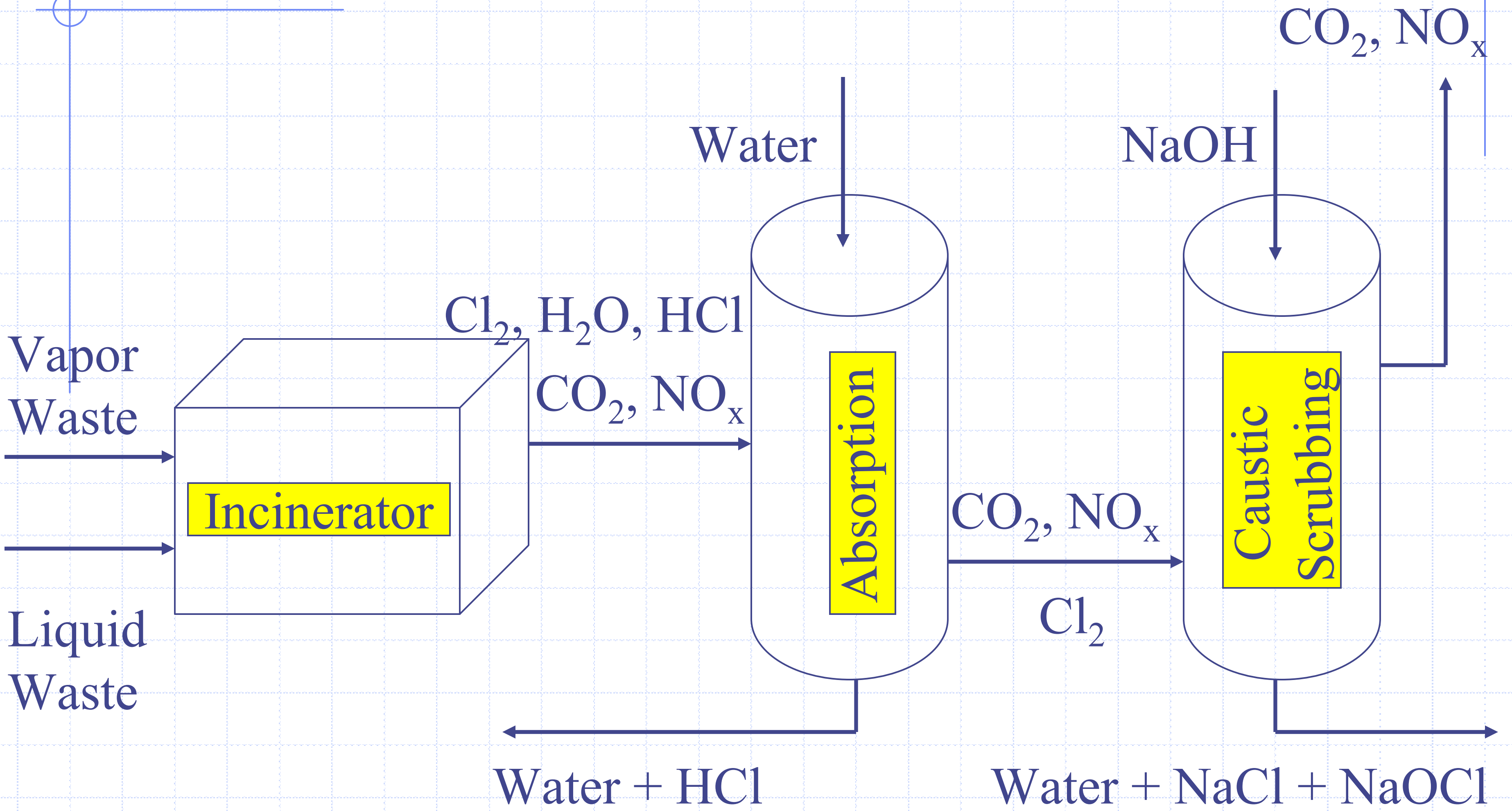
Types of Waste Treatment

- Condenser
- Catalytic Incinerator
- Absorber/Scrubber
- Thermal Incinerator
- Flare

Waste Treatment Selected

- Multiple Treatment Process Selected
- Consists of thermal incineration, absorption column, and caustic scrubbing unit

Treatment PFD



Products of Waste Treatment

- Water and HCl (solution)
- Water, NaCl, and Sodium Hypochlorite (solution)
- Carbon Dioxide and Nitrous Oxides

Incineration Unit Design

Auxiliary Fuel Flowrate Needed (Q_f)

- $Q_f = Q_w$ (X/Y) where,

$X = 1.1C_{po}(T_c - T_r) - C_{pi}(T_i - T_r) - h_w$

$Y = h_f - 1.1C_{po}(T_c - T_r)$

$Q_f = 331$ lb/hr

Absorption Column Design

Amount of Solvent (Water)

- $L = G*(Y_i - Y_o)/(X_o - X_i)$

L = 154,000 lbs/hr

Column Diameter (D_t)

- $$D_T = \frac{4VM_v}{fU_f\pi(1 - A_d / A)\rho_v}$$

D_t = 5.7 ft

Absorption Column Design Cont'd

Number of Theoretical Stages (N_{OG})

$$N_{OG} = \frac{\ln\{[(A-1)/A][(Y_i - KX_i)/(Y_O - KX_i)] + (1/A)\}}{(A-1)/A}$$

$N_{OG} = 20$

Overall Height of a Transfer Unit (H_{OG})

- $H_{OG} = G/K_y aS$

$H_{OG} = .75$

Absorption Column Design Cont’d

Packing Height

- $H_{pack} = N_{OG}*(H_{OG})$

$H_{pack} = 15$ ft

Caustic Scrubbing Design

Design

- L = 45,000 lbs/hr
- D_T = 4.5 ft
- N_{OG} = 12
- H_{OG} = .83
- H_{pack} = 10 ft

Waste Water Treatment

Waste Water Streams

	DC Caustic Scrubber (L/hr)	Water Wash Drum (L/hr)
Water	280	41,000
NaCl	48	0
HCl	-	200
Chloral	-	26
EDC	-	680
CCl_4	-	180
TCE	-	170

