Generation & Evaluation of Sustainable Process (retrofit) Alternatives

CAPEC

Rafiqul Gani

CAPEC, Department of Chemical Engineering
Technical University of Denmark
DK-2800 Lyngby, Denmark
http://www.capec.kt.dtu.dk

Outline

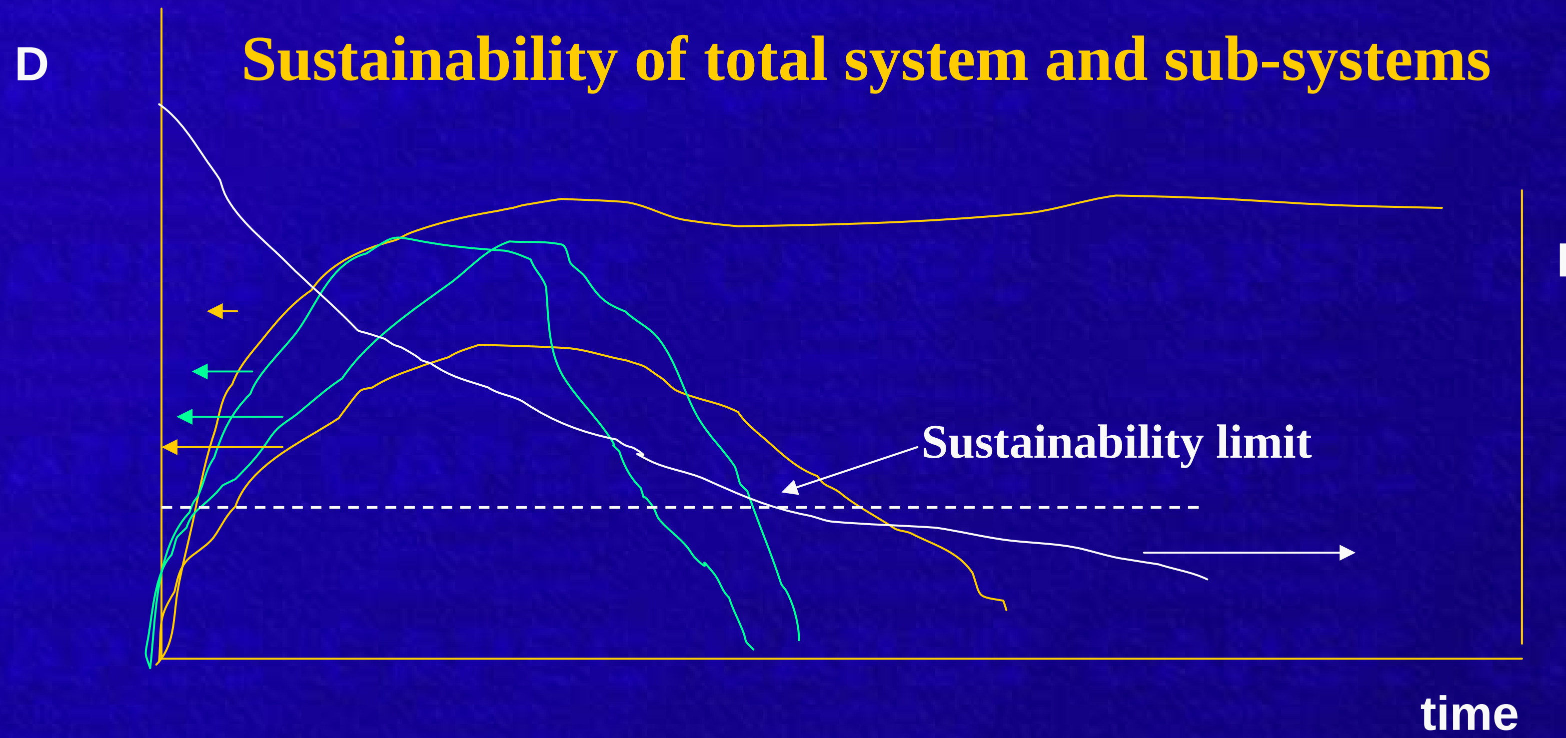
- Introduction – Concepts
- Definition of “indicators”
- Systematic methodology
- Case studies
- Conclusions

Introduction - Concepts

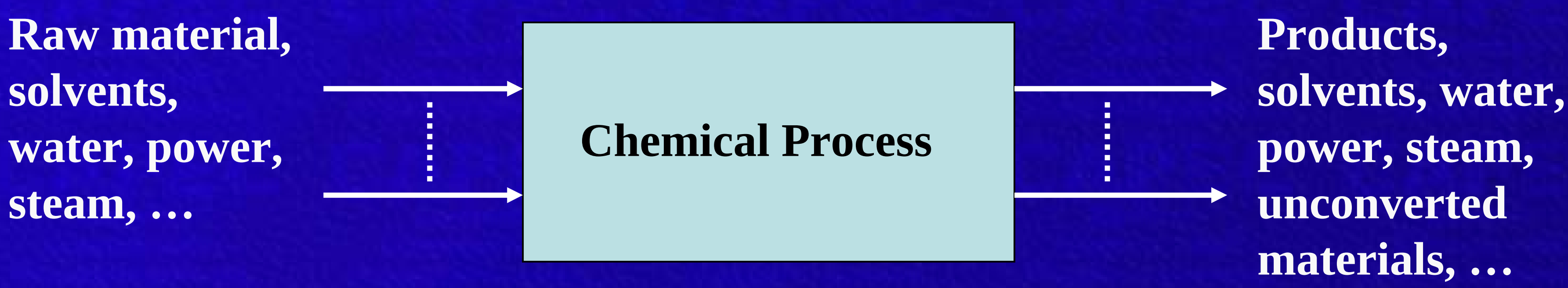
Raw material, solvents, water, power, steam, …

