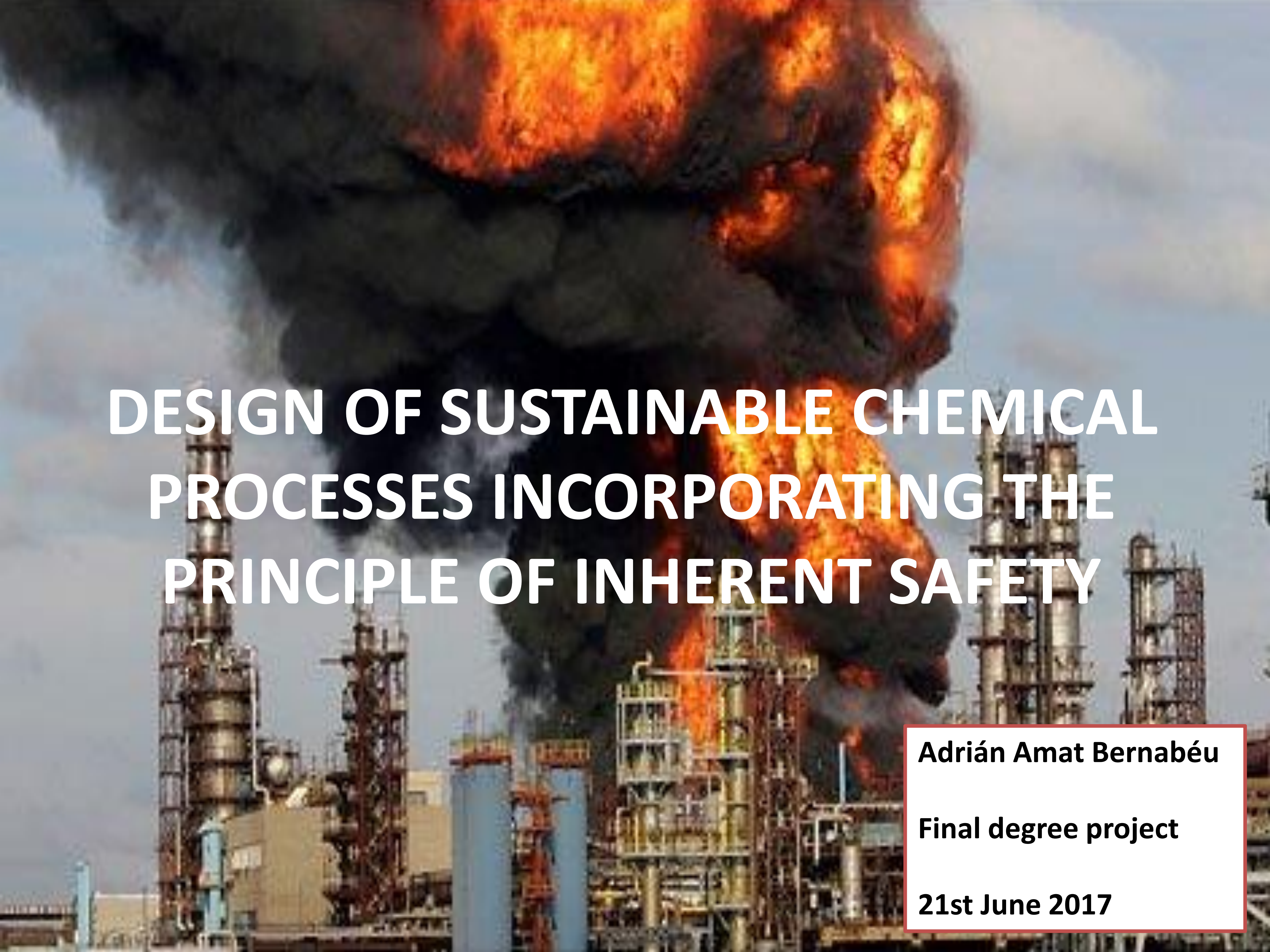

DESIGN OF SUSTAINABLE CHEMICAL PROCESSES INCORPORATING THE PRINCIPLE OF INHERENT SAFETY

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Final degree project

21st June 2017

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- Optimization model reformulation
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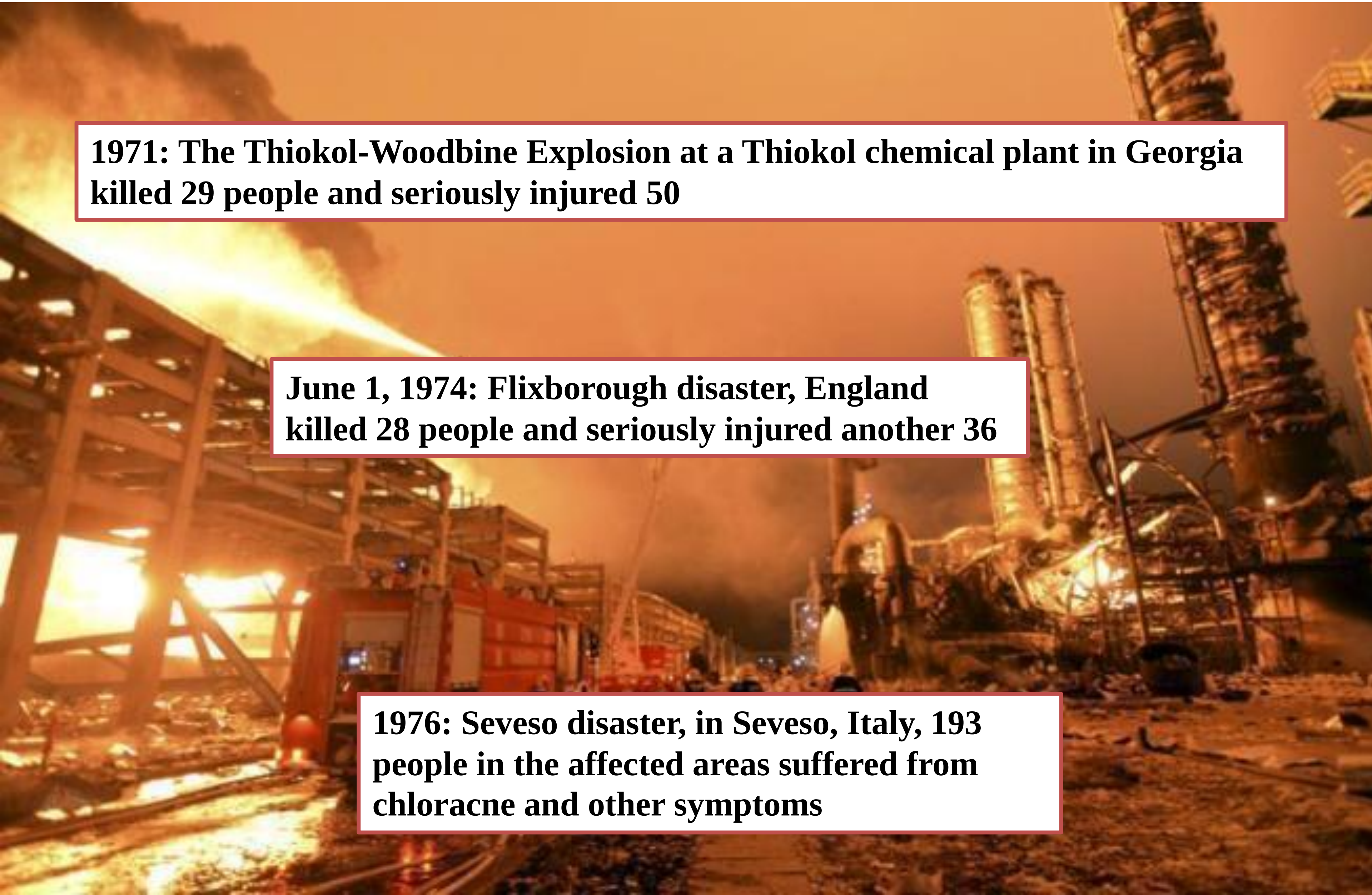
Introduction



1971: The Thiokol-Woodbine Explosion at a Thiokol chemical plant in Georgia killed 29 people and seriously injured 50

June 1, 1974: Flixborough disaster, England killed 28 people and seriously injured another 36

1976: Seveso disaster, in Seveso, Italy, 193 people in the affected areas suffered from chloracne and other symptoms

Motivation

- Process plants can be dangerous places
  - Energy products and chemical transformations that are driven by energy.
  - Hazardous substances or operation conditions.
  - Fuels and industrial chemicals can be hazardous:
    - Fuels burn readily with the release of energy.
    - Chemical reactions often involve large amounts of energy.

- Response
  - Hazard identification and analysis techniques to reduce the frequency and consequences of accidents.

Risk mitigation strategies

- Common method to mitigate risk
  - Adding layers of protection with safety devices (later phases of the process design).
  - These protective layers increase the complexity of the process.
  - Do not eliminate the hazards (can provoke an unanticipated potential incident).

Alternative method

- Another design philosophy of risk management is based on the concept **Inherently Safer Design**.

DOW'S FIRE & EXPLOSION INDEX

- Inherent safety performance of each design alternative has been assessed by the Dow's Fire and Explosion index (*Dow, 1994*).

