CASE STUDY FOR CONCEPTUAL DESIGN OF A SAFER, INTENSIFIED PROCESSING PLANT

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TU Delft

Learning objectives of the project

- Judge which process intensification technologies are suitable to (at least partially) address different kinds of safety risks and process bottlenecks in a chemical plant
- Identify appropriate selection criteria for comparison of different process intensification technologies on given applications
- Compare process intensification technologies on the basis of a set of selection criteria
- Perform basic dimensionalization of process intensification technologies

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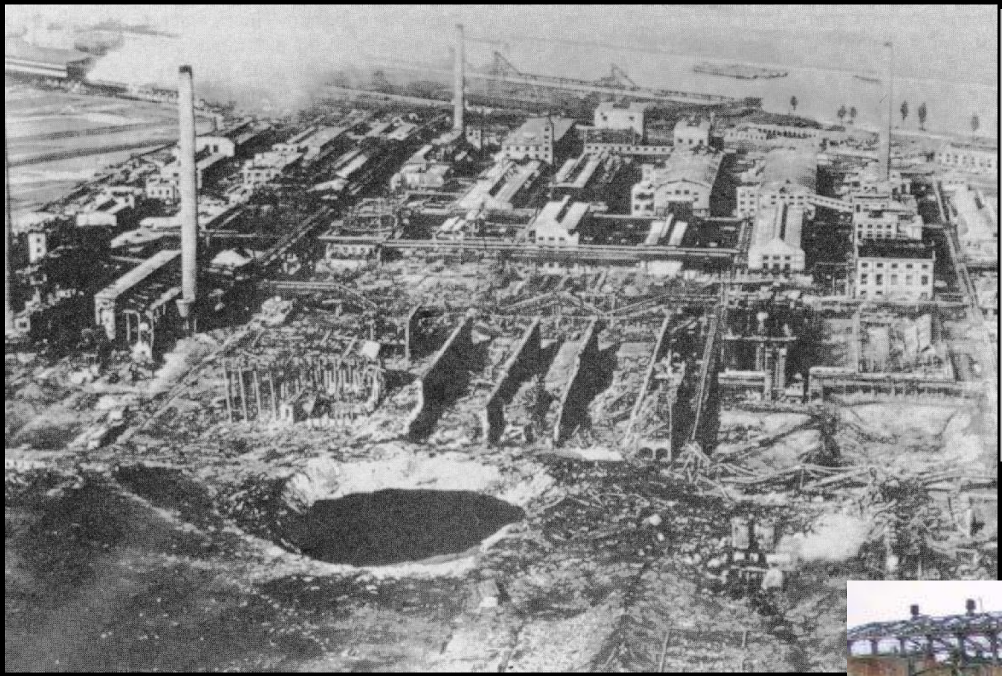
ISSUES OF CONCERN FOR CHEMICAL INDUSTRY: SAFETY



BASF, Oppau/Ludwigshafen, September 21, 1921

Crater: 80 m diameter, 16 m deep

>500 dead, 1500 injured

Countless buldings destroyed

Any lessons learned?

AZF, Toulouse, September 21, 2001

Crater: 50 m diameter, 10 m deep

30 dead, 10000 injured

Improved safety

SMALLER *is* SAFER!