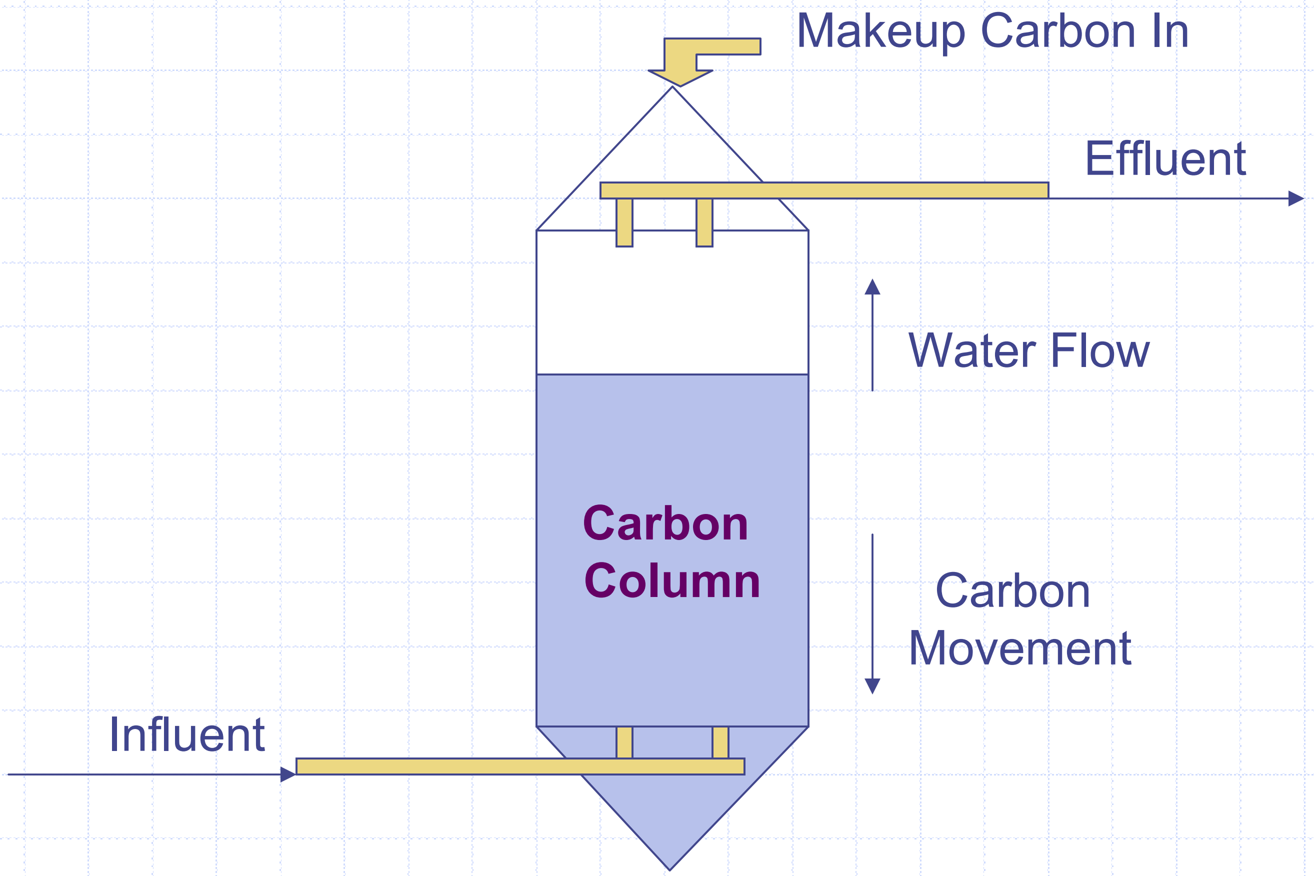
Limits and Treatment Options

	EPA Limit (mg/L)	Treatment Options
HCl	5	–GAC
Chloral	1	–Incinerator w/Afterburner –GAC
EDC	.005	-GAC –Boiling
CCl_4	.005	-GAC –Fluidized Bed Incineration
TCE	.005	-Incineration -GAC

Granular Activated Carbon

- EPA Recommended Control Technology
- Ability to remove > 99% of contaminants
- Simple design and operation
- No hazardous waste byproducts
- Ability to operate at low temperatures and pressures

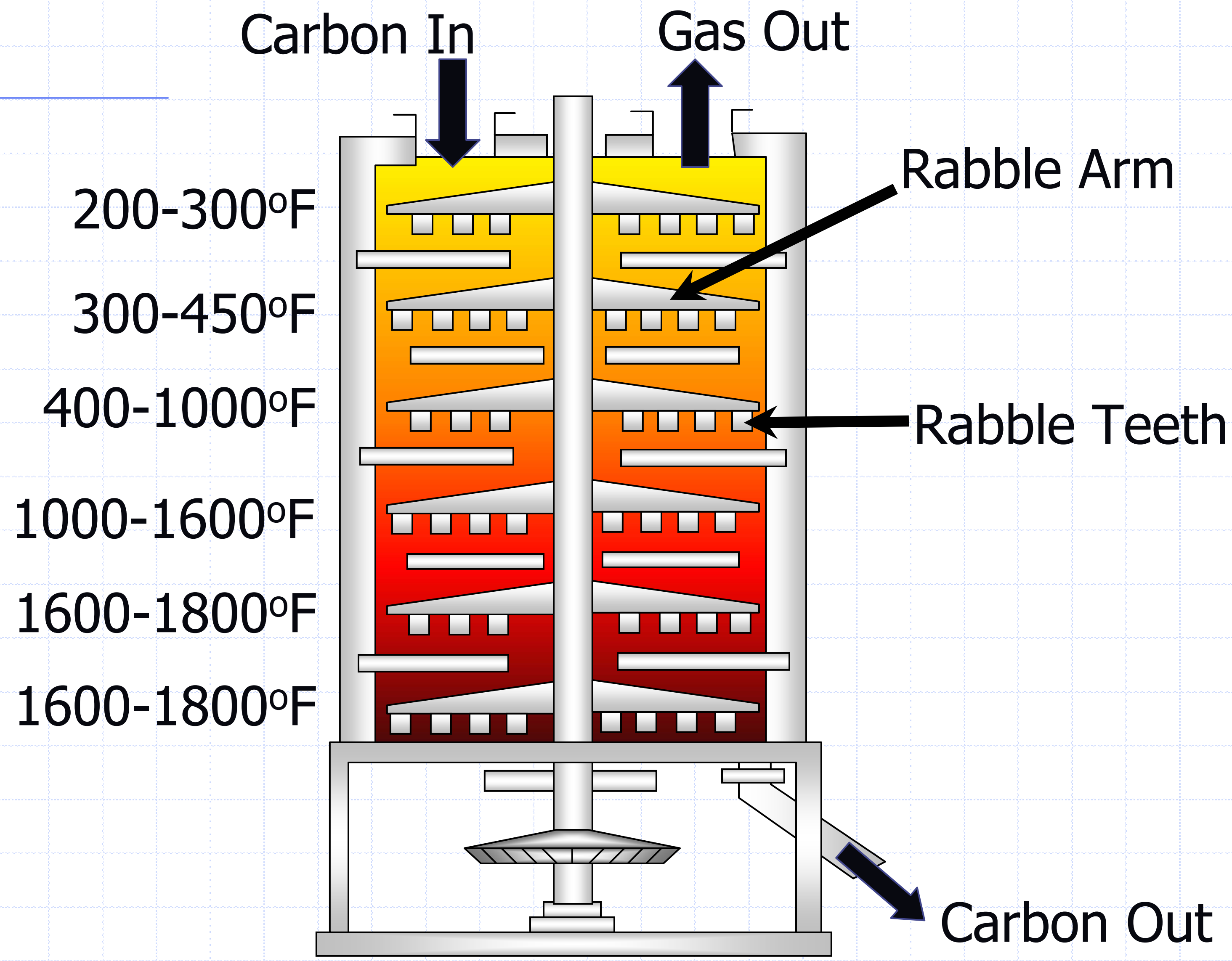
GAC Operation



Column Specifications

Carbon Mass	21000 lb
Adsorber Volume	170 ft^3
Adsorber Area	36 ft^2
Velocity	7 ft/min
Contact Time	27 min
Equilibrium Saturation	19 days