- Suggested by *Kletz (1998)* and also used by other authors (*Al-Mutairi et al., 2008, Suardin et al., 2007)* as a an inherent safety metric.

AREA / COUNTRY	Business group	LOCATION	DATE
SITE	MANUFACTURING UNIT	PROCESS UNIT	
PREPARED BY:	APPROVED BY: (Production Manager)	BUILDING	
REVIEWED BY: (Management)	REVIEWED BY: (Technology)	REVIEWED BY: (Safety/Environment)	
MATERIALS IN PROCESS UNIT			
STATE OF OPERATION ___ DESIGN ___ START UP___ NORMAL OPERATION ___ SHUTDOWN		BASIC MATERIAL(S) FOR MATERIAL FACTOR	
MATERIAL FACTOR (See Table 1 or Appendices A or B) Note requirements when unit temperature over 140 °F (60 °C)			

1. General Process Hazards	Penalty Factor Range	Penalty Factor Used(1)
Base Factor	1.00	1.00
A. Exothermic Chemical Reactions	0.00 to 1.25	0.3
B. Endothermic Processes	0.00 to 0.40	-
C. Material Handling and Transfer	0.00 to 1.05	-
D. Enclosed or Indoor Process Units	0.00 to 0.90	-
E. Access	0.00 to 0.35	-
F. Drainage and Spill Control ________ gal or cu.m.	0.00 to 0.50	-
General Process Hazards Factor (F_1) (SUM A to F)		1.3
2. Special Process Hazards		
Base Factor	1.00	1.00
A. Toxic Material(s)	0.0 to 0.80	1.00
B. Sub-Atmospheric Pressure (< 500 mm Hg)	0.50	
C. Operation In or Near Flammable Range ___ Inerted ___ Not Inerted		
1. Tank Farms Storage Flammable Liquids	0.50	
2. Process Upset or Purge Failure	0.30	0.3
3. Always in Flammable Range	0.80	
D. Dust Explosion (See Table 3)	0.00 to 2.00	
E. Pressure (See Figure 2) Operating Pressure 720.1 psig or ~~kPa~~ gauge; Relief Setting 793.6 psig or ~~kPa~~ gauge		0.90
F. Low Temperature	0.0 to 0.30	
G. Quantity of Flammable/Unstable Material: Quantity 16815 lb or ~~kg~~; H_C = 16051 BTU/lb or ~~kcal/kg~~		
1. Liquids or Gases in Process (See Figure 3)		0.59
2. Liquids or Gases in Storage (See Figure 4)		
3. Combustible Solids in Storage, Dust in Process (See Figure 5)		
H. Corrosion and Erosion	0.00 to 0.75	
I. Leakage – Joints and Packing	0.00 to 1.50	
J. Use of Fired Equipment (See Figure 6)		
K. Hot Oil Heat Exchange System (See Table 5)	0.00 to 1.15	
L. Rotating Equipment	0.00 - 0.50	0.5
Special Process Hazards Factor (F_2) (A to L)		3.89
Process Unit Hazards Factor (F_1 x F_2) = F_3		5.06
Fire and Explosion Index (F_3 x MF = F&EI)		106.27

DOW'S FIRE & EXPLOSION INDEX

1. **Select the process units.**
2. **Determine MF.**
3. **Determine risk factors.**
   - General Process Hazards (F1)
   - Special process Hazards (F2)

1. General Process Hazards		Penalty Factor Range	Penalty Factor Used(1)
Base Factor		1.00	1.00
A. Exothermic Chemical Reactions		0.30 to 1.25	
B. Endothermic Processes		0.20 to 0.40	
C. Material Handling and Transfer		0.25 to 1.05	
D. Enclosed or Indoor Process Units		0.25 to 0.90	
E. Access		0.20 to 0.35	
F. Drainage and Spill Control	______ gal or cu.m.	0.25 to 0.50	
General Process Hazards Factor (F_1)			

DOW'S FIRE & EXPLOSION INDEX

- Special Process Hazards

2. **Special Process Hazards**		
Base Factor	1.00	1.00
A. Toxic Material(s)	0.20 to 0.80	
B. Sub-Atmospheric Pressure (< 500 mm Hg)	0.50	
C. Operation In or Near Flammable Range ___ Inerted ___ Not Inerted		
1. Tank Farms Storage Flammable Liquids	0.50	
2. Process Upset or Purge Failure	0.30	
3. Always in Flammable Range	0.80	
D. Dust Explosion (See Table 3)	0.25 to 2.00	
E. Pressure (See Figure 2) Operating Pressure ________ psig or kPa gauge Relief Setting ________ psig or kPa gauge		
F. Low Temperature	0.20 to 0.30	
G. Quantity of Flammable/Unstable Material: Quantity _____ lb or kg H_C = _____BTU/lb or kcal/kg		
1. Liquids or Gases in Process (See Figure 3)		
2. Liquids or Gases in Storage (See Figure 4)		
3. Combustible Solids in Storage, Dust in Process (See Figure 5)		
H. Corrosion and Erosion	0.10 to 0.75	
I. Leakage – Joints and Packing	0.10 to 1.50	
J. Use of Fired Equipment (See Figure 6)		
K. Hot Oil Heat Exchange System (See Table 5)	0.15 to 1.15	
L. Rotating Equipment	0.50	
Special Process Hazards Factor (F_2)		

DOW'S FIRE & EXPLOSION INDEX

$$F_1 = 1 + \sum penalties$$ Process Hazard

$$F_2 = 1 + \sum penalties$$ Special Process Hazard

AREA / COUNTRY	Business group	LOCATION	DATE
SITE	MANUFACTURING UNIT	PROCESS UNIT	
PREPARED BY:	APPROVED BY: (Production Manager)	BUILDING	
REVIEWED BY: (Management)	REVIEWED BY: (Technology)	REVIEWED BY: (Safety/Environment)	
MATERIALS IN PROCESS UNIT			
STATE OF OPERATION ___ DESIGN ___ START UP___ NORMAL OPERATION ___ SHUTDOWN		BASIC MATERIAL(S) FOR MATERIAL FACTOR	
MATERIAL FACTOR (See Table 1 or Appendices A or B) Note requirements when unit temperature over 140 ºF (60 ºC)			

1. General Process Hazards	Penalty Factor Range	Penalty Factor Used(1)
Base Factor	1.00	1.00
A. Exothermic Chemical Reactions	0.00 to 1.25	0.3
B. Endothermic Processes	0.00 to 0.40	-
C. Material Handling and Transfer	0.00 to 1.05	-
D. Enclosed or Indoor Process Units	0.00 to 0.90	-
E. Access	0.00 to 0.35	-
F. Drainage and Spill Control ________ gal or cu.m.	0.00 to 0.50	-
General Process Hazards Factor (F_1) (SUM A to F)		1.3
2. Special Process Hazards		
Base Factor	1.00	1.00
A. Toxic Material(s)	0.0 to 0.80	1.00
B. Sub-Atmospheric Pressure (< 500 mm Hg)	0.50	
C. Operation In or Near Flammable Range ___ Inerted ___ Not Inerted		
1. Tank Farms Storage Flammable Liquids	0.50	

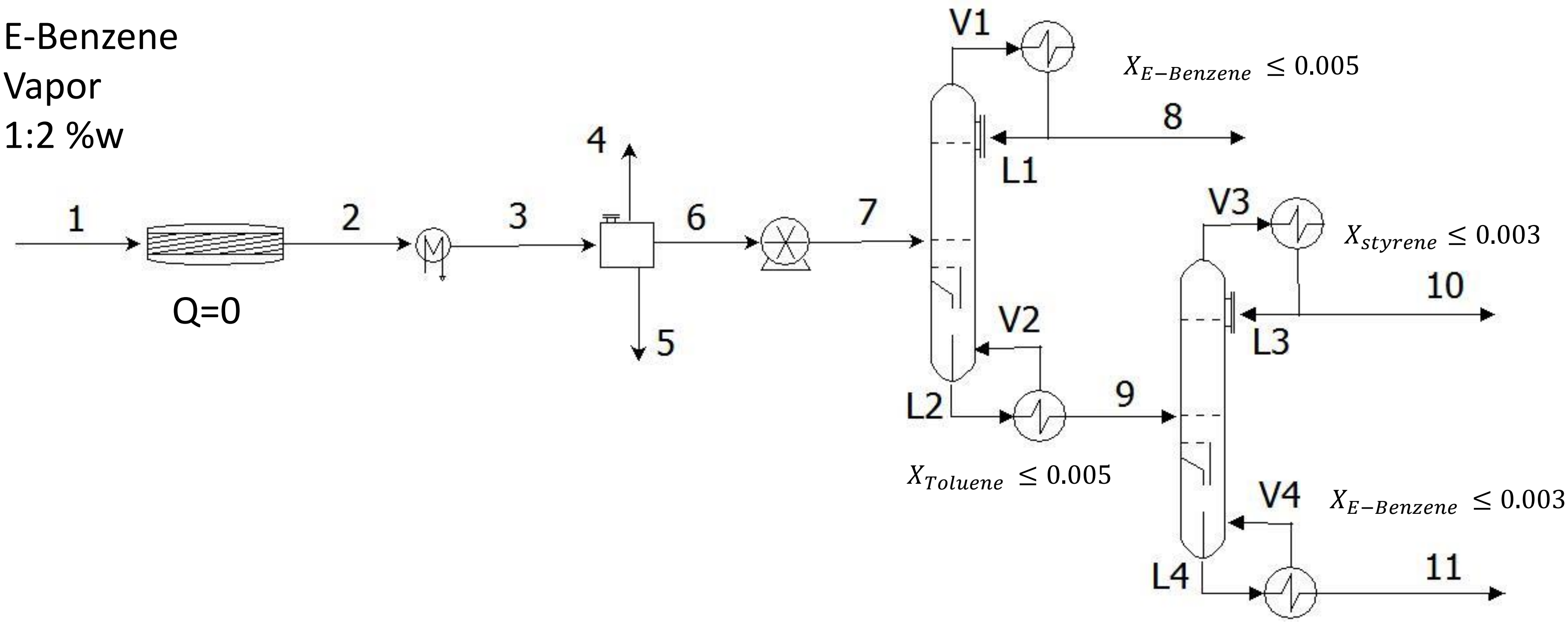
Special Process Hazards Factor (F_2)	
Process Unit Hazards Factor (F_1 x F_2) = F_3	
Fire and Explosion Index (F_3 x MF = F&EI)	