→ **Chemical Process** →

Products, solvents, water, power, steam, unconverted materials, …

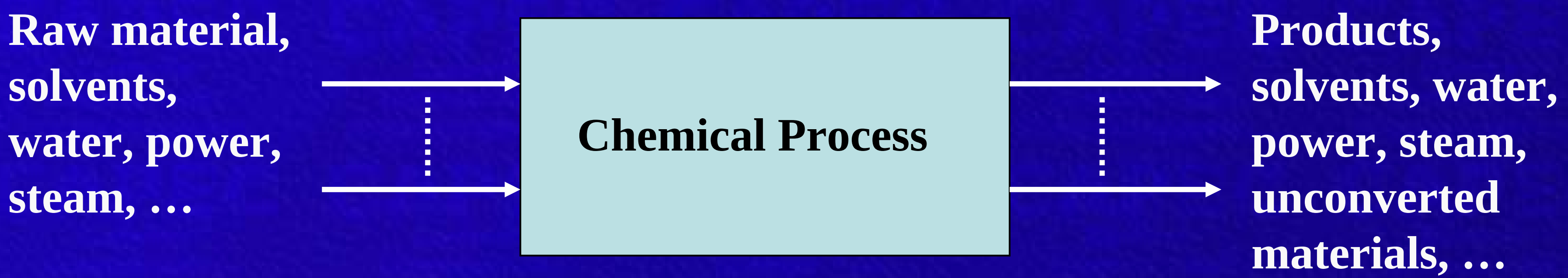


Introduction - I



- **Boundary:** process and its connections
- **Compared to a base-case design, generate alternatives that improve the following**
  - Operability, energy consumption, waste reduction, environmental impact, safety, cost, ….
- **Sustainability metrics** (as defined by IChemE): 49 Environmental (resource usage; emissions, effluents, waste), economic (profit, value, tax; investments), societal (workplace, society)

Introduction - II



- **Improve the following**
  - **Operability, energy consumption, waste reduction, environmental impact, safety, cost, ….**
- **Sustainability metrics (as defined by IChemE)**

Apply a systematic analysis of the mass and energy paths within the process to determine a set of mass and energy indicators that will help to define attainable targets for improvement; generate alternatives that meet these targets through a "reverse" approach

Sustainability Metrics

Sustainability Metrics: Energy

Total Net Primary Energy Usage Rate = Imports – Exports (GJ/y)

Percentage Total Net Primary Sourced from Renewals (%)

Total Net Primary Energy Usage Rate per kg Product (kJ/kg)

Total Net Primary Energy Usage per Unit Value Added (kJ/$)

Sustainability Metrics: Material

Total raw materials used per kg product (kg/kg)

Total raw materials used per unit value added (kg/$)

Fraction of raw materials recycled within company (kg/kg)

Fraction of raw materials recycled from consumers (kg/kg)

Hazardous raw material per kg product (kg/kg)

Sustainability Metrics: Water

Net water consumed per unit mass of product (kg/kg)

Net water consumed per unit value added (kg/$)

Environmental Impact

Physical potential impacts (acidification, greenhouse enhancement, ozone depletion and photochemical oxidant depletion)

Human toxicity effects (air, water and soil) and eco-toxicity effects (aquatic and terrestrial)

The important parameters are:

HTPI (Human Toxicity Potential by Ingestion)

HTPE (Human Toxicity Potential by Exposure both Dermal and Inhalation)

TTP (Terrestrial Toxicity Potential)

ATP (Aquatic Toxicity Potential)

GWP (Global Warming Potential)

ODP (Ozone Depletion Potential)

PCOP (Photochemical Oxidation Potential)

AP (Acidification Potential)

Total **PEI** (Total Potential Environmental Impact), which indicates the unrealised effect or impact that the emission of mass and energy would have on the environment on average

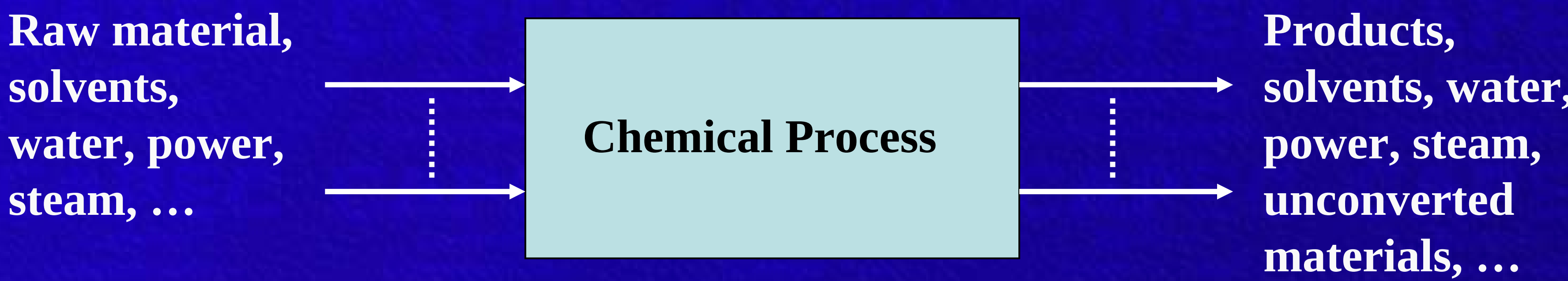
US-EPA War Algorithm (Young et al. 2000)

Safety Factors

Total Inherent Safety Index (ISI)			
Chemical Inherent Safety Index, I_{ci}	**Score**	**Process Inherent Safety Index, I_{pi}**	**Score**
Sub-indices for reactions Hazards		*Sub-indices for process conditions*	
Heat of the main reaction, I_{rm}	0-4	Inventory, I_i	0-5
Heat of the side reactions, Irs	0-4	Temperature, I_t	0-4
Chemical interactions, I_{int}	0-4	Pressure, I_p	0-4
Sub-indices for hazardous substances		*Sub-indices for process conditions*	
Flammability, I_{fl}	0-4	Equipment, I_{eq}	
Explosiveness, I_{ex}	0-4	I_{ISBL}	0-4
Toxicity, I_{tox}	0-6	I_{OSBL}	0-3
Corrosivity, I_{cor}	0-2	Process structure, I_{st}	0-5
Maximum I_{ci} score	*28*	*Maximum I_{pi} score*	*25*
Maximum I_{si} score 53			