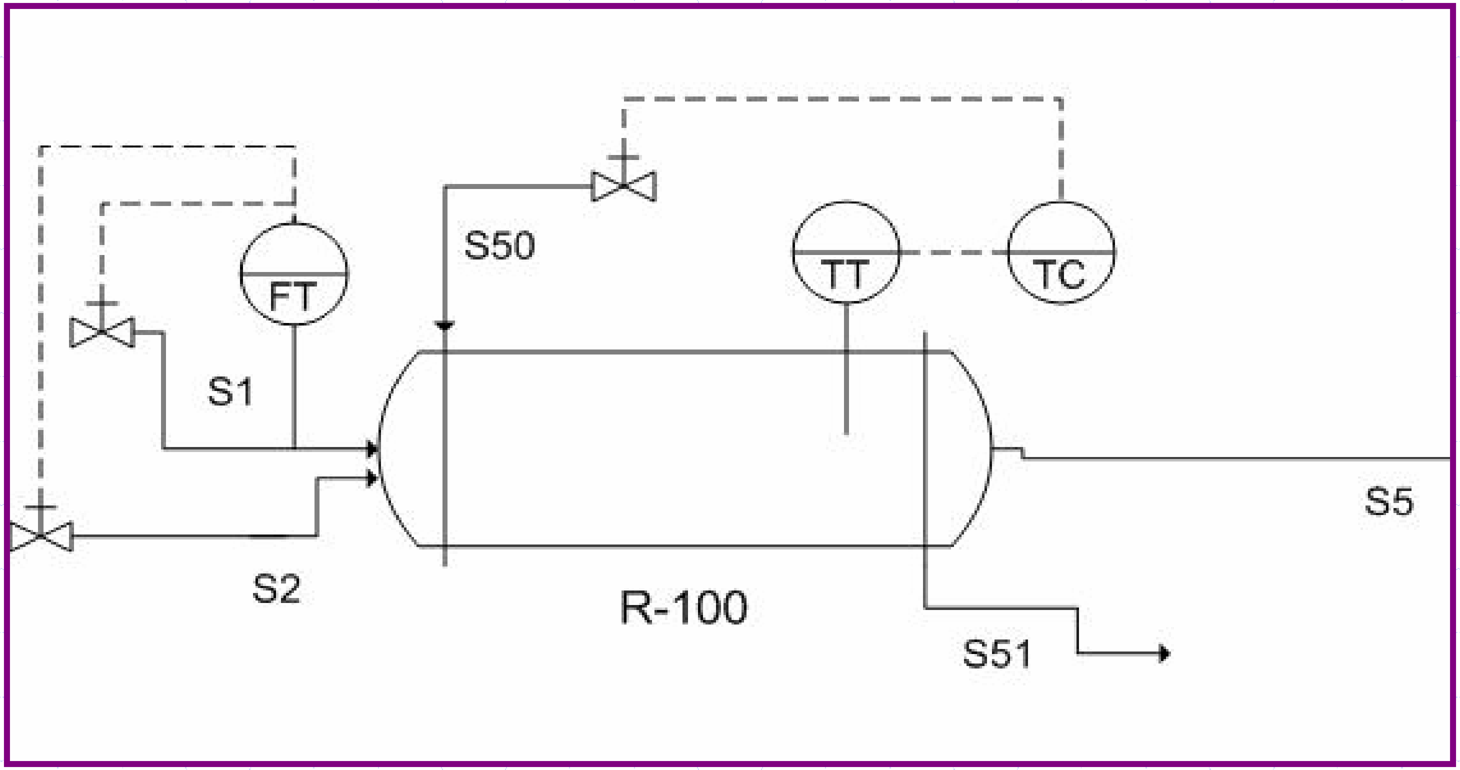
Carbon Regeneration



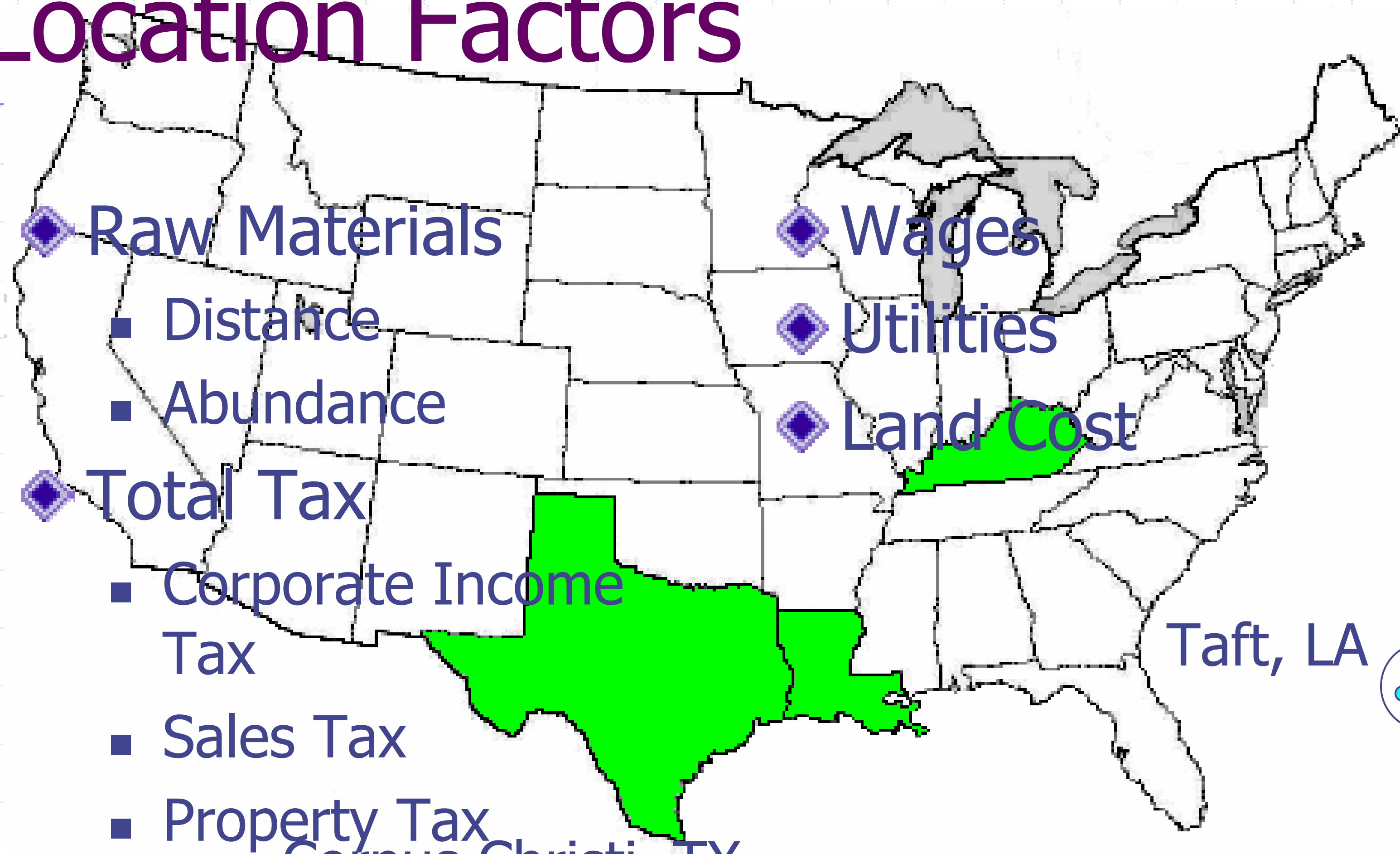
HAZOP Studies- Safety Concern

- Purpose: Reduce risk at workplace
- Identify risks, prevent and reduce impact
- Subdivide into small sections
- Deviations, Causes, Consequences, Safe Guard and Actions