K. Hot Oil Heat Exchange System (See Table 5)	0.00 to 1.15	
L. Rotating Equipment	0.00 - 0.50	0.5
Special Process Hazards Factor (F_2) (A to L)		3.89
Process Unit Hazards Factor (F_1 x F_2) = F_3		5.06
Fire and Explosion Index (F_3 x MF = F&EI)		106.27

$$F\&EI = MF\ F_1\ F_2^{cte} + MF\ F_1 E_2(P) + MF\ F_1 G_2(V)$$

Problem statement

Case study on a styrene production plant



850 kg/h styrene

Problem statement

$$\underset{\text{E-Benzene}}{C_6H_5CH_2CH_3} \leftrightarrow \underset{\text{Styrene}}{C_6H_5CHCH_2} + H_2$$

$$r_1 = A_1 \exp\left(-\frac{E_1}{RT}\right)\left(p_{EB} - \frac{p_{ST}p_{H_2}}{K'}\right)$$

$$\underset{\text{E-Benzene}}{C_6H_5CH_2CH_3} \rightarrow \underset{\text{Benzene}}{C_6H_6} + \underset{\text{Ethylene}}{C_2H_4}$$

$$r_2 = A_2 \exp\left(-\frac{E_2}{RT}\right) p_{EB}$$

$$\underset{\text{E-Benzene}}{C_6H_5CH_2CH_3} \rightarrow \underset{\text{Toluene}}{C_6H_5CH_3} + \underset{\text{Methane}}{CH_4}$$

$$r_3 = A_3 \exp\left(-\frac{E_3}{RT}\right) p_{EB}\, p_{H_2}$$

$$2H_2O + C_2H_4 \rightarrow 2CO + 4H_2$$

$$r_4 = A_4 \exp\left(-\frac{E_4}{RT}\right) p_{Ethyl}\, p_{H_2O}^2$$

$$H_2O + CH_4 \rightarrow CO + 3H_2$$

$$r_5 = A_5 \exp\left(-\frac{E_5}{RT}\right) p_{Met}\, p_{H_2O}$$

$$H_2O + CO \rightarrow CO_2 + H_2$$

$$r_6 = A_6 \exp\left(-\frac{E_6}{RT}\right) p_{CO}\, p_{H_2O}$$

Problem statement

Goal

Determine the optimal process layout and its operating conditions (pressures, areas, reactor length, flow rates) that minimize the hazard (**F&EI**) and total annualised cost (**TAC**).

Multi-objective problem

Optimization model reformulation

Optimization model reformulation

- SAFETY

$$F\&EI = MF\ F_1\ F_2^{cte} + MF\ F_1 E_2(P) + MF\ F_1 G_2(V)$$

E. Pressure relief

$$Y = 0.16109 + 1.61503\left(\frac{X}{1000}\right) - 1.42879\left(\frac{X}{1000}\right)^2 + 0.5172\left(\frac{X}{1000}\right)^3$$

$$E = 1.2\frac{Y^2(operating\ pressure)}{Y(realief\ pressure)}$$

G. Inflammable Material

$$logY = 0.17179 + 0.42988(1ogX) - 0.37244(1ogX)^2 + 0.17712(1og\,X)^3 - 0.029984(1ogX)^4$$

$$X \geq V_{equipment} \cdot \sum_j C_j^{average} \cdot H_{cj}$$

$$X \geq H_{cj} \cdot m_j \cdot t$$

- # INHERENT SAFETY

$$F\&EI = 128.52 + 40.8\left[1.2\frac{Y(P_{operating})^2}{Y(P_{realive})} + G_2(V)\right]$$

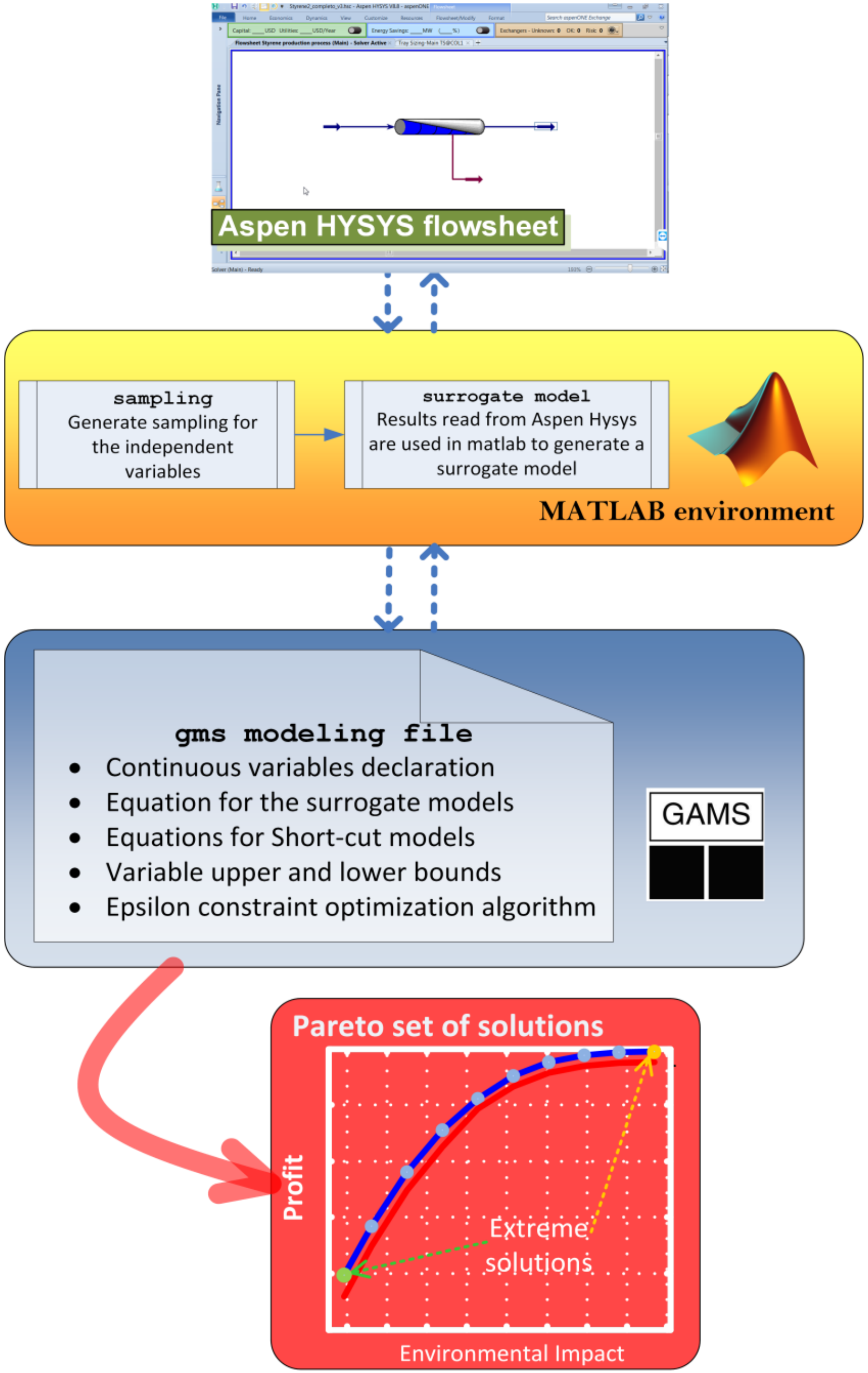
$$G_2 = \frac{2.509x + 0.01545}{x + 0.6932}$$

$$1 < X < 9 \quad BTU \cdot 10^9$$

Material Factor	24
1. General Process Hazards	
Base Factor	1
A. Exothermic Chemical Reactions	0.3
B. Endothermic Processes	0.4
C. Material Handling and Transfer	0
D. Enclosed or Indoor Process Units	0
E. Access	0
F. Drainage and Spill Control	0
General Process Hazards Factor (F1)	1.7
2. Special Process Hazards	
Base Factor	
A. Toxic Marial(s)	0.6
B. Sub-Atmospheric Pressure (<500 mmHg)	0
C. Operation In or Near Flammable Range	
1. Tank Farms Storage Flammable Liquids	-
2. Process Upset or Purge Failure	-
3. Always in Flammable Range	0.8
D. Dust Explosion	0
E. Pressure	Equation
F. Low Temperature	0
G. Quantity of Flammable/Unstable Material	
1. Liquid or Gases in Process	Equation
2. Liquids or Gases in Storage	-
3. Combustible Solids in Storage, Dust in Process	-
H. Corrosion and Erosion	0.75
I. Leakage-Joints and Packing	0
J. Use of Fired Equipment	1
K. Hot Oil Heat Exchange System	0
L. Rotating Equipment	0
Special Process Hazards Factor (F2)	3.15
Process Unit Hazards Factor (F1xF2)=F3	5.355