Heikkilä, 1999; Dow Index

Systematic Methodology for Design & Analysis



Start with a reference design

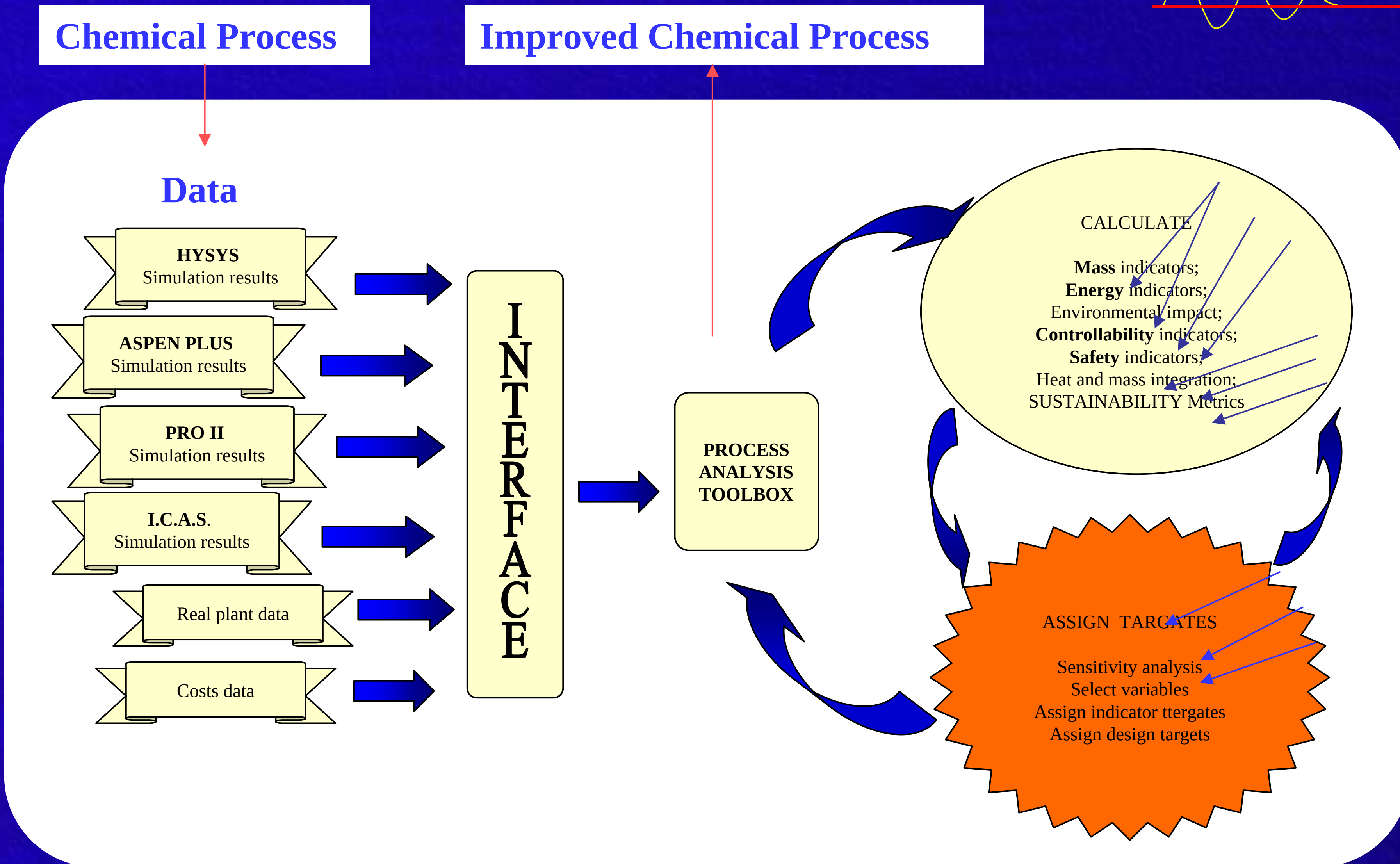
Calculate sustainability metrics, safety factors plus mass & energy indicators

Identify attainable design targets

- **Indicator targets (for process improvements)**
- **Driving forces targets (for generation of alternatives)**

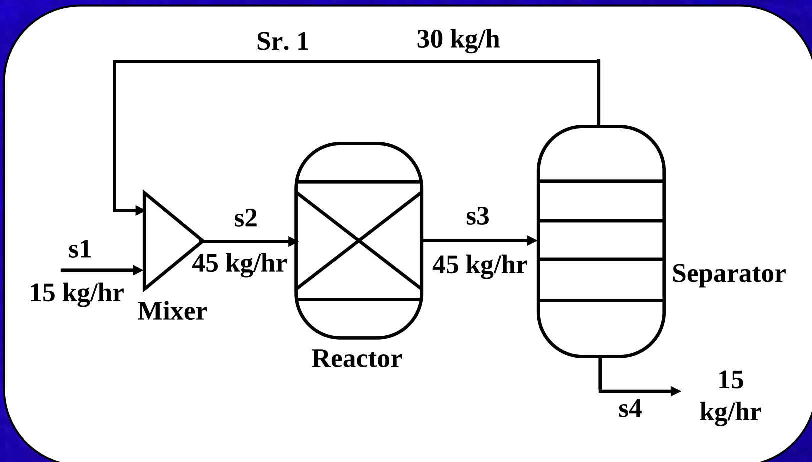
Apply reverse approach to match design targets

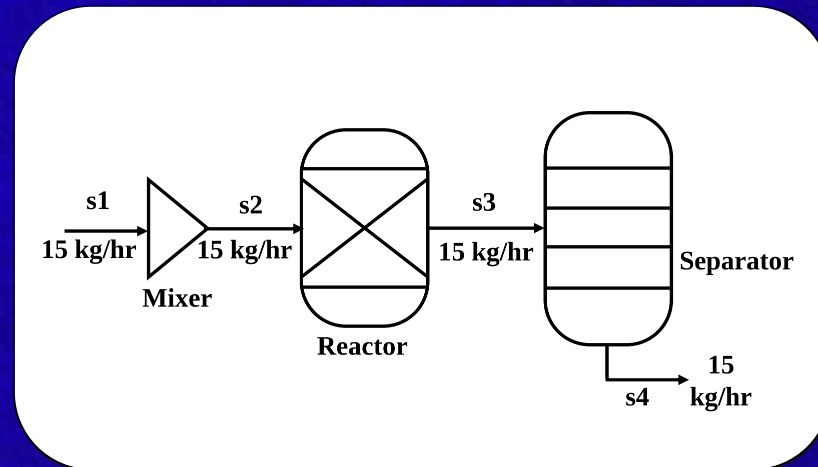
Order all feasible solutions to find optimal (conflict resolution)