PFTR Reactor

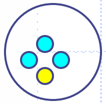


Plant Location
Location Factors

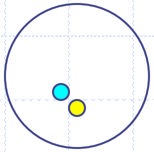


- Raw Materials
  - Distance
  - Abundance
- Total Tax
  - Corporate Income Tax
  - Sales Tax
  - Property Tax
- Wages
- Utilities
- Land Cost

Taft, LA



Corpus Christi, TX



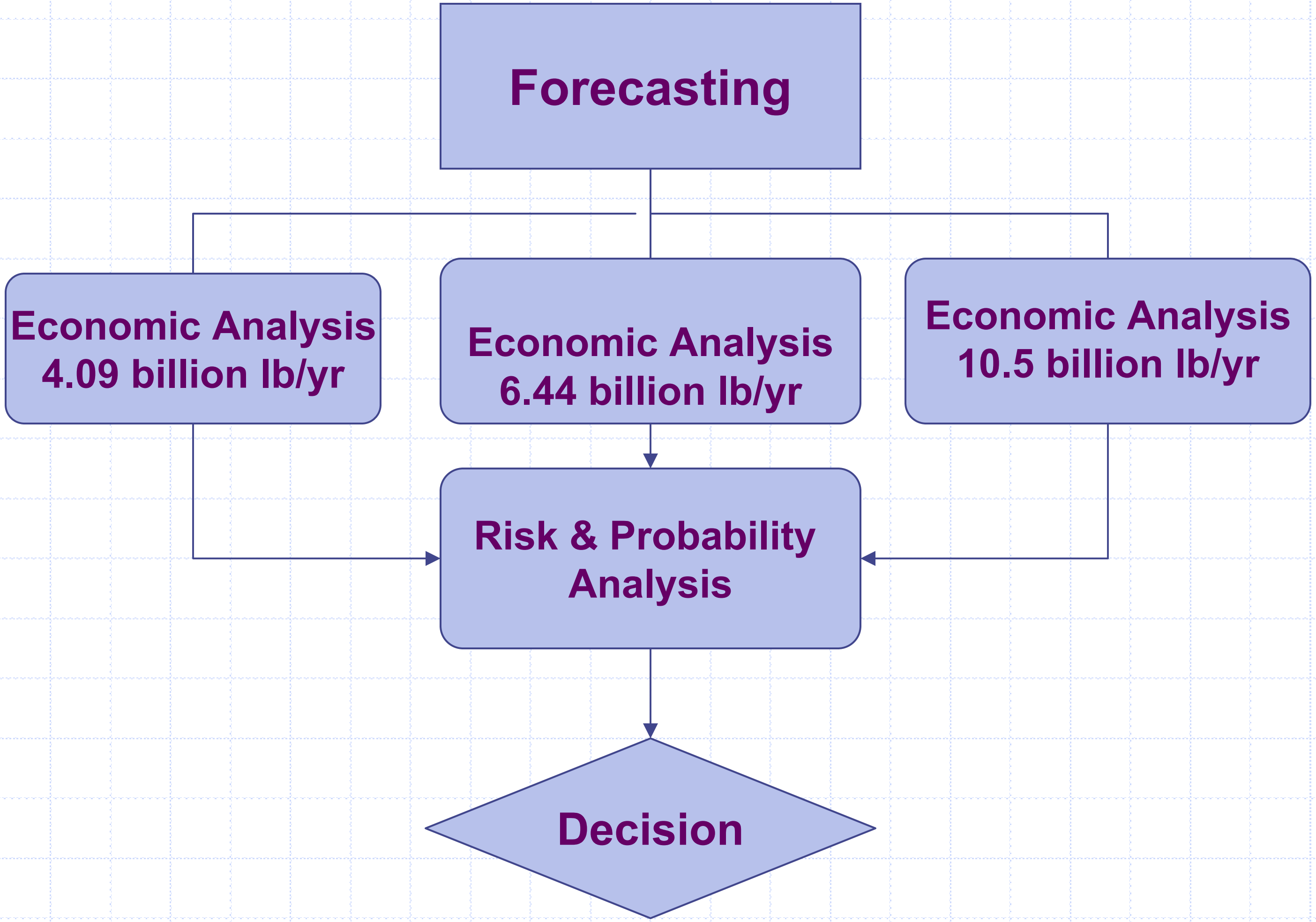
Factor Rating Maximization

Factor	Weight %	LA	TX
Raw Material			
Distance	30	3 miles	17 miles
Abundance	25	4	2
Total Tax	20	32%	40%
Wages	12	0.95	1.03
Utilities	8	$2.7/MMBtu	$2.5/MMBtu
Land Cost	5	$1270/acre	$640/acre