- # EQUIPMENT DESIGN

Reactor



Optimization model reformulation

- EQUIPMENT DESIGN

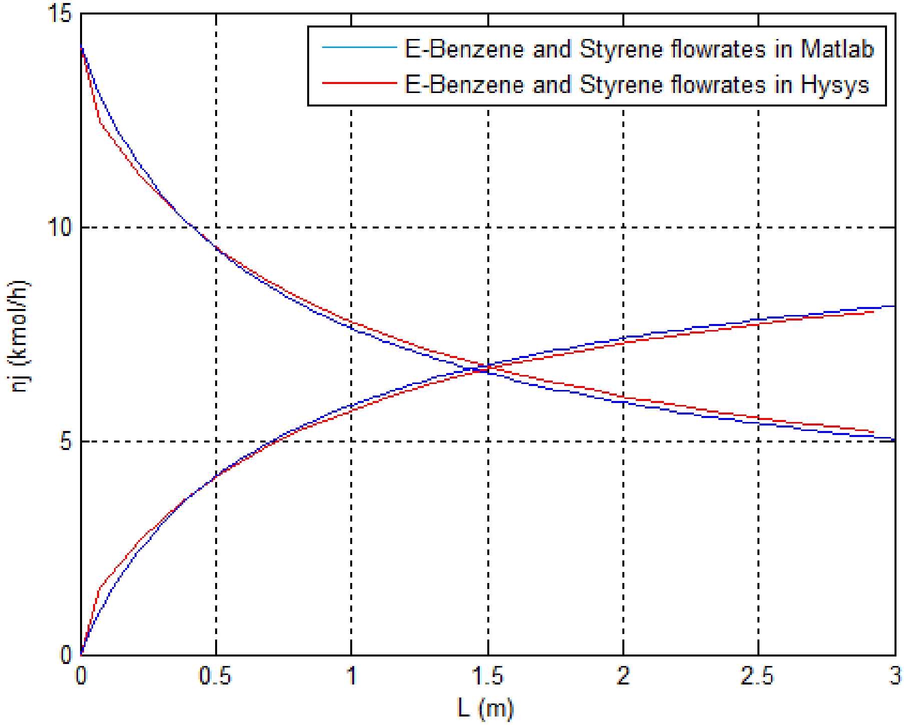
Reactor

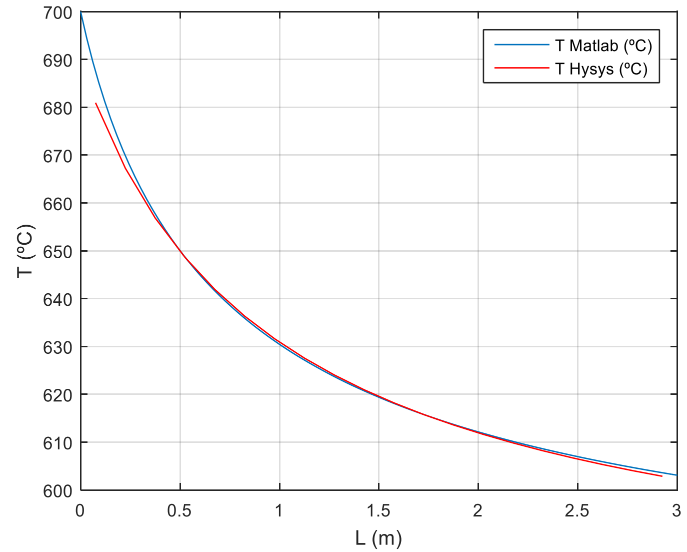
$$\left.\begin{aligned}
&\frac{dn_j}{dL} = Ar_j \\
&\frac{dT}{dL} = \frac{Ua(T_a - T) - A\sum_{i=1}^{R} r_i \Delta H_i}{\sum_{j=1}^{S} n_j C_{pj}} \\
&\frac{dP}{dL} = -\frac{G}{\rho g_c D_p}\left(\frac{1-\varepsilon}{\varepsilon^3}\right)\left[\frac{150(1-\varepsilon)\mu}{D_p} + 1.75G\right]
\end{aligned}\right\}$$