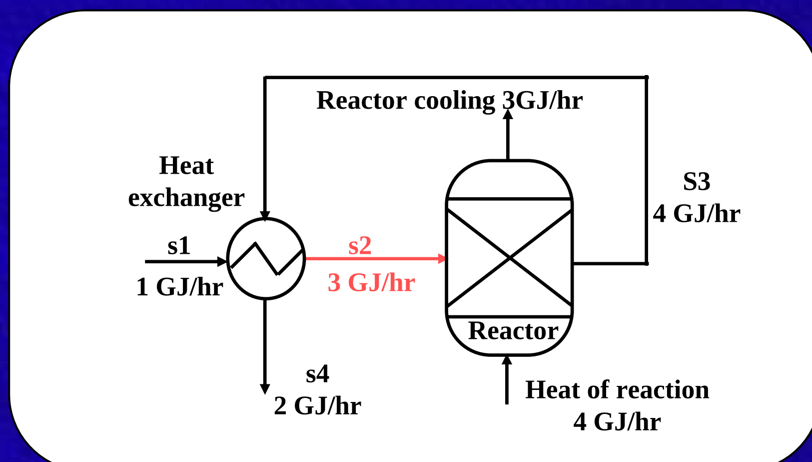


Flow diagram of indicator-based methodology

Mass & Energy Open- & Closed-paths







Mass & Energy Indicators - I

Indicator	Description	Definition
MVA	Material Value Added Mass; Open-path	MVA = $M_T * (P_{sale} - P_{cost})$
EWC	Energy and Waste Cost Mass; open- & cyclic-path	EWC = $E P_E M_i \theta_i / (\Sigma_i M_i \theta_i)$
TVA	Total Value Added cost	TVA = MVA - EWC
RQ	Reaction Quality Mass; open- & cyclic-path	RQ = $R_x \theta_R / (\Sigma_p M_p)$
AF	Accumulation Factor Mass; cyclic-path	AF = $M_{i\text{-cycle}} / (\Sigma_{k\text{-cycle}} M_{k\text{-cycle}})$
REF	Reusable Energy Factor Energy; cyclic-path	REF = $E_{used\text{-cycle}} / E_{exit\text{-cycle}}$
DC	Demand Cost Energy; open-path	DC = $P_{utility} E_{open\text{-path}}$
TDC	Total Demand Cost Energy; open-path	TDC = ΣDC_k

Mj = Mass flow; Pj = Price; E = Energy flow; θ = Property or Parameter
Subscripts: T=total; E=energy; i=component ID; x=reaction extent ; k=cycle-path

Mass & Energy Indicators - II

Indicator	**Negative value**	**Positive value**
MVA	Value lost in path	Value gained in path
RQ	Negative impact on plant productivity	Positive impact on plant productivity
TVA	High potential for improvement	Low potential for improvement
	Low value	**High value**
EWC	Low energy & waste reduction potential	High energy & waste reduction potential
AF	Low accumulation of component	High accumulation of component
EAF	Low energy utilization	High energy utilization
TDC	Low energy loss	High energy loss

REF	Represents the amount of reusable energy with respect to the total recycled energy	Increase
DC	Represents the associated cost for an energy open path	Decrease
TDC	Represents the total cost associated with an output from a process	Decrease