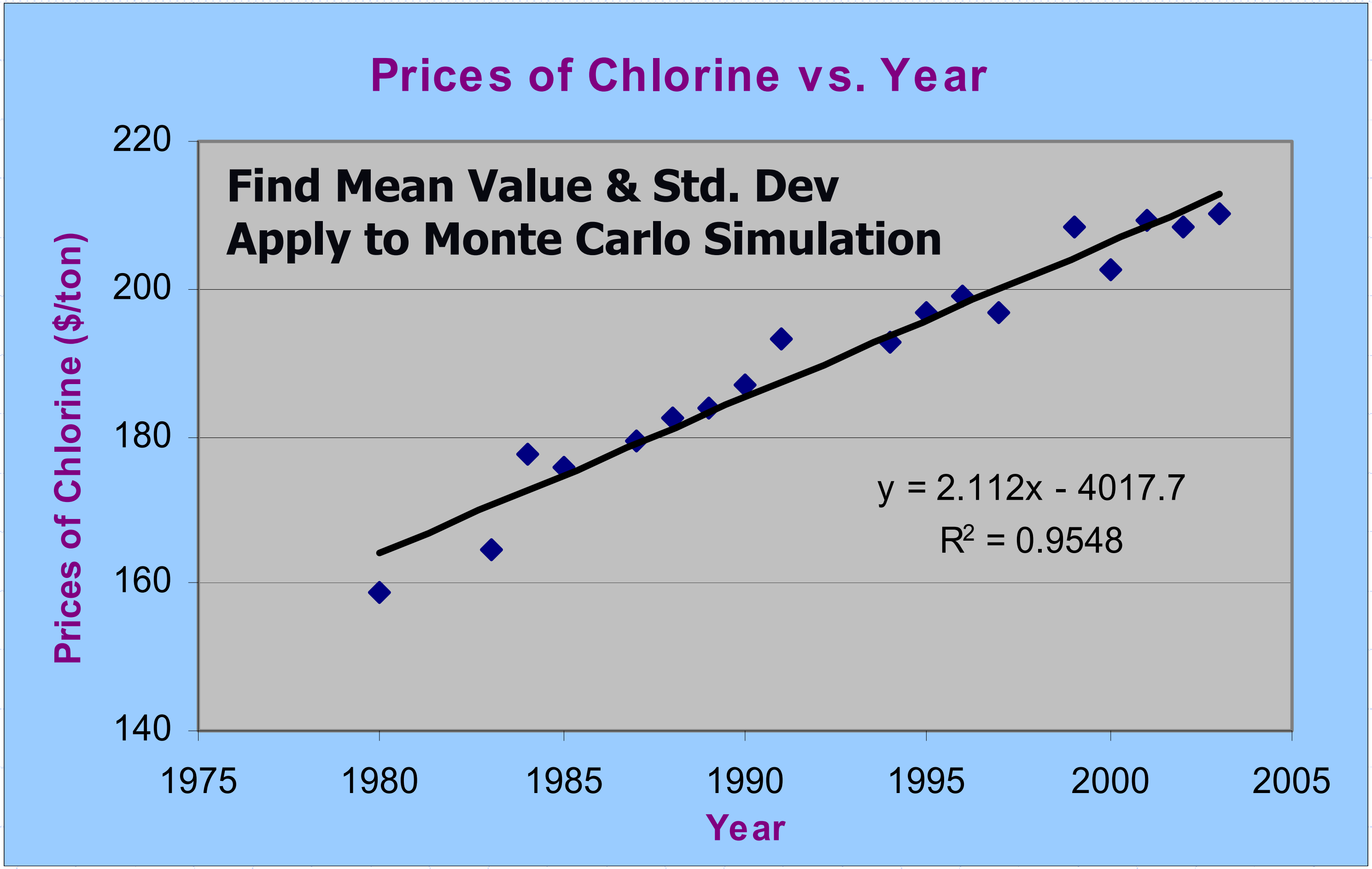
Factor Rating Maximization

- Weight % x Value % = Factor Rating
- Taft, LA
  - 0.64
- Corpus Christi, TX
  - 0.96

Plant Capacity



Forecasting



Forecasting

Year	Ethylene ($/ton)	Chlorine ($/ton)	Oxygen ($/ft^3)	VCM ($/ton)
2004	492.5	212.2	0.001445	499.2
2005	499.4	214.1	0.001436	506.2
2006	506.2	216.1	0.001427	513.2
2007	513.1	218.0	0.001418	520.2
2008	519.9	219.9	0.001409	527.2
2009	526.7	221.8	0.001400	529.2
2010	533.6	223.8	0.001391	535.2
2011	540.4	225.7	0.001382	543.21
Std. Dev.	24.17	10.56	0.000102	26.15

NPW & ROI

$$NPW = \sum_{k=1}^{n-1} \frac{CF_k}{(1+i)^k} + \frac{CF_n + V_S + I_W}{(1+i)^n} - TCI$$

$$TCI = \sum_{k=1}^{n} CF_k (1+r)^{-k} + (V_s + I_w)(1+r)^{-n}$$

Where

TCI= total capital investment

CF = cash flow

i = interest rate = 0.05

V_s = savage value

I_w = working capital

Economic Analysis

Plant Capacity	4.09 billion lb/yr	6.44 billion lb/yr	10.5 billion lb/yr
TCI	$47,110,000	$68,886,000	$77,154,000
NPW	$133,739,000	$284,828,000	$161,759,000
ROI	0.24	0.25	0.20

Risk Analysis

- Monte-Carlo simulation
    - Mean and Standard Deviation
    - Random Number Generation
    - NPW
    - Risk Measurement
    - Probability
- Decision: Plant Capacity
- Detailed Economic Analysis