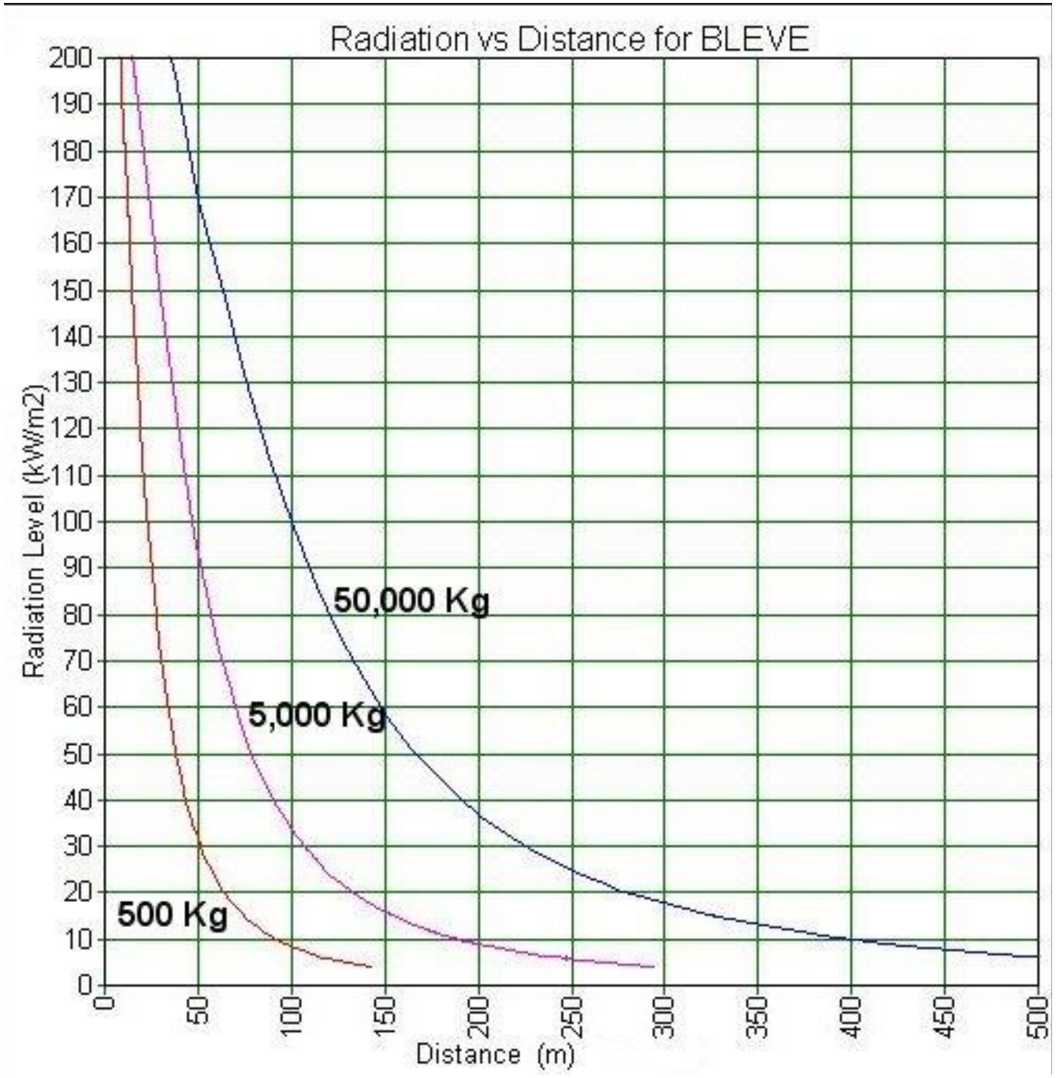
PLACE	DATE	CHEMICAL	ESTIMATED AMOUNT	CASUALTIES
Oppau/Ludwigshafen	September 21, 1921	ammonium sulfate, ammonium nitrate	4,500 t exploded	ca. 550 + 50 dead, 1,500 injured
Flixborough	June 1, 1974	cyclohexane	400 ton inventory, 40 ton escaped	28 dead, 36 + 53 injured
Beek	November 7, 1975	(mainly) propylene	> 10,000 m^3 inventory, 5.5 ton escaped	14 dead, 104 + 3 injured
Seveso	July 10, 1976	2,4,5 trichlorophenol, dioxin	7 ton inventory, 3 ton escaped	no direct casualties, ca. 37,000 people exposed
San Juan, Mexico City	November 19, 1984	LPG	> 10,000 m^3 inventory	5 + ca. 500 dead, 2 + 7000 injured (mainly outside the plant)
Bhopal	December 3, 1984	methyl isocyanate	41 ton released	3,800 dead, 2,720 permanently disabled
Pasadena	October 23, 1989	ethylene, isobutane, hexene, hydrogen	33 ton escaped	23 dead, 130-300 injured
Toulouse	September 21, 2001	ammonium nitrate	200-300 ton	31 dead, 2442 injured

Inherently Safer Design of Process Plants

Basic strategies:

- **Intensification** (minimization) – what you don't have can't leak ⇐ **PI**
- **Substitution** – safer material in place of hazardous one
- **Moderation** (attenuation) – hazardous material under the least hazardous conditions
- **Simplification** – fewer opportunities for error, less equipment that can fail

Intensification (minimization)