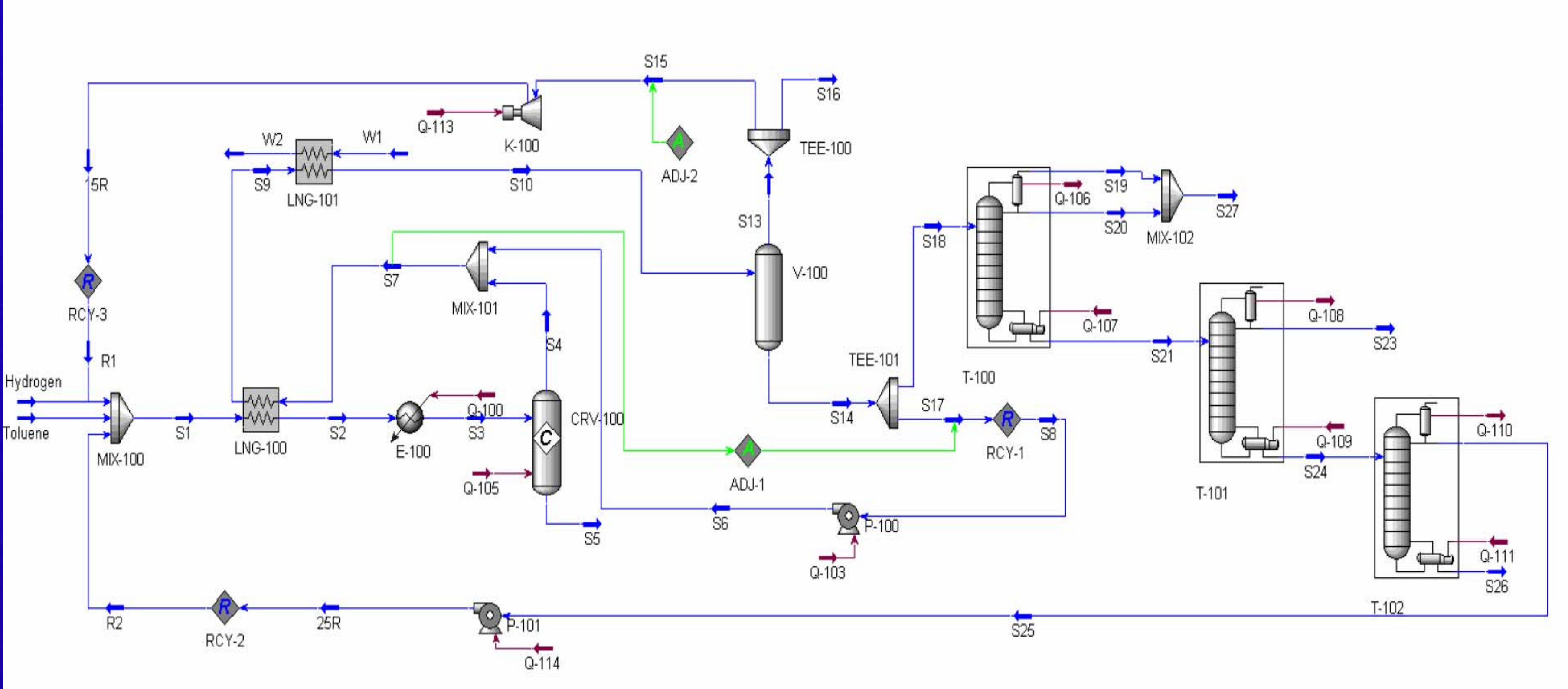
Mass & Energy Indicators - III

Component path flows	**Design (retrofit) action**	**Indicators that me be affected**
All categories	Reduce duty by changing temperatures, by reducing flows or through heat integration	*EWC, MVA*
Category 1: Open path flows, $RQ \leq 0$	Reduce/remove flows	*EWC, MVA*
	Improve separation	*EWC, MVA*
	Increase value of the open path	*MVA*
	Introduce a separation method	*EWC, MVA*
	Change conversion	*EWC, MVA, RQ*
Category 2: Open path flows, $RQ > 0$	Reduce flow if no consumed in reactor	*EWC, MVA*
	Recycle the open path	*EWC, MVA*
	Improve separation	*EWC, MVA*
	Increase value of the open path	*MVA*
Category 3: Cycle path flows, $RQ \leq 0$		
b) $AF > 1$	Reduce flow	*EWC, AF*
	Change catalyst	*EWC, RQ, AF*
	Reduce AF by increased purge	*EWC, AF*
	Remove path at source	*EWC, AF*
	Reroute path (change to open path)	*EWC, AF*
b) $AF \leq 1$	Remove path at source	*EWC, AF*
	Reduce flow	*EWC, AF*
	Reroute path (change to open path)	*EWC, AF*
Category 4: Cycle paths, $RQ > 0$	Optimise the flow rate	*EWC, AF*
	Increase conversion	*EWC, AF, RQ*

Model structural analysis

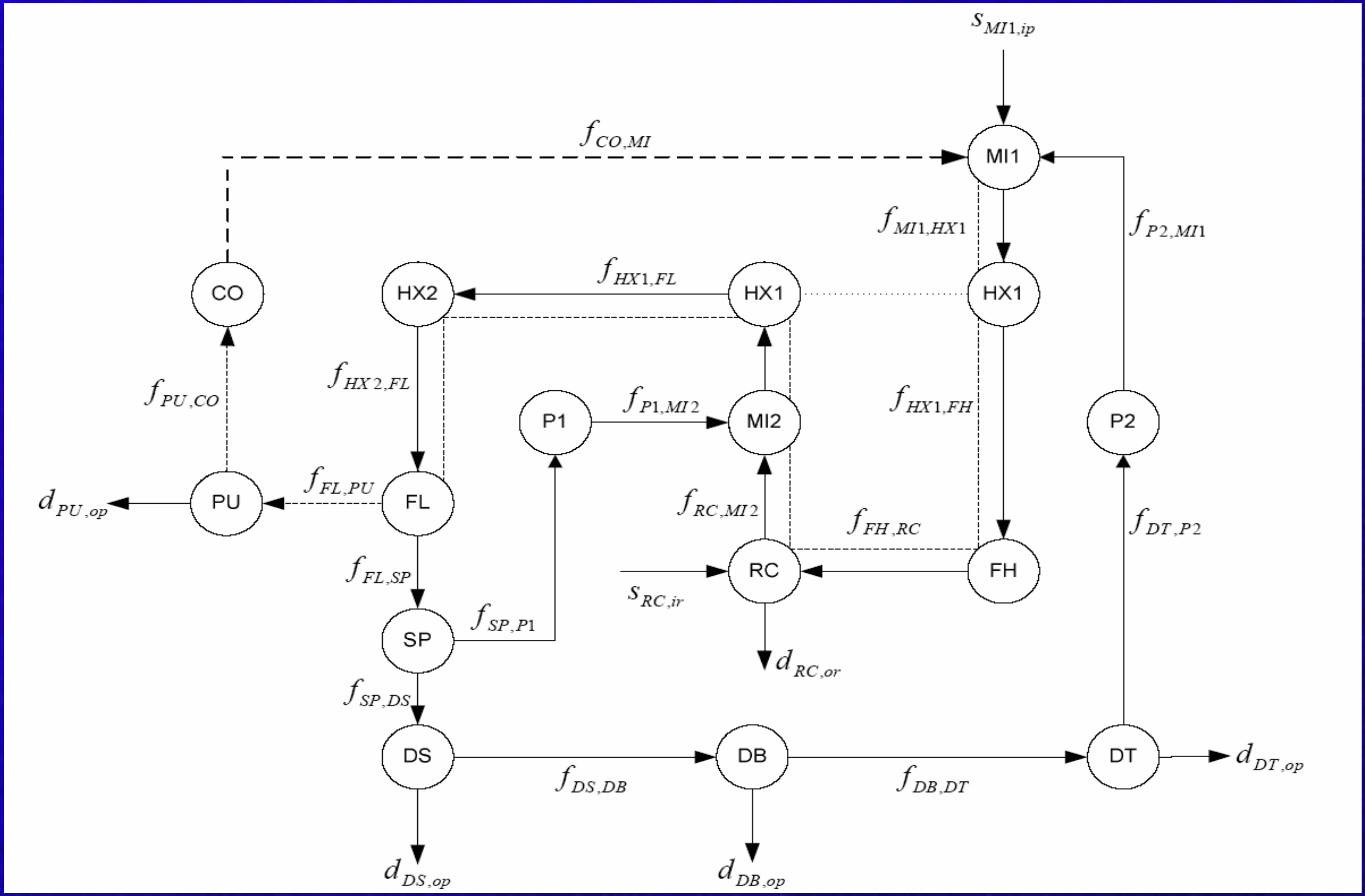
Known variables																										
variables			Prices & Other										Process unrelated variables													
	$\xi_{r,rk,k}$ reaction/s extend (1)	$E_{r,rk,k}$ reaction parameter (1)	PP, comp sales price (1)	PR, comp. purchase price (1)	PR^{rm}, raw materials purchase price (1)	PS, steam price (generated) (1)	PE_u, utily prices (1)	WAV_{cj}, volume specificallocation cost (1)	WAM_{cj}, mass specificallocation cost (1)	WAC_{cj}, concentration specific allocation cost (1)	η_e, energy conversions efficiency (1)	η^c, combustion efficiency (1)	ΔH_{comb}, combustion heat	M^c, molecular weight	ΔH_{vap}^{H2O}, vaporization heat	ΔH_r, heat of main reaction/s	ΔH_r, heat of side reaction/s	H_f, heat of formation	PEI_i, unit potential environment impact	f^p, flash point	UEL, upper explosion limit	LEL, lower explosion limit	TLV, threshold, limit value	SBL, steel's breakage limit	equipment type	experienced-based data
Safety Indicators																										
$I_m = f(\Delta H_r^m)$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	X	0	0	0	0	0	0	0	0	0	0
$I_{rs} = f(\Delta H_r^s)$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	X	0	0	0	0	0	0	0	0	0
$I_{int} = f(H^f)$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	X	0	0	0	0	0	0	0	0
$I_{fl} = f(f^p)$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	X	0	0	0	0	0	0
$I_{ex} = f(UEL, LEL)$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	X	X	0	0	0	0
$I_{tox} = f(TLV)$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	X	0	0	0
$I_{cor} = f(SBL)$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	X	0	0
$I_I = f(m^{rm}, m^p)$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$I_p = f(p^{max})$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
$I_t = f(t^{max})$	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
I_{sbl}=f(equipment type)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	X	0
O_{sbl}=f(equipment type)	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	X	0