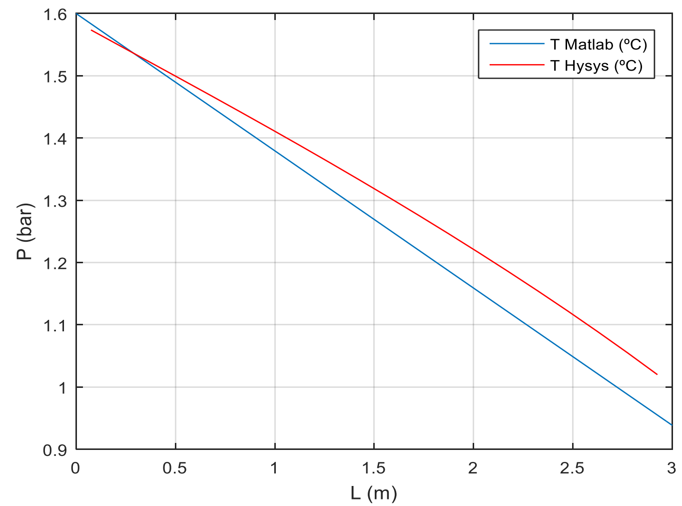
Optimization model reformulation

- EQUIPMENT DESIGN

Reactor





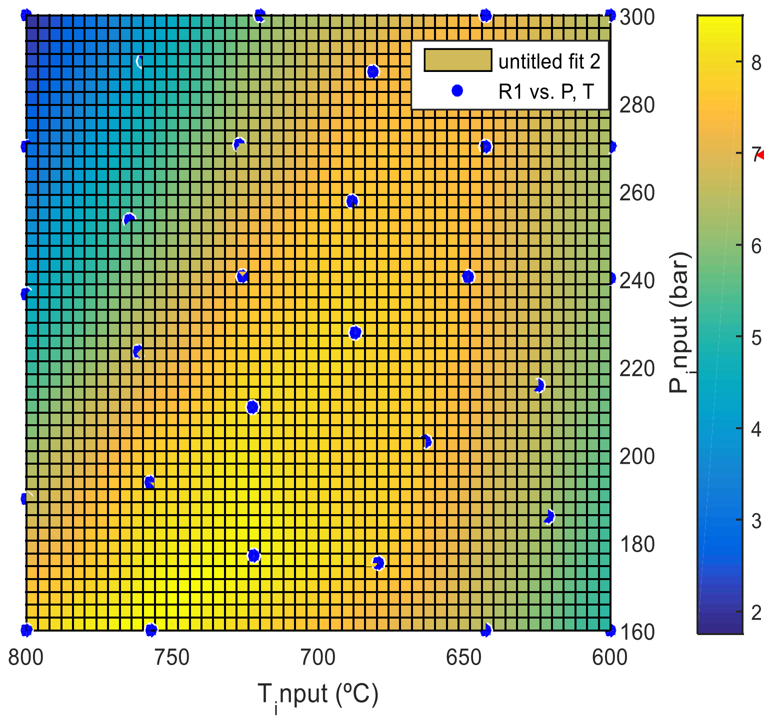


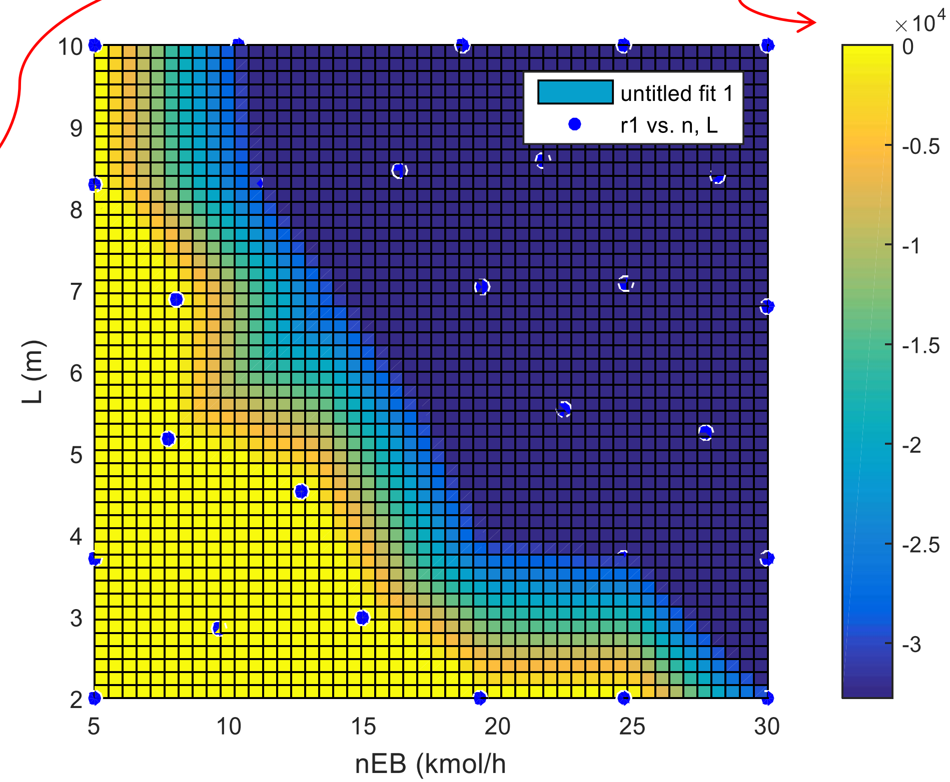
Optimization model reformulation

- EQUIPMENT DESIGN

Reactor $T_{input}, P_{input}, L_{reactor}, nEB_{in}$

Extent of reaction $(R1)(kmol/h)$



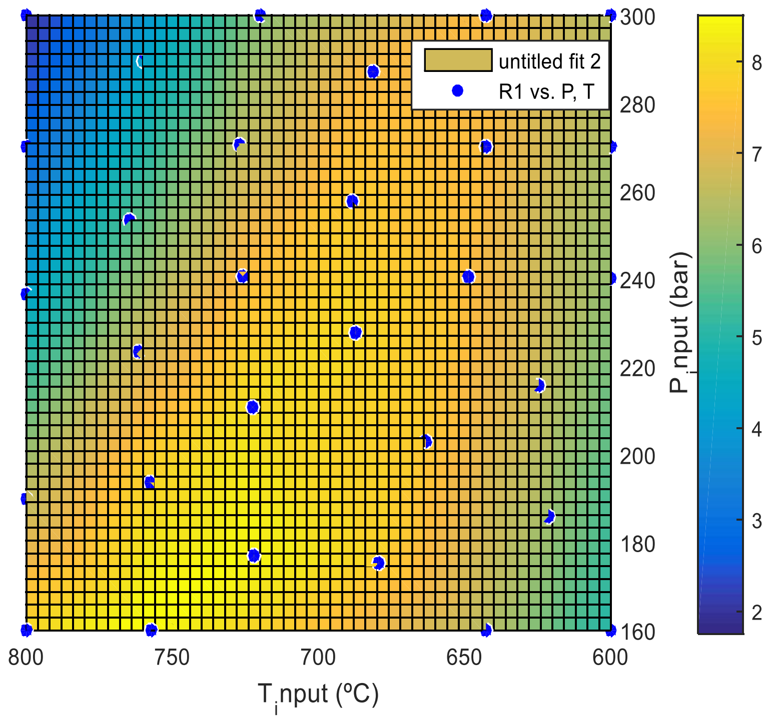


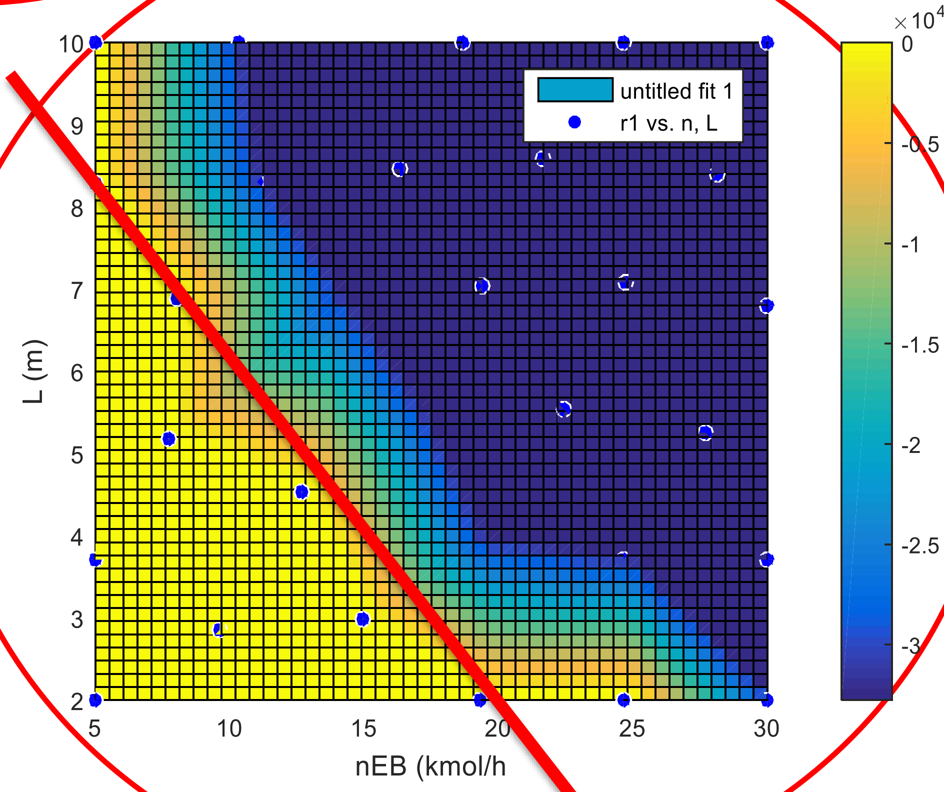
Optimization model reformulation

- EQUIPMENT DESIGN

Independent variables

Reactor $T_{input}, P_{input}, L_{reactor}, nEB_{in}$





$T_{input} = 700°C$

$P_{input} = 1.6$ bar

$$L_{reactor} \leq -0.4 \cdot n_{EB}{}^{feed}_{reactor} + 10$$

Optimization model reformulation

- Equipment design

Cooler

A_{cooler}

$$A_{cooler} = \frac{Q_{cooler}}{U \Delta T_{ml}}$$

Q_{cooler}

$$Q_{cooler} = m_{product} C_p^{product} \left(T_{out}^{reactor} - T_{out}^{cooler} \right)$$

Chen's approximation

ΔT_{ml}

$$\Delta T_{ml} = [0.5 \cdot (\Delta T_1 \cdot \Delta T_2) \cdot (\Delta T_1 + \Delta T_2)]^{1/3}$$

Distillation columns

NP

Molokanov Equation

$$\frac{NP - N_{min}}{NP + 1} = 1 - \exp\left[\frac{1 + 54.4X}{11 + 117.2X} \cdot \frac{X - 1}{X^{0.5}}\right]$$

Kirkbride Equation

NR

$$\frac{NR}{NS} = \left[\frac{z_{HK}}{z_{LK}} \cdot \frac{x_{LK,B}^2}{x_{HK,D}^2} \cdot \frac{B}{D}\right]^{0.206}$$

Fair correlation

D_{column}

$$A_{column} = \frac{M_V}{(\rho_L \cdot \rho_V)^{0.5}} \cdot \frac{1}{0.7} \cdot \frac{1}{C_o} \cdot \frac{A}{A_n} \cdot V_{real}$$

Optimization model reformulation

- Economic evaluation

$$TAC\left(\frac{M\$}{year}\right) = (OPEX + CAPEX \cdot F) \cdot 10^{-6}$$

Optimization model reformulation

- Economic evaluation

Vessel Catalyst cost
Cooler
Tower
Trays
Condenser
Reboiler

$$TAC\left(\frac{M\$}{year}\right) = (\underbrace{OPEX}_{\left(\frac{\$}{year}\right)} + \underbrace{CAPEX}_{(\$)} \cdot F) \cdot 10^{-6}$$