Radiation intensity from a BLEVE (boiling liquid expanding vapor explosion) as a function of distance for propylene storage tanks in three different sizes

(Source: D. Hendershot, in: “Re-engineering the Chemical Processing Plant”, Marcel Dekker, 2003)

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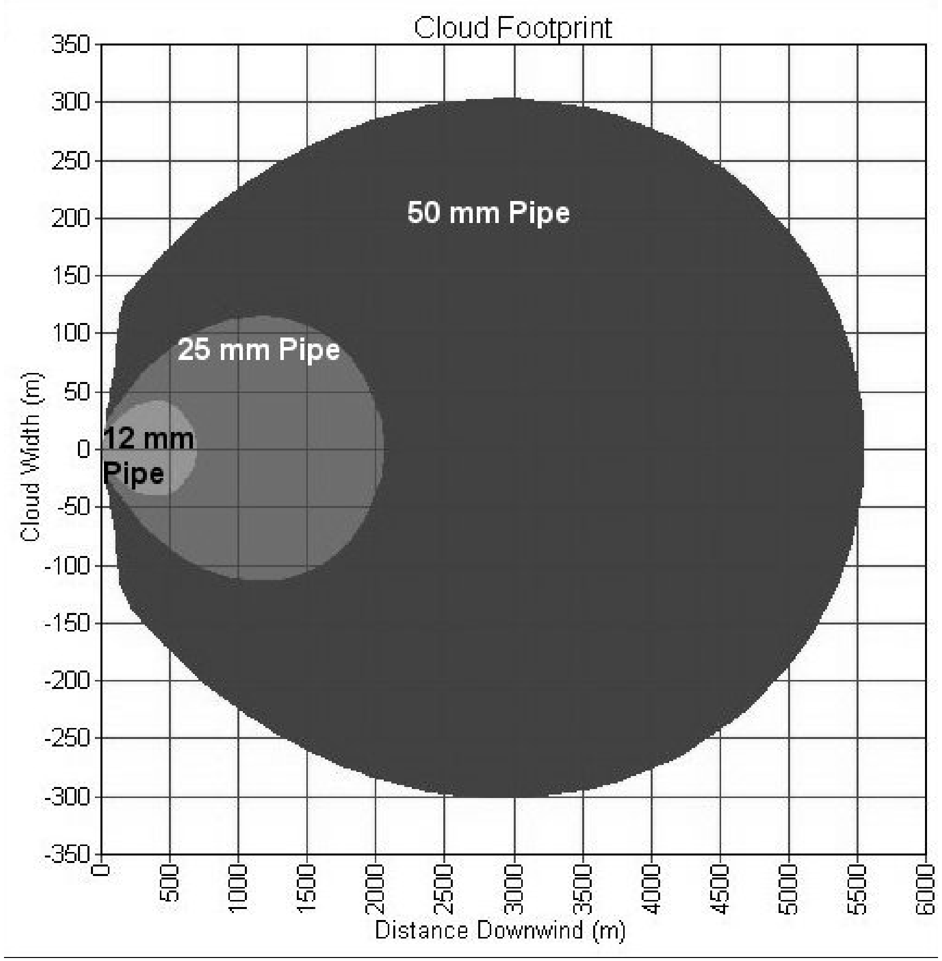
Intensification (minimization)



Cloud footprint to atmospheric concentration of 1ppm resulting from the rupture of three sizes of phosgene pipe

(Source: D. Hendershot, in: “Re-engineering the Chemical Processing Plant”, Marcel Dekker, 2003)

Intensification (minimization)

Think of:

- **Reactors** (type, size, heat removal, etc.)
- **Separation equipment** (type, size, energy consumption, integration with reaction processes)
- **Heat Transfer Equipment** (compactness, efficiency, etc.)
- **Storage** (necessary size, cooling systems, transfer piping, etc.)

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Substitution (elimination)

Think of:

Choosing less hazardous process routes (e.g. alternative chemistry, reaction steps etc.)

Using safer non-reactive agents (e.g. refrigerants, solvents, propellants, firefighting agents, etc.)