HDA Case Study



Hydrogen reacts with Toluene to produce Benzene. Methane is present as impurity and Biphenyl is produced as a by-product

HDA case study: Open- & Closed Paths



HDA case study: Mass Indicators

Indicators for open paths

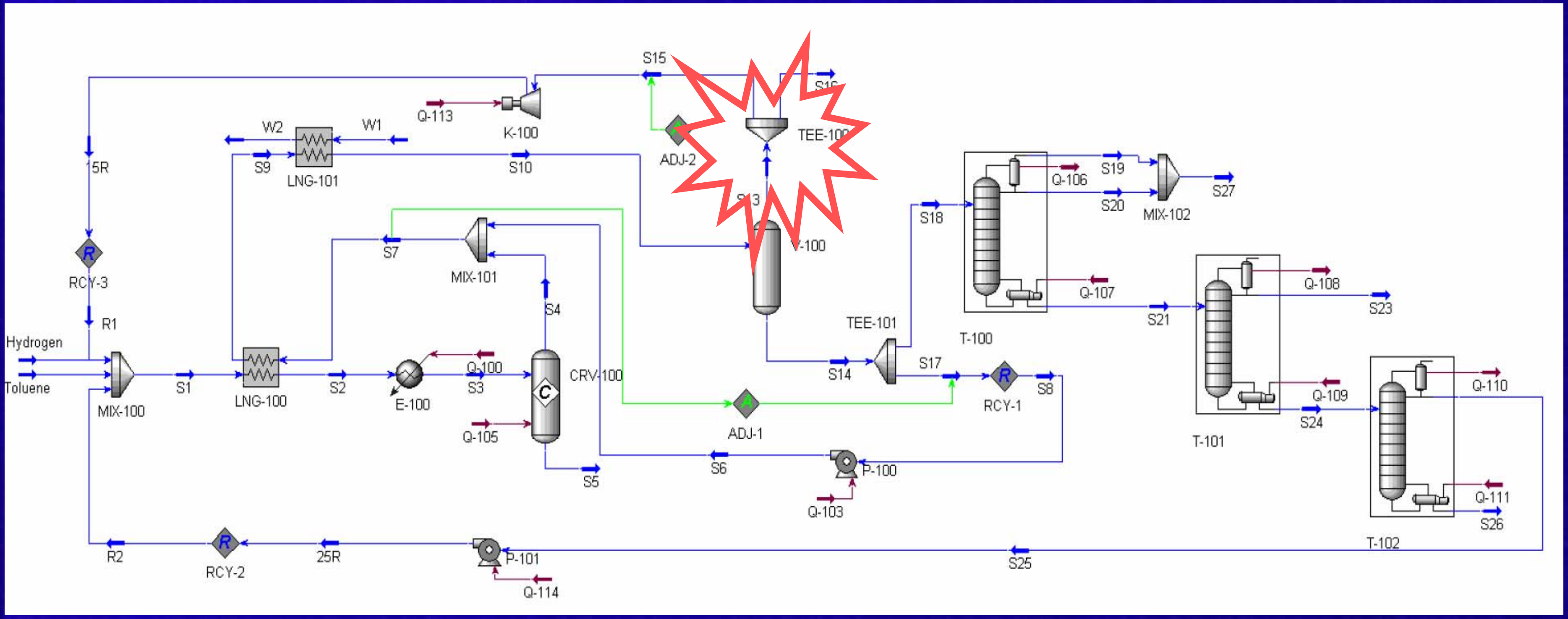
Open path #	Component	Path	Flowrate (kg	RQ	MVA (10^3 $	EWC (10^3 $	TVA (10^3 $/yr)
O1	Methane	sMI1,ip-dPU,op	195.72	0.000	321.30	7.19	314.10
O2	Hydrogen	sMI1,ip-dPU,op	244.30	1.037	-2947.75	33.99	-2981.74
O3	Benzene	sRC,ir-dPU,op	134.57	0.000	-78.43	0.30	-78.72
O4	Biphenyl	sRC,ir-dPU,op	0.00	0.000	0.00	0.00	0.00
O5	Toluene	sMI1,ip-dPU,op	18.33	1.037	-18.50	0.43	-18.93
O6	Methane	sRC,ir-dPU,op	1887.71	0.000	-8747.91	7.78	-8755.70
O7	Methane	sMI1,ip-dDS,op	10.78	0.000	17.70	0.40	17.30
O8	Hydrogen	sMI1,ip-dDS,op	1.35	1.060	-16.31	0.19	-16.49
O9	Benzene	sRC,ir-dDS,op	3.80	0.000	-2.22	0.44	-2.66
O10	Biphenyl	sRC,ir-dDS,op	0.00	0.000	0.00	0.00	0.00
O11	Toluene	sMI1,ip-dDS,op	0.00	1.011	0.00	0.00	0.00
O12	Methane	sRC,ir-dDS,op	103.99	0.000	-481.88	0.43	-482.31
O13	Benzene	sRC,ir-dDB,op	9348.60	0.000	14629.37	626.29	14003.08
O14	Biphenyl	sRC,ir-dDB,op	0.00	0.000	0.00	0.00	0.00
O15	Toluene	sMI1,ip-dDB,op	2.68	1.037	-6.42	0.20	-6.62
O16	Benzene	sRC,ir-dDT,op	0.00	0.000	0.00	0.00	0.00
O17	Biphenyl	sRC,ir-dDT,op	207.23	0.000	-13.41	266.80	-280.21
O18	Toluene	sRC,ir-dDT,op	0.38	1.037	-0.38	0.58	-0.96
O19	Hydrogen	sMI1,ip-dRC,or	247.66	1.037	not defined	28.83	-28.83
O20	Toluene	sMI1,ip-dRC,or	11442.91	1.037	not defined	243.07	-243.07