$coolingWaterCost$
$SteamCost$

$$Equipment_{CBM}^{update} = Equipment_{CBM} \cdot UpdateFactor$$

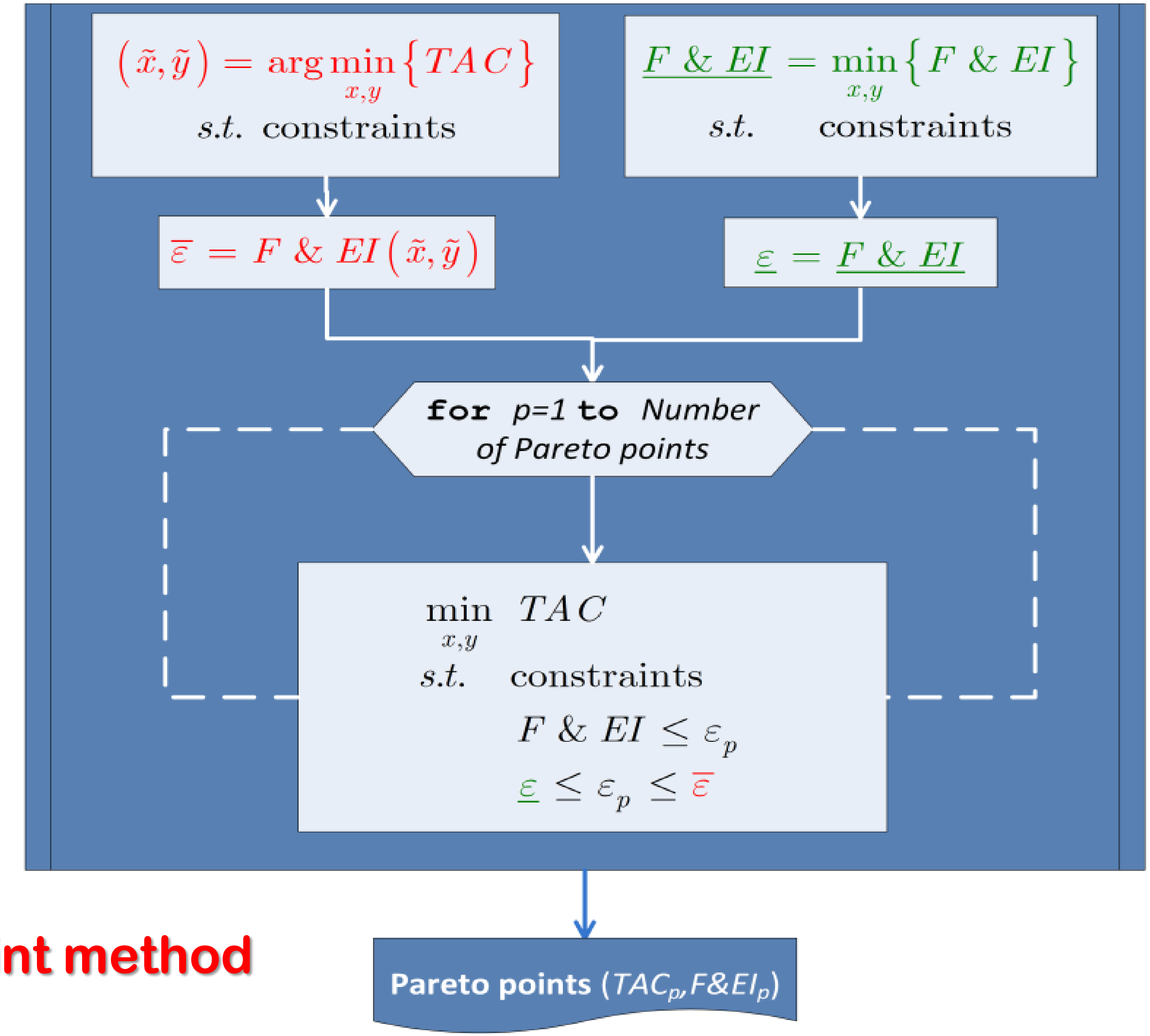
$$Equipment_{CBM} = Equipment_{Cp0} \cdot FBM_{equipment}$$

$$Equipment_{Cp0} = 10^{K_1 + K_2 \cdot \log_{10} X + K_3 [\log_{10} X]^2}$$

$$FBM_{equipment} = B_1 + B_2 \cdot F_M \cdot F_P$$

Richard Turton, R. C. (s.f.). Analysys, Synthesis and Design of Chemical Processes.