Moderation (attenuation)

Think of:

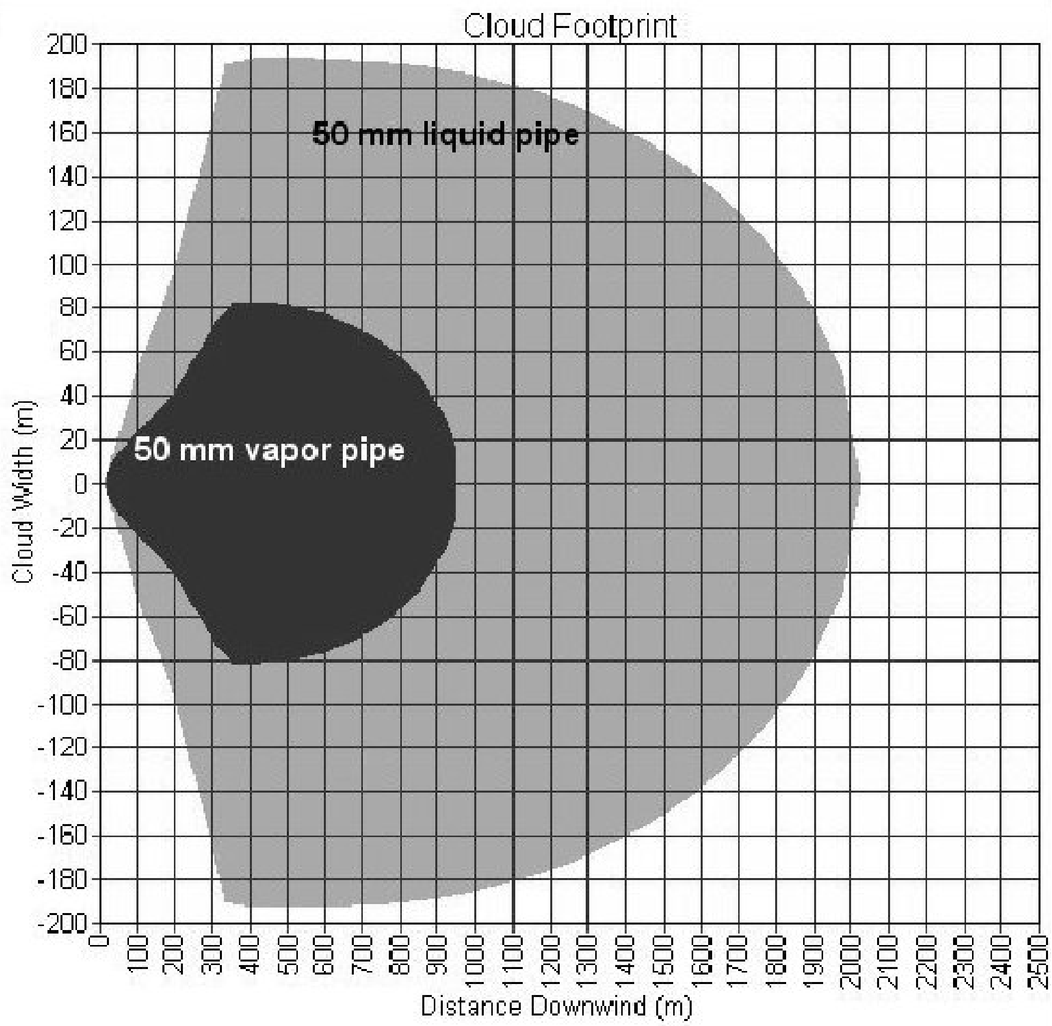
Dilution

Refrigeration

Pressure (lower)

Alternative catalysts (to lower temperature)

Moderation (attenuation)



Cloud footprint to an atmospheric concentration of 20 ppm resulting from the rupture of a 50 mm diameter chlorine pipe containing either chlorine liquid or chlorine vapor

(Source: D. Hendershot, in: "Re-engineering the Chemical Processing Plant", Marcel Dekker, 2003)

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Simplification (and error tolerance)

Think of:

Leaving things out

Avoiding moving parts

Vessels geometries

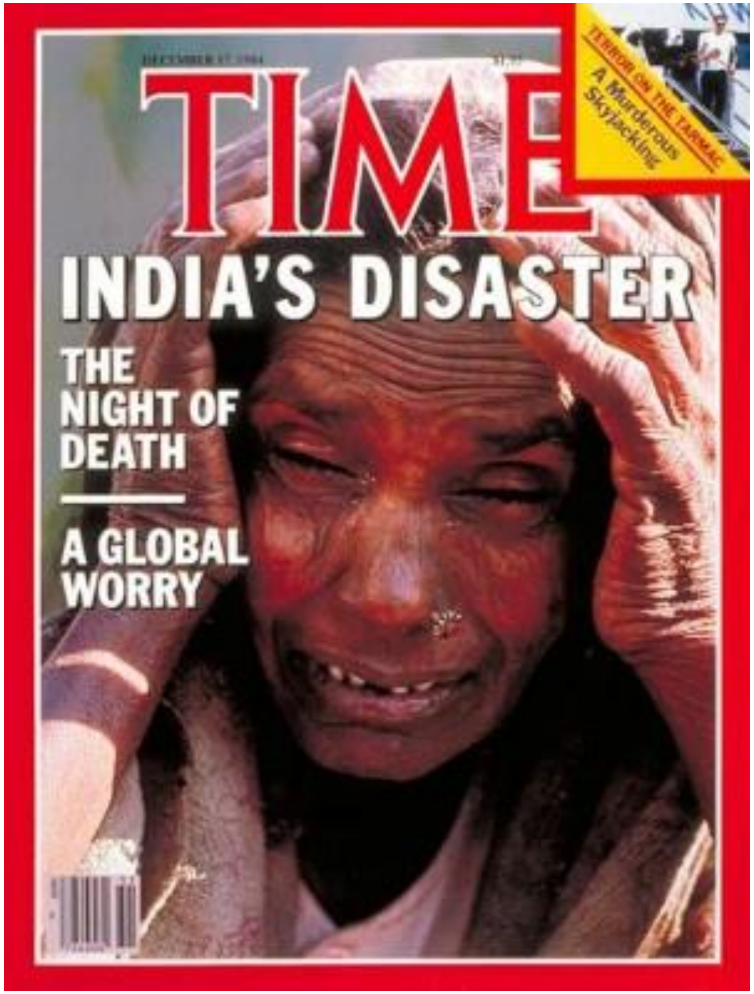
Flanges, joints, etc.

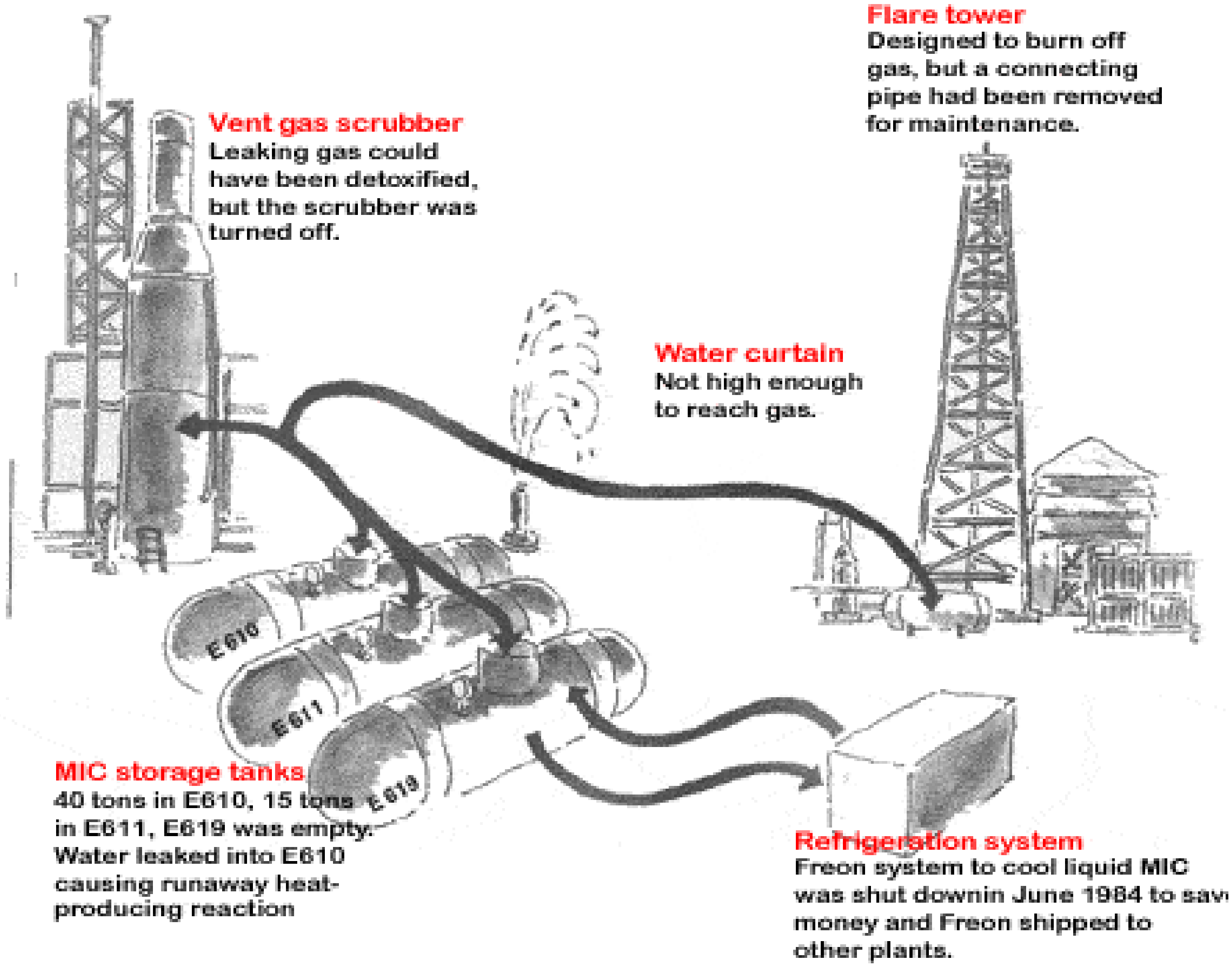
Instrumentation (more complex is not necessarily better)