HDA case study: Mass Indicators

Indicators for mass cycle paths

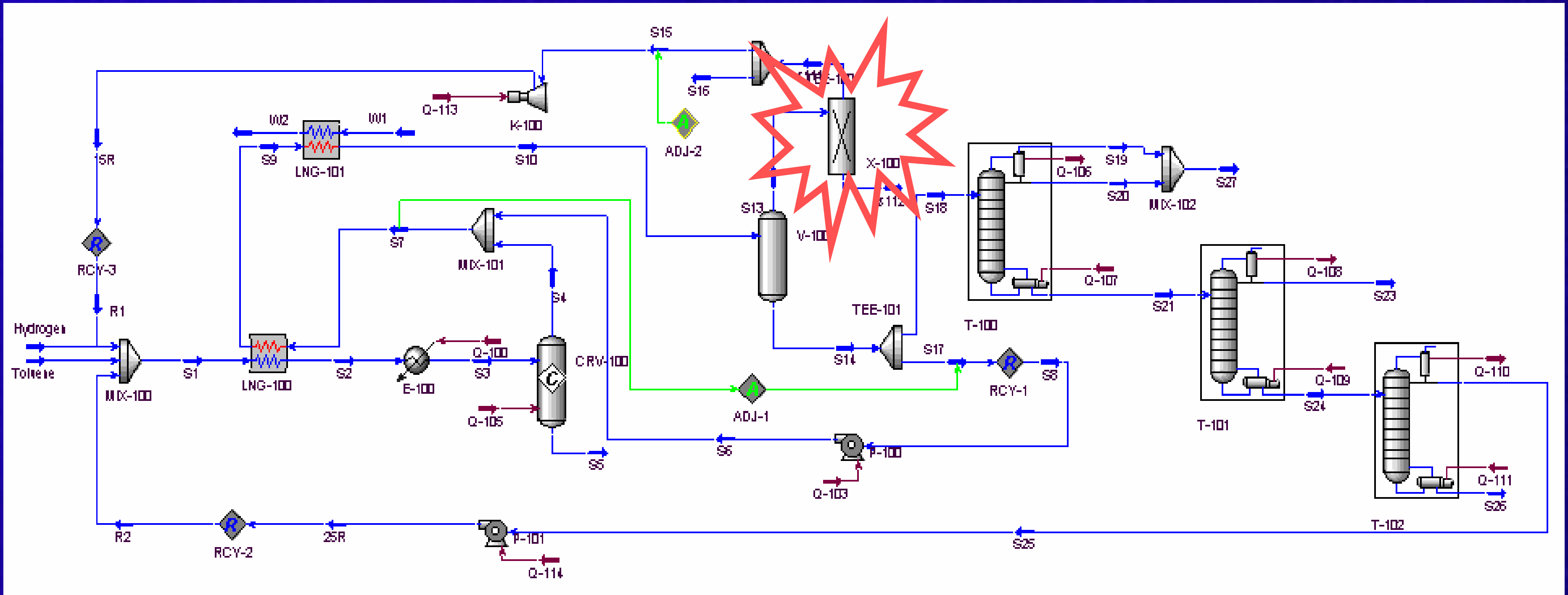
Cycle path	Component	Path	Flowrate (kg	AF	RQ	EWC (10^3 $	TVA (10^3 $/
C1	Methane	Gas cycle	10926.69	4.878	0.00	484.53	-484.53
C2	Hydrogen	Gas cycle	1281.22	5.205	1.06	179.40	-179.40
C3	Benzene	Gas cycle	705.75	0.054	-0.03	16.00	-16.00
C4	Biphenyl	Gas cycle	0.01	0.000	0.03	0.00	0.00
C5	Toluene	Gas cycle	96.16	0.019	1.04	2.28	-2.28
C6	Methane	Liquid cycle	0.00	0.000	0.00	0.00	0.00
C7	Hydrogen	Liquid cycle	0.00	0.000	1.04	0.00	0.00
C8	Benzene	Liquid cycle	94.41	0.007	-0.03	51.81	-51.81
C9	Biphenyl	Liquid cycle	0.00	0.000	0.03	0.00	0.00
C10	Toluene	Liquid cycle	3695.37	2.515	1.04	1828.87	-1828.87
C11	Methane	Quench cycle	41.94	0.003	0.00	0.17	-0.17
C12	Hydrogen	Quench cycle	0.49	0.000	0.00	0.01	-0.01
C13	Benzene	Quench cycle	3452.12	0.336	0.00	7.67	-7.67
C14	Biphenyl	Quench cycle	75.73	0.365	0.00	0.29	-0.29
C15	Toluene	Quench cycle	1351.51	0.354	0.00	3.14	-3.14

HDA case study



The "base case" for the HDA process flow sheet[2]

HDA case study



The retrofit alternative design for the HDA process flow sheet[2]

HDA case study: Alternative design (open path)