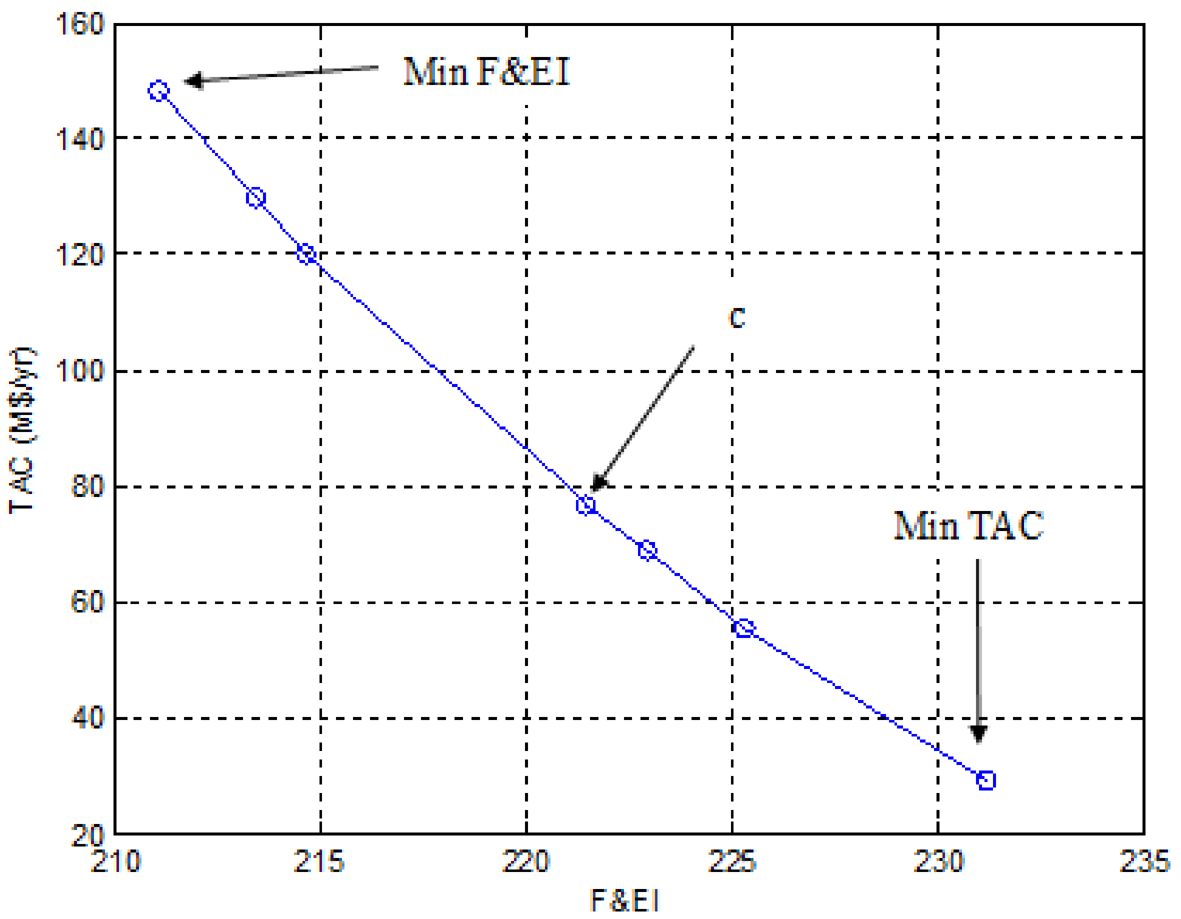
Multi-objective optimization algorithm



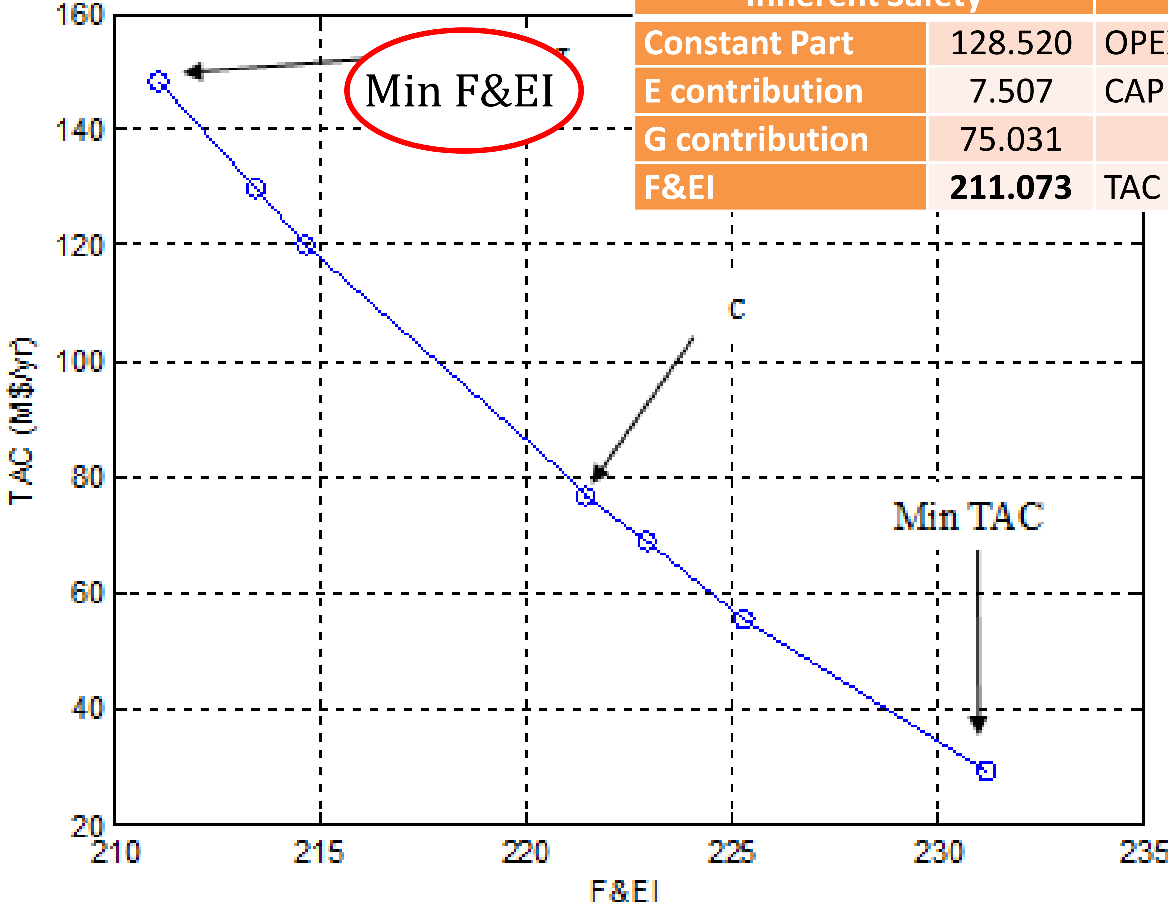
ε-constraint method

Results

Pareto optimal frontier

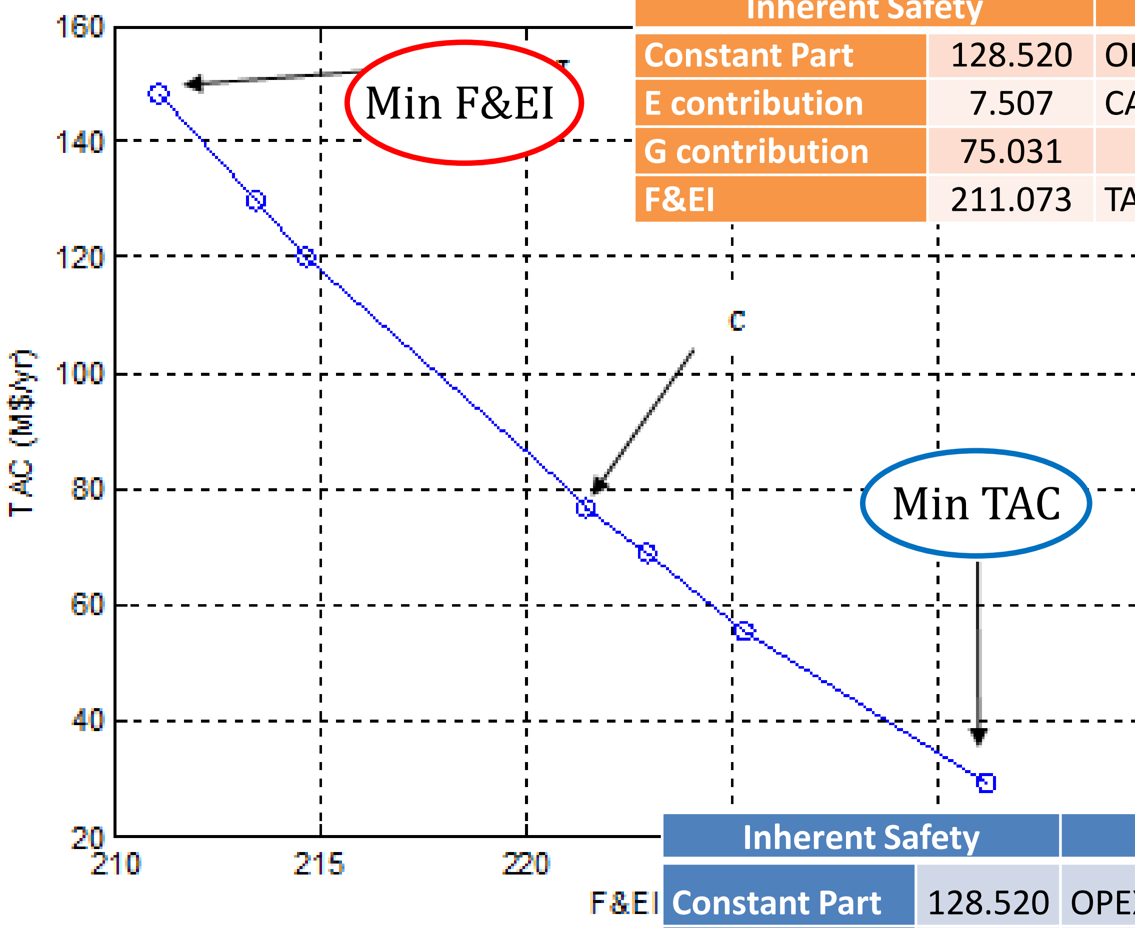


Results



Inherent Safety		Economic	
Constant Part	128.520	OPEX (M$/yr)	146.820
E contribution	7.507	CAPEX (M$/yr)	1.713
G contribution	75.031		-
F&EI	**211.073**	TAC (M$/yr)	**148.530**

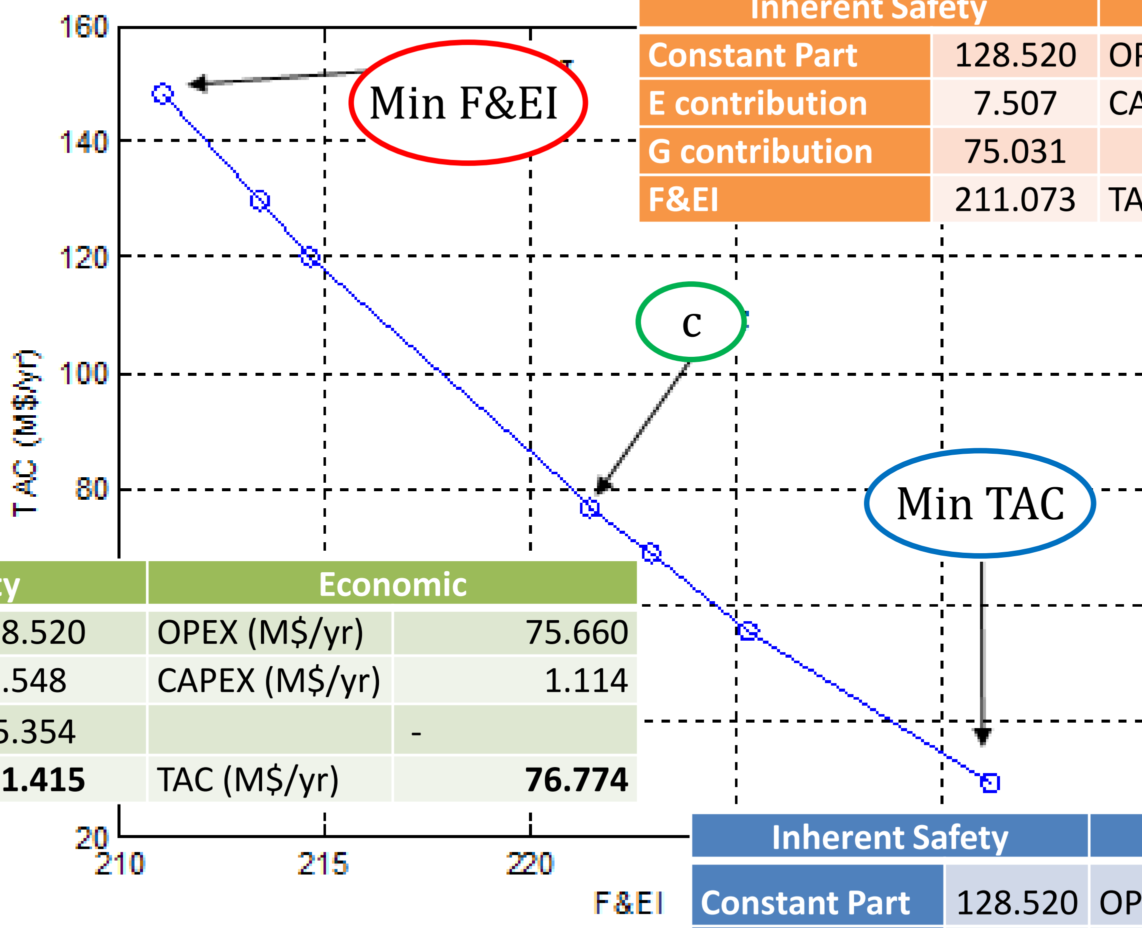
Results



Inherent Safety		Economic	
Constant Part	128.520	OPEX (M$/yr)	146.820
E contribution	7.507	CAPEX (M$/yr)	1.713
G contribution	75.031		-
F&EI	211.073	TAC (M$/yr)	148.530

Inherent Safety		Economic	
Constant Part	128.520	OPEX (M$/yr)	28.113
E contribution	7.507	CAPEX (M$/yr)	0.941
G contribution	95.105		-
F&EI	**231.156**	TAC (M$/yr)	**29.055**

Results



Inherent Safety		Economic	
Constant Part	128.520	OPEX (M$/yr)	146.820
E contribution	7.507	CAPEX (M$/yr)	1.713
G contribution	75.031		-
F&EI	211.073	TAC (M$/yr)	148.530

Inherent Safety		Economic	
Constant Part	128.520	OPEX (M$/yr)	75.660
E contribution	7.548	CAPEX (M$/yr)	1.114
G contribution	85.354		-
F&EI	**221.415**	TAC (M$/yr)	**76.774**

Inherent Safety		Economic	
Constant Part	128.520	OPEX (M$/yr)	28.113
E contribution	7.507	CAPEX (M$/yr)	0.941
G contribution	95.105		-
F&EI	231.156	TAC (M$/yr)	29.055

Results

Increase in the level of hazard

Min F&EI

	Column1	Column 2
$D\ (m)$	1.554	1.417
NP	24	55
L (m)	18.007	38.128
V (m^3)	33.711	60.105