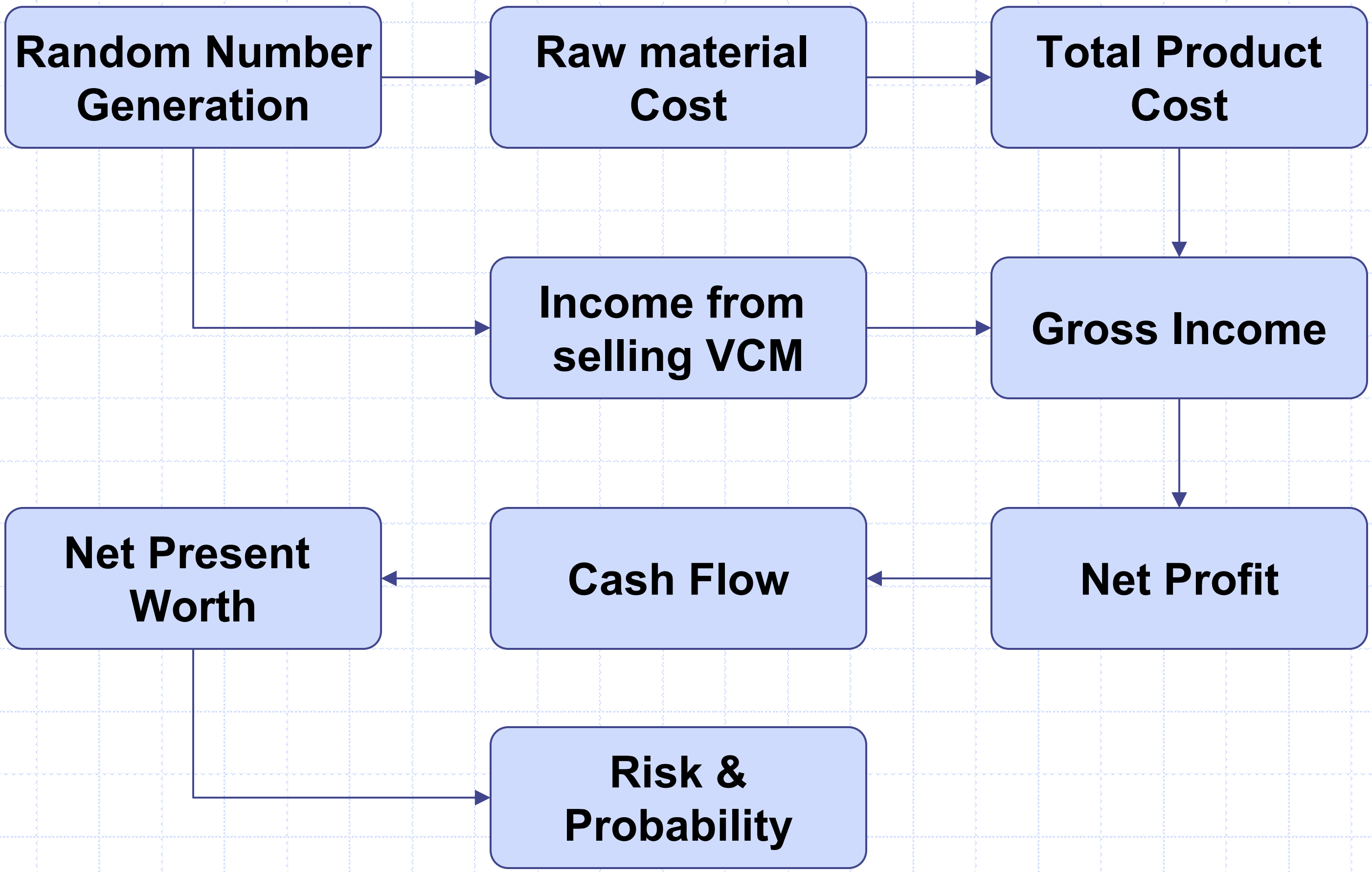
Monte Carlo

- Assume normal distribution
- Perform random walks

  Norminv(Rand(), Mean, Std. Dev.)
- Stop the iterations when the data converges

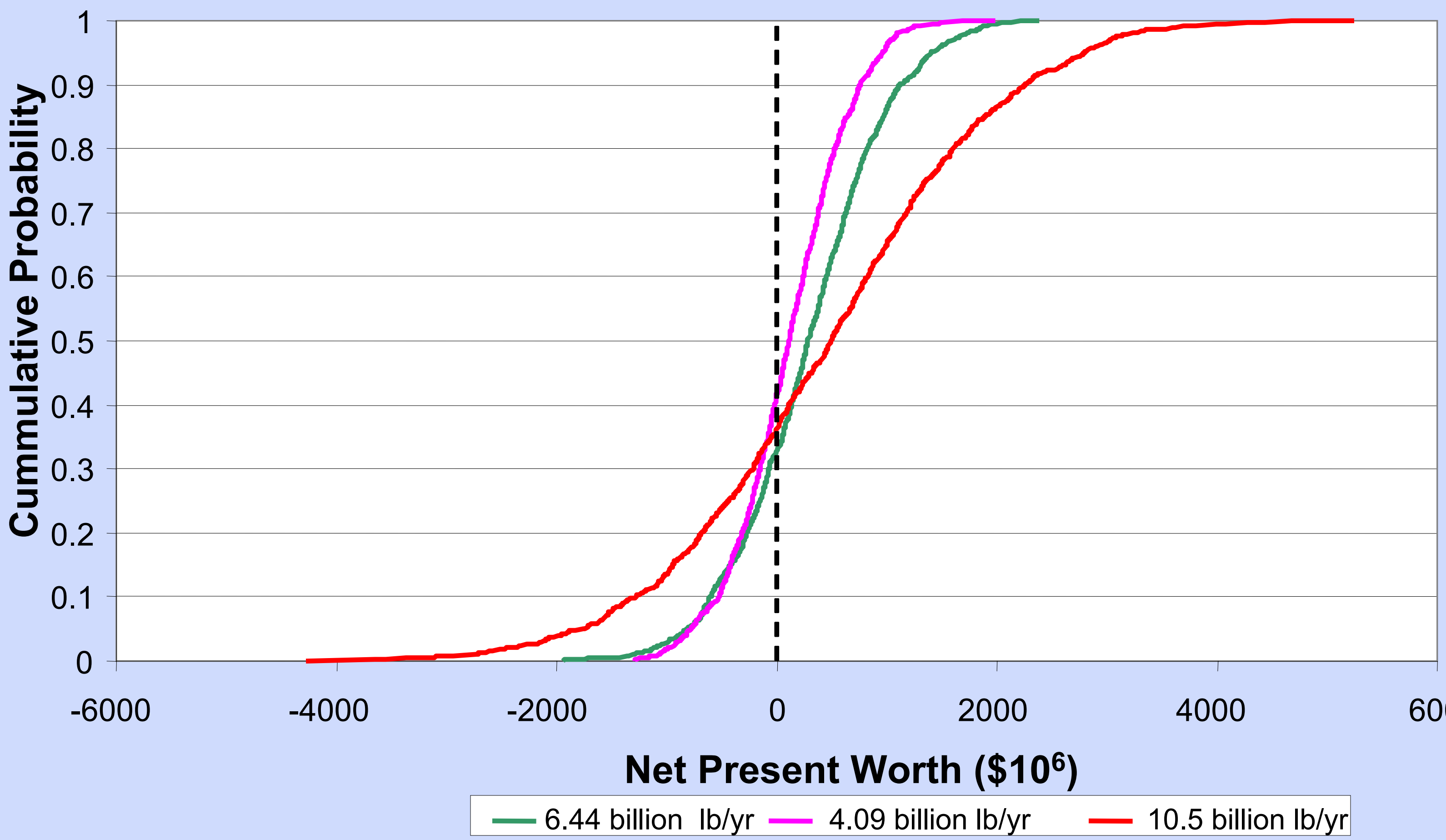
  Approximately 1000 trials
- Reduce error compared to analytical approach

Procedure



Random Number Generation
Raw material Cost
Total Product Cost
Income from selling VCM
Gross Income
Net Present Worth
Cash Flow
Net Profit
Risk & Probability

Project Risk Curves



Comments

- Capacity of 4.09 billion lb/yr:

  41.7% chance of negative NPW

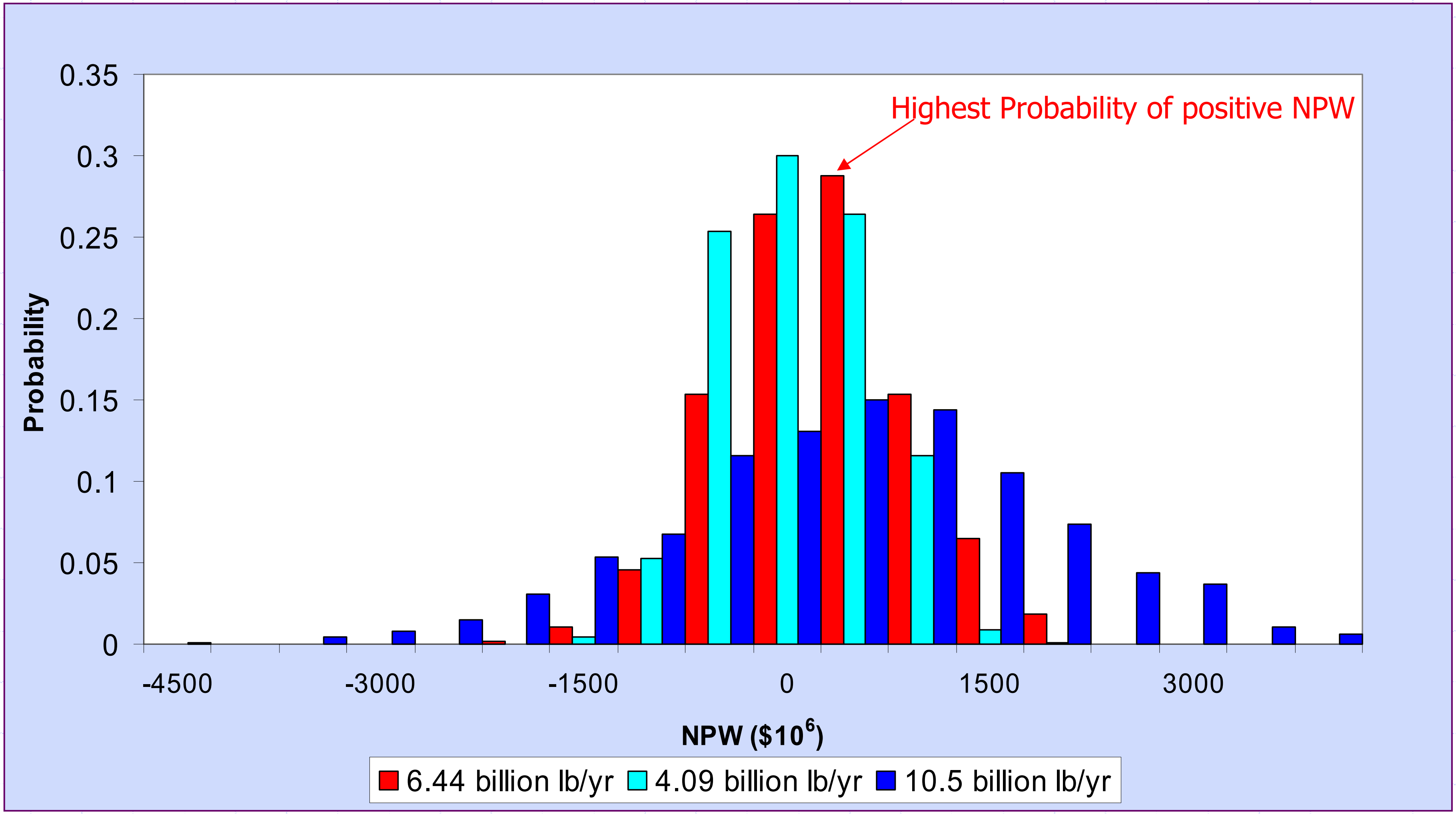
- Capacity of 6.44 billion lb/yr:

  31.5% chance of negative NPW

- Capacity of 10.5 billion lb/yr:

  36.8% chance of negative NPW

Probability vs. Net Present Worth



Decision

Plant Capacity of 6.44 billion lb/yr:

- Highest NPW
- Highest ROI
- Lowest risk: 31.5 % of losing money
- High probability of making money

Detailed Economic Analysis

Plant Capacity: 6.44 billion lb/yr

Plant Equipment:

- Four Heat Exchangers
- Four Distillation Towers
- Seven Flash Tanks
- Three Reactors
- Adsorption System
- Incineration Unit

- Total Equipment Cost: $15.3M

Total Capital Investment		
Total Equipment Cost		$15,284,100
Variables	**Description**	**Cost ($)**
Equipment Installed	47% of TEC (P&T)	7,183,527
Incineration Unit (install)	Flow Rate Correlation	10,500
Instrumentation & Control	18% of TEC (P&T)	2,751,138
Piping (installed)	50% of TEC (P&T)	7,642,050
Electrical (installed)	11% of TEC (P&T)	1,681,251
Total		19,268,466
Building Cost		
Office	$45/ft^2 (Brick Building) in 3000 ft^2	135,000
Process Building (5-Unit)	$15/ ft^2 (Steel Building)in 4600 ft^2/Unit	375,000
Service Building	$45/ ft^2 (Brick Building) in 2000 ft^2	90,000
Storage Building	$15/ ft^2 (Steel Building)in 4000 ft^2/Unit	62,500
Maintenance Unit/Shop	$45/ ft^2 (Brick Building) in 1500 ft^2	67,500
Administration/Accounting	$45/ ft^2 (Brick Building) in 2500 ft^2	112,500
Environment/Research	$45/ ft^2 (Brick Building) in 3000 ft^2	135,000
Total		977,500
Yard Improvement		
Site Cleaning	$4400/acre (total of 50 acres)	220,000
Grading	$465/acre (total of 10 acres)	4,650
Fencing	$9/ft (total of 9000 ft)	81,000
Walkways	$4.50/ ft^2 (total of 5000 ft^2)	22,500
Total		328,150
Land Cost	$1270/acre (total of 50 acres)	63,500
Total Direct Plant Cost		35,921,716
Engineering & Supervision	32% of TEC (P&T)	4,890,912
Construction Expenses	41% of TEC (P&T)	6,266,481
Contractor's Fee	21% of TEC (P&T)	3,209,661
Contingency	42% of TEC (P&T)	6,419,322
Total Indirect Cost		20,786,376
Fixed Capital Investment	Direct+Indirect	56,708,092
Working Capital	86% of TEC (P&T)	13,144,326
Total Capital Investment	Direct+Indirect+Working Capital	69,852,418

Employee	# of Employee	$/yr	Total
Plant Chairman	1	$105,000	$105,000
Managers			
Plant Manager	1	$80,000	$80,000
Unit Managers	5	$73,000	$365,000
Operational Engineers			
Computer Programmer	1	$62,890	$62,890
Computer Engineer	2	$74,310	$148,620
Chemical Engineers	5	$72,780	$363,900
Process Engineers	5	$73,000	$365,000
Electrical Engineers	3	$68,630	$205,890
Environment Engineers	3	$62,000	$186,000
Industrial Engineers	3	$61,900	$185,700
Mechinical Engineers	2	$63,500	$127,000
Maintainance Engineers	2	$30,000	$60,000
Operator	30	$68,000	$2,040,000
Supervisor	5	$70,000	$350,000
Administration			
Financial Manager	1	$60,000	$60,000
Production Manager	1	$68,000	$68,000
Sales Manager	1	$60,000	$60,000
Accounting			
Budget Analysts	2	$53,000	$106,000
Finantial Analysts	1	$62,000	$62,000
Tax Preparers	2	$33,000	$66,000
Auditor	2	$35,000	$70,000
Total			**$5,137,000**

Economic Summary

- Total Product Cost-$1.59 billion
- Net Profit- $26.2 million
- NPW- $265 million
- ROI-23.7%