Indicators for open paths							
Open path #	Component	Path	Flowrate (kg	RQ	MVA (10^3 $	EWC (10^3 $	TVA (10^3 $/yr)
O1	Methane	sMI1,ip-dPU,op	103.3000	0.0000	169.5000	2.9470	166.5000
O2	Hydrogen	sMI1,ip-dPU,op	0.6210	1.0430	-7.4880	0.0670	-7.5500
O3	Benzene	sRC,ir-dPU,op	134.5682	0.0000	0.0000	0.0000	0.0000
O4	Biphenyl	sRC,ir-dPU,op	0.0028	0.0000	-0.0002	0.0000	-0.0002
O5	Toluene	sMI1,ip-dPU,op	0.0220	1.0220	-0.0022	0.0004	-0.0020
O6	Methane	sRC,ir-dPU,op	1960.0000	0.0000	-9085.0000	6.4490	-9092.0000
O7	Methane	sMI1,ip-dDS,op	1.8070	0.0000	2.9600	0.0052	2.9140
O8	Hydrogen	sMI1,ip-dDS,op	2.2200	1.0430	-26.8000	0.2400	-27.0400
O9	Benzene	sRC,ir-dDS,op	3.8600	0.0000	-2.2500	0.1660	-2.4200
O10	Biphenyl	sRC,ir-dDS,op	0.0000	0.0000	0.0000	0.0000	0.0000
O11	Toluene	sMI1,ip-dDS,op	0.0028	1.0430	-0.0029	0.0004	-0.0032
O12	Methane	sRC,ir-dDS,op	34.3100	0.0000	-159.0000	0.1130	-159.1000
O13	Benzene	sRC,ir-dDB,op	9505.0000	0.0000	14870.0000	629.3000	14240.0000
O14	Biphenyl	sRC,ir-dDB,op	0.0000	0.0000	0.0000	0.0000	0.0000
O15	Toluene	sMI1,ip-dDB,op	2.7200	1.0220	-6.5380	0.1900	-6.7270
O16	Benzene	sRC,ir-dDT,op	0.0000	0.0000	0.0000	0.0000	0.0000
O17	Biphenyl	sRC,ir-dDT,op	200.7000	0.0000	-12.9900	267.2000	-280.2088
O18	Toluene	sRC,ir-dDT,op	0.3880	1.0220	-0.3920	0.6070	-0.9980
O19	Hydrogen	sMI1,ip-dRC,or	248.0000	1.0430	not defined	22.1900	-22.1900
O20	Toluene	sMI1,ip-dRC,or	11460.0000	1.0220	not defined	187.9000	-187.9000

HDA case study

Indicators for mass cycle paths							
Cycle path	Component	Path	Flowrate (k	AF	RQ	EWC (10^3 $	TVA (10^3 $/
C1	Methane	Gas cycle	0.0000	0.0000	0.0000	0.0000	0.0000
C2	Hydrogen	Gas cycle	1338.0000	154.7000	1.0430	183.5000	-183.5000
C3	Benzene	Gas cycle	358.9000	0.0149	-0.0214	11.0300	-11.0300
C4	Biphenyl	Gas cycle	0.0000	0.0000	0.0000	0.0000	0.0000
C5	Toluene	Gas cycle	47.6200	0.0048	1.0220	1.1290	-1.1290
C6	Methane	Liquid cycle	0.0000	0.0000	0.0000	0.0000	0.0000
C7	Hydrogen	Liquid cycle	0.0000	0.0000	0.0000	0.0000	0.0000
C8	Benzene	Liquid cycle	95.9900	0.0097	-0.0214	52.1900	-52.1900
C9	Biphenyl	Liquid cycle	0.0000	0.0000	0.0000	0.0000	0.0000
C10	Toluene	Liquid cycle	3768.0000	74.2400	1.0220	1845.0000	-1845.0000
C11	Methane	Quench cycle	7.3390	0.0035	0.0000	0.0241	-0.0241
C12	Hydrogen	Quench cycle	0.4510	0.0003	0.0000	0.0083	-0.0083
C13	Benzene	Quench cycle	1950.0000	0.1960	0.0000	3.3100	-3.3100
C14	Biphenyl	Quench cycle	40.7400	0.2030	0.0000	0.1200	-0.1200
C15	Toluene	Quench cycle	765.6000	0.2010	0.0000	1.3690	-1.3690

Mass indicators value for cycle paths in the alternative design

HDA case study

- A simple economical study including all the associate cost with the HDA process was performed also:
- The values shows the improvement obtained by mass indicators analysis

The base design:

•Benefit = -1579 (k$/year)

The alternative design:

•Benefit = 2309 (k$/year)

Sustainability Metrics

Base Case

Total Net Primary Energy Usage Rate = Imports – Exports -75.09e^{+4} GJ/y

Total Net Primary Energy Usage Rate per kg Product -78.58e^{+6} kJ/kg

Total raw materials used per kg product 1.27 kg/kg

Hazardous raw material per kg product 1.22 kg/kg

Net water consumed per unit mass of product 184.62 kg/kg

Generated Alternative

Total Net Primary Energy Usage Rate = Imports – Exports -53.61e^{+4} GJ/y

Total Net Primary Energy Usage Rate per kg Product -55.24e^{+6} kJ/kg

Total raw materials used per kg product 1.22 kg/kg

Hazardous raw material per kg product 1.19 kg/kg

Net water consumed per unit mass of product 171.35 kg/kg

Environmental Impact

Stream No	Total PEI	HTPI	HTPE	ATP	TTP	GWP	ODP	PCOP	AP

Base Case

Impact generated	-825772,00	8082,70	77298,30	11711,90	8082,70	111,55	0	-931059,00	0

Generated Alternative

Impact generated	-827968,00	8018,95	77157,60	11362,70	8018,95	111,76	0	-932637,00	0

Safety Factors

Base Case & Generated Alternative

	Total inherent safety index (ISI)				
Chemical inherent safety index, Ici		*Score*	*Process inherent safety index, Ipi*		Score
Subindices for reactions hazards			Subindices for process conditions		
	Heat of the main reaction, Irm	1		Inventory, Ii	3
	Heat of the side reactions, Irs	0		Process temperature, It	4
	Chemical Interaction, Iint	4		Process pressure, Ip	2
Subindices for hazardous substances			Subindices for process system		
	Flammability, Ifl	4		Equipment, Ieq	
	Explosiveness, Iex	1		Isbl	3
	Toxicity, Itox	4		Osbl	2
	Corrosivity, Icor	1		Process structure, Ist	2
	Ici	15		*Ipi*	16
		ISI	**31**	**Out of 53**	

Dow CEI = 801.6 mg/m^3; HD$_1$ > 10000 m, HD$_2$= 8016.4 m

Conclusions and future work

- **A systematic model-based method to generate alternatives that make the improves the ability of the process to be flexible and adapt to future demands has been developed and tested – use of models in "reverse" approach**
- **The indicators point to process/operation alternatives that affects the sustainability metrics parameters in the desired direction, avoiding, thereby, tradeoffs in design (decisions)**
- **The models and methodology are generic and can easily be applied in other sectors – targeted design**
- **Methods and tools from various groups have been integrated to generate sustainable alternatives**
- **Industrial process flowsheets are being labelled in terms of their potential for improvement**

Acknowledgements

Collaboration:

ETH-Zurich, Texas A&M

Methods & Tools:

US-EPA, CapSolva, PhD- & MSc-students

Funding:

Danish Funding Agency, CAPEC member companies