Distributed control systems

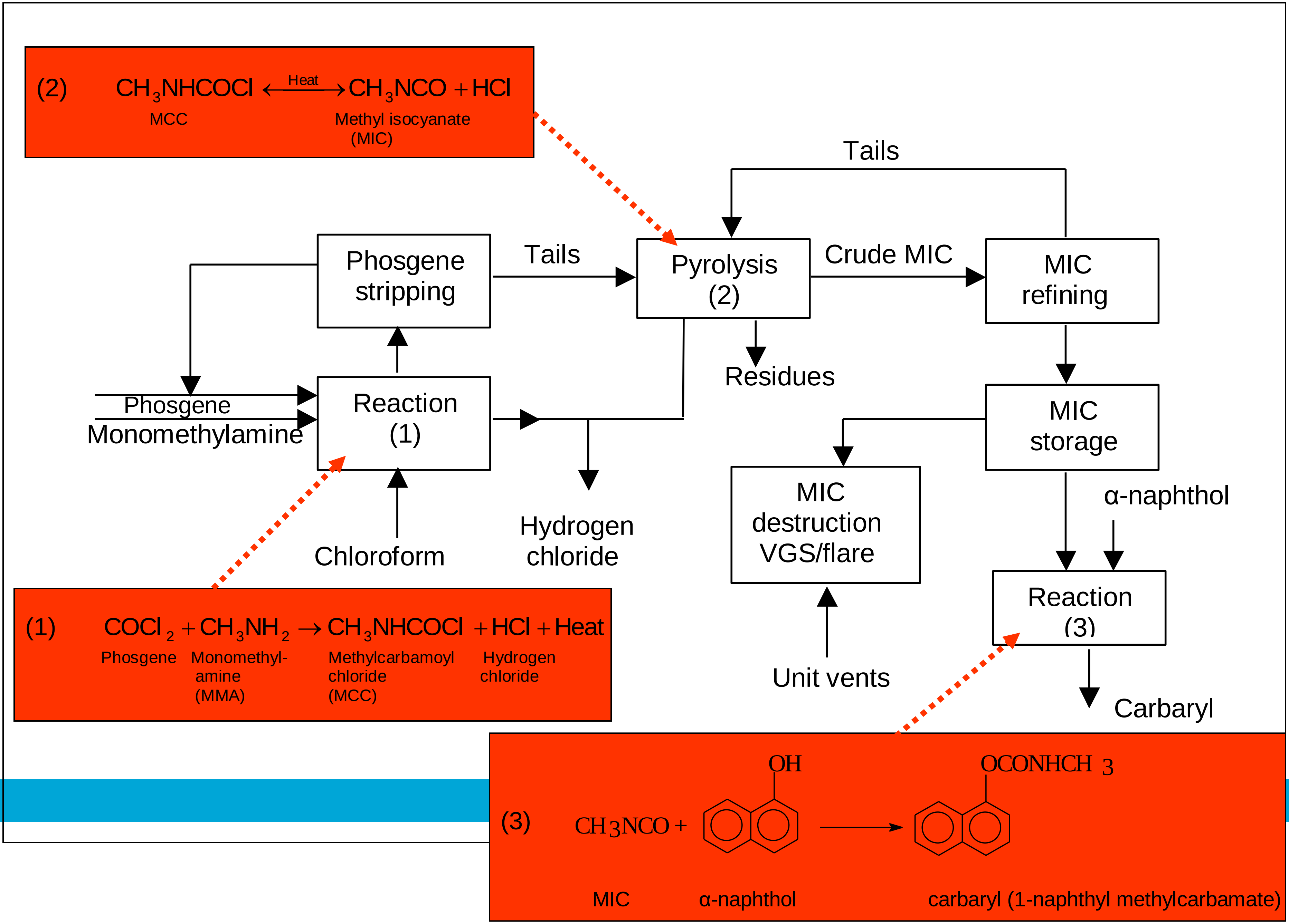
Separation of process steps

BHOPAL: COULD WE HAVE AVOIDED IT?




Flare tower
Designed to burn off gas, but a connecting pipe had been removed for maintenance.
Vent gas scrubber
Leaking gas could have been detoxified, but the scrubber was turned off.
Water curtain
Not high enough to reach gas.
E610
E611
E619
MIC storage tanks
40 tons in E610, 15 tons in E611, E619 was empty. Water leaked into E610 causing runaway heat-producing reaction
Refrigeration system
Freon system to cool liquid MIC was shut downin June 1984 to save money and Freon shipped to other plants.

Bhopal – scheme of Union Carbide *carbaryl/sevin* process



YOUR ASSIGNMENT

1. The Bhopal process consists of 3 sections: the MCC synthesis, MCC pyrolysis and the carbaryl synthesis. Each section will be investigated by a different team.

2. Conduct analysis of the Bhopal plant and redesign the Union Carbide process assuming the targeted plant capacity as licensed in 1983 (5250 t/yr). The analysis should address the bottlenecks in the process by applying the generic PI-principles. In the generation of PI-concepts make use of four fundamental approaches of Process Intensification in the spatial, thermodynamic, functional and temporal domains. Consider all scales, from molecular to the scale of processing units. Redesign by applying process-intensive equipment and methods and to minimize the risk to humans and environment. Do not change the chemistry.