Min TAC

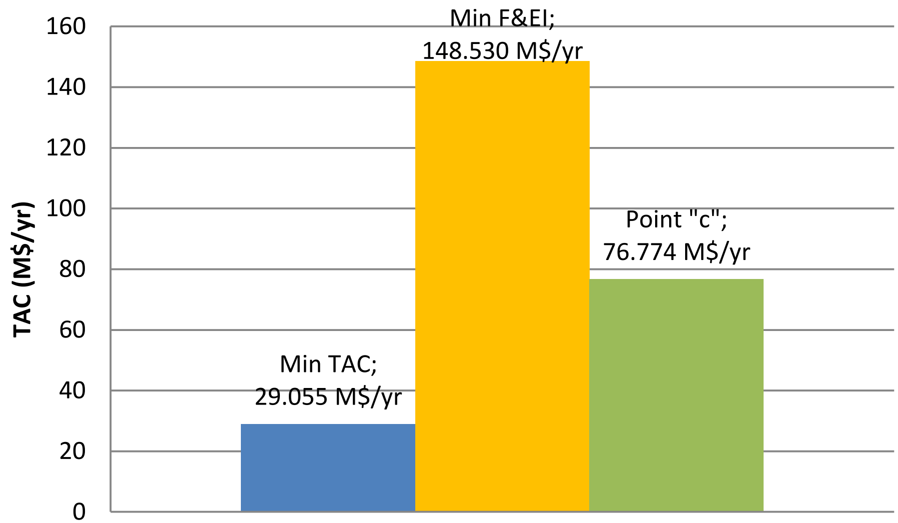
	Column1	Column 2
$D\ (m)$	3.639	3.174
NP	24	55
$L\ (m)$	17.300	36.393
$V\ (m^3)$	179.963	287.873

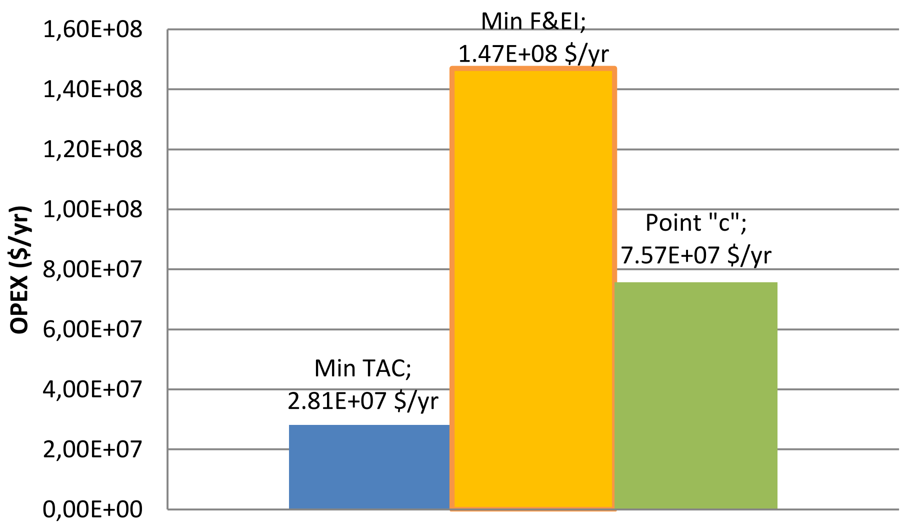
Point "c"

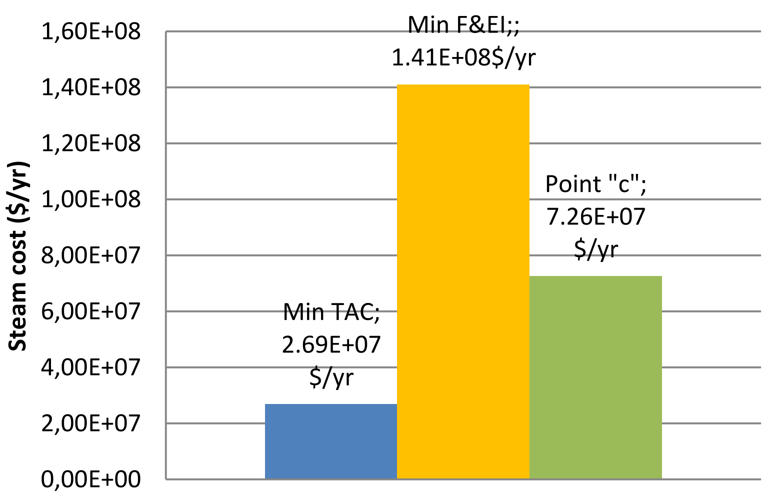
	Column1	Column 2
$D\ (m)$	2.195	1.946
NP	24	55
$L\ (m)$	17.538	36.976
$V\ (m^3)$	66.394	110.03

Results

TAC and OPEX comparison among solutions



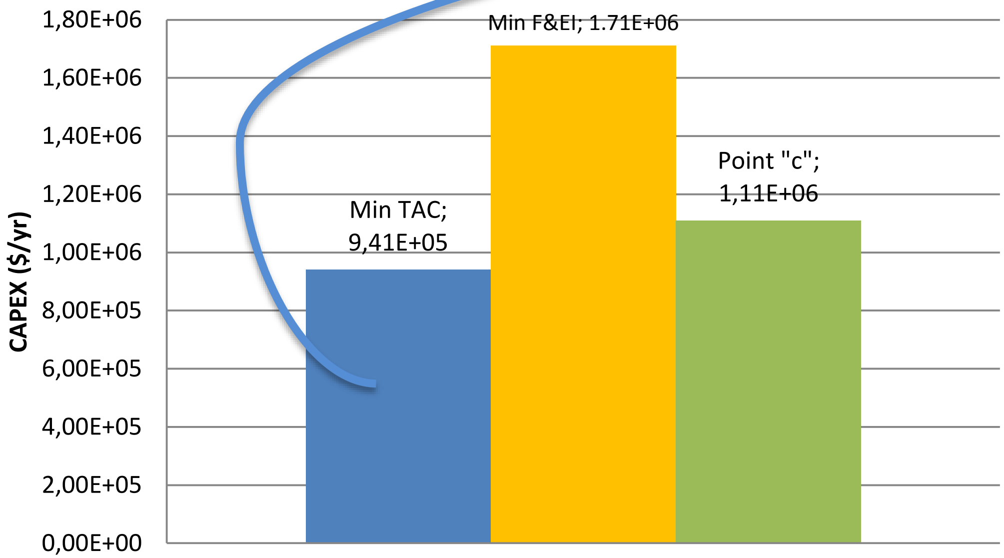


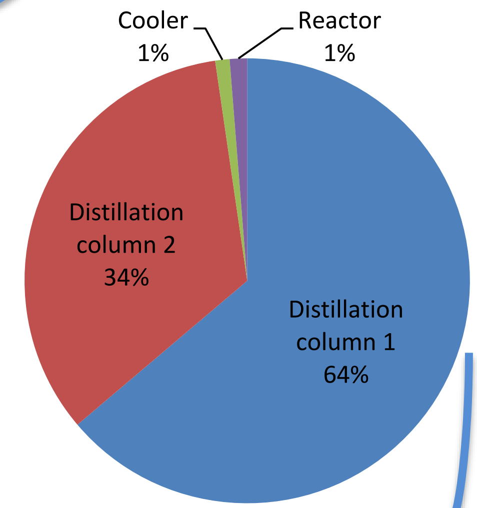


Results

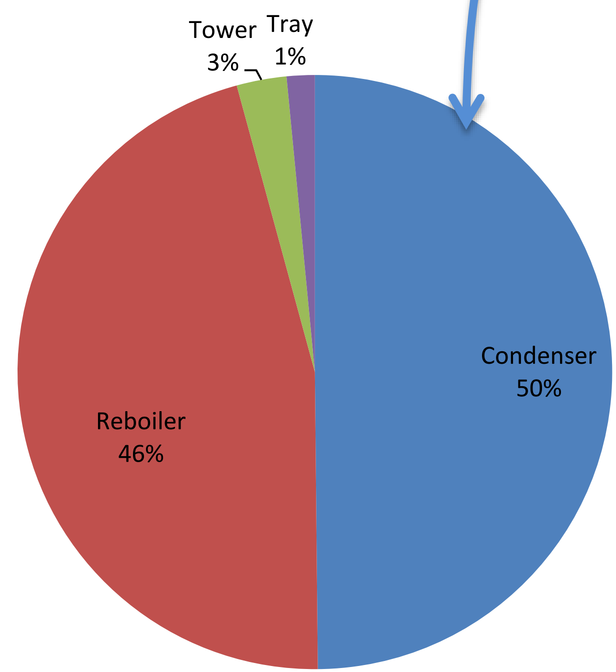
CAPEX

CAPEX distribution at the minimum TAC extreme solution





Distillation column



Conclusions

- Methodology is useful to incorporate and quantify inherent safety into chemical plants design.
- A set of Pareto solutions are presented, there is not a unique optimal solution.
- In the case study, the most economic plant is not the safest inherently design according to F&EI methodology.
- An economic analysis has been carried out for the calculation economic objective.
- The applied optimization approach achieves the best design (equipment parameters and operation conditions) of a styrene production plant That is to say, it is not just a styrene production plant feasible design, hence its importance.