Environmental Impact vs. Profit

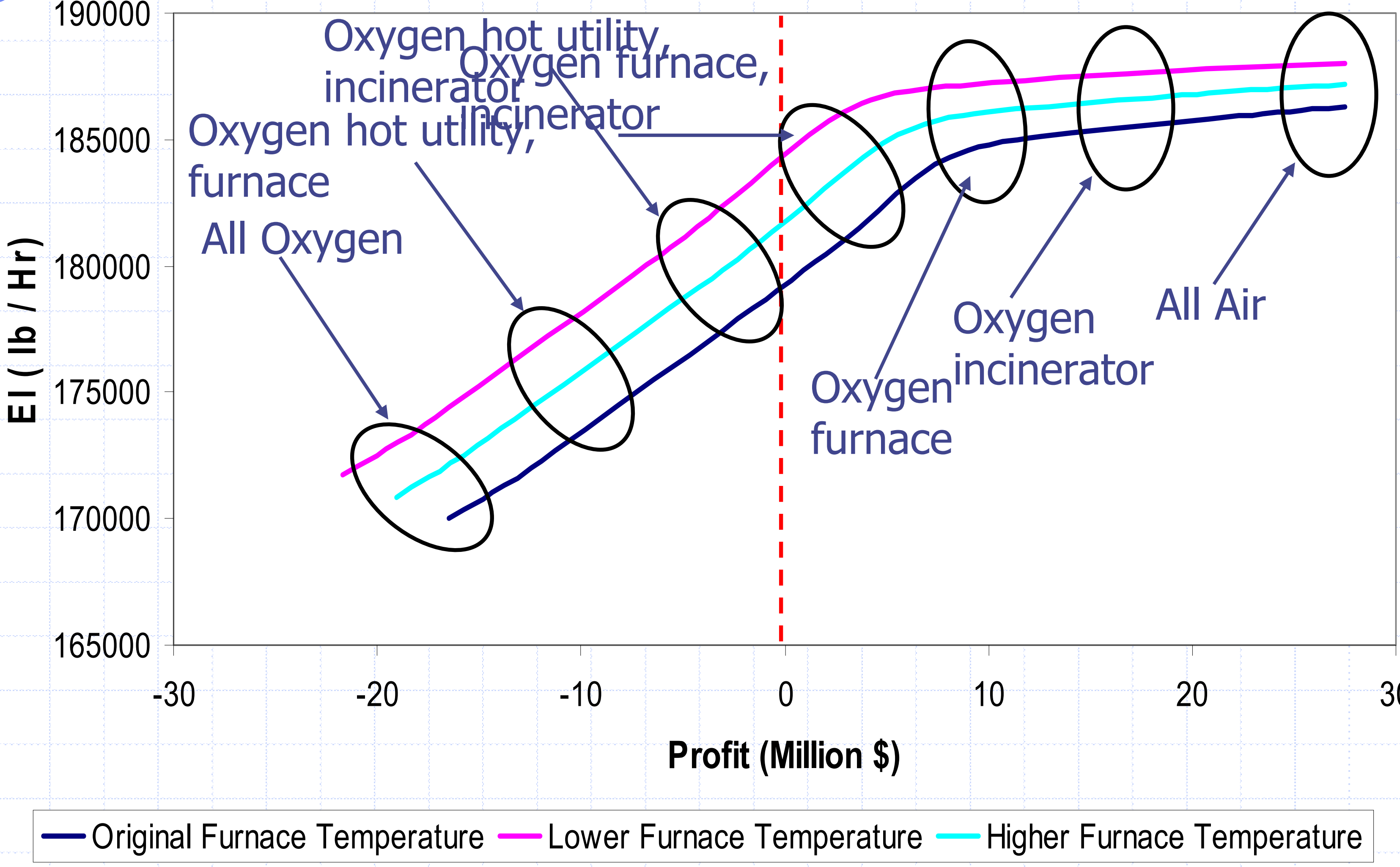
Waste Reduction Algorithm

- Evaluate effects of design changes on environment
- Reactors can not be varied
  - Exothermic reactions allow heat integration
- Variable design parameters
  - Oxygen usage
  - Furnace temperature

Impact Calculations

- Impact/hr
- $I_i = \Sigma M_j \times \Sigma x_{kj} \Psi_k$
  - M_j = mass flow rate of stream j
  - x_{kj} = mass fraction of chemical k in stream j
  - $-\Psi_k$ = characteristic potential impact of chemical k

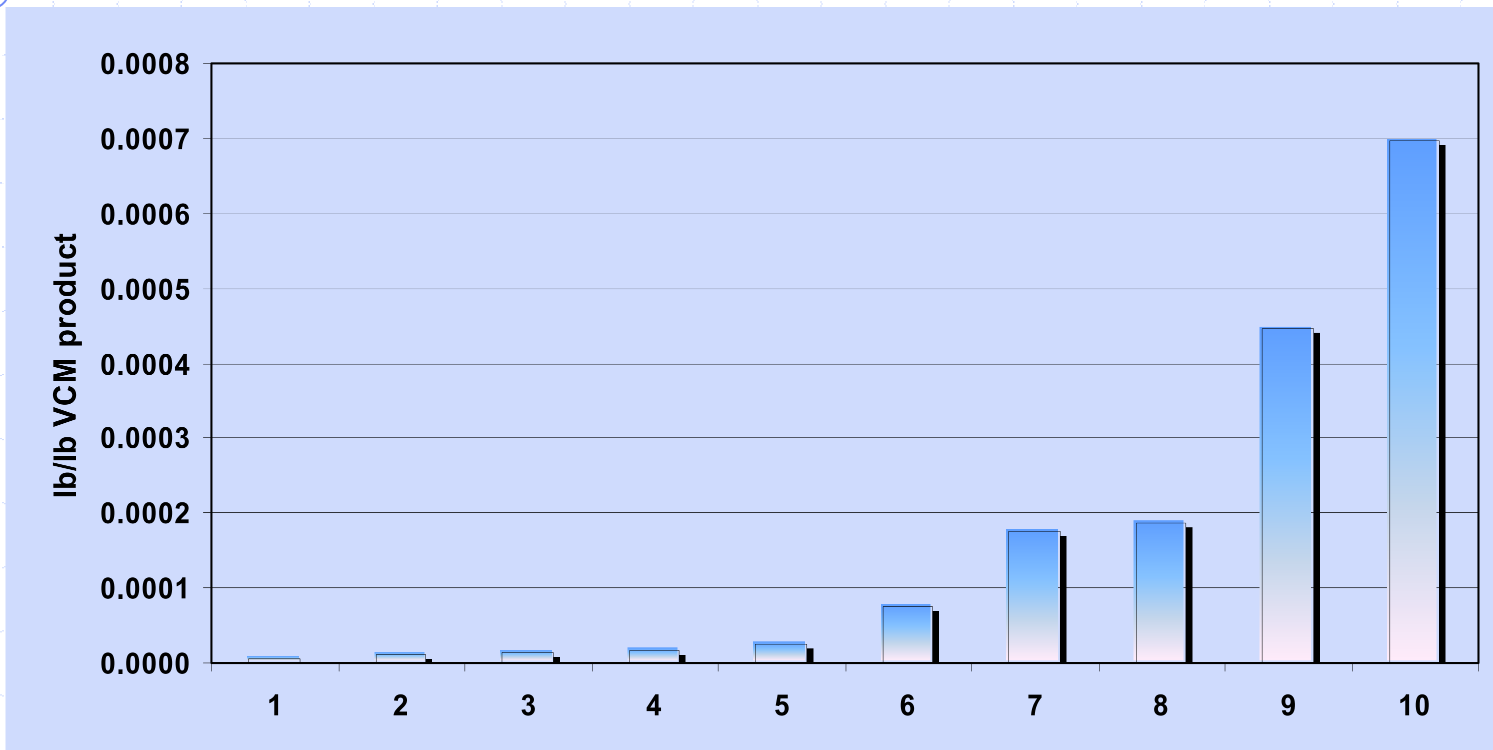
Environmental Impact vs. Profit



Sequestering CO_2 Emissions

- Enhanced oil recovery
- Brine aquifers injection
- Located beneath shale layer
- 3100 ft
- FCI is a function of CO_2 flow rate
  - 27.753 $/(kg/hr) = $11.4 million
- OC is a function of CO_2 flow rate and depth
  - 0.0000912 $/(kg/hr)(ft) = $183,000/yr

VCM Plant Emissions in the United States



2 Formosa-LA
5 Georgia Gulf-LA
8 Borden-LA

Capital Investment to achieve this emission reduction = $2.5 Million

Decreased Net Profit = $1.3 Million/year

3 Oxyvinyls-D-TX
6 Westlake Monomers-KY
9 Dow-LA

4 Oxyvinyls-L-TX
7 Formosa-TX
10 Dow-TX

Conclusion

- Balanced Process
- Incineration and Carbon Adsorption
- 6.4 billion lbs/year
- Taft, LA
- Sequestration of CO_2