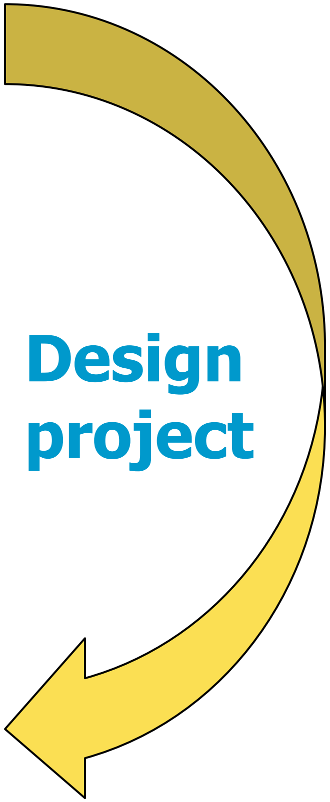
Deliverables

1. Analysis of the original plant design

- Chemistry (do not change), chemical kinetics
- Required operating conditions: temperatures, pressures, concentrations, flow rates/superficial velocities, residence times
- Process Flow Diagram (PFD)
- Rough dimensionalization
- Product specifications: purity, state (solute/crystallized/…)
- Weak spots in the design, hazards, bottlenecks

2. New plant design

- Improved and safer process
- PFD of intensified process equipment
- Rough dimensionalization, intensification factors



Design methodology

To rationalize and manage design projects

- Manage: time planning, division of work.
- Rationalize: to brings design efforts into the conscious mind.

Making sure you're not forgetting something important

Design methodology

4 steps

1. Define the problem: analysis of the original plant design.
2. Find solutions: applying the PI-principles, selecting intensified technologies.
3. Evaluate and select solutions
4. Implementation: main process characteristics, rough dimensionalization, intensification factors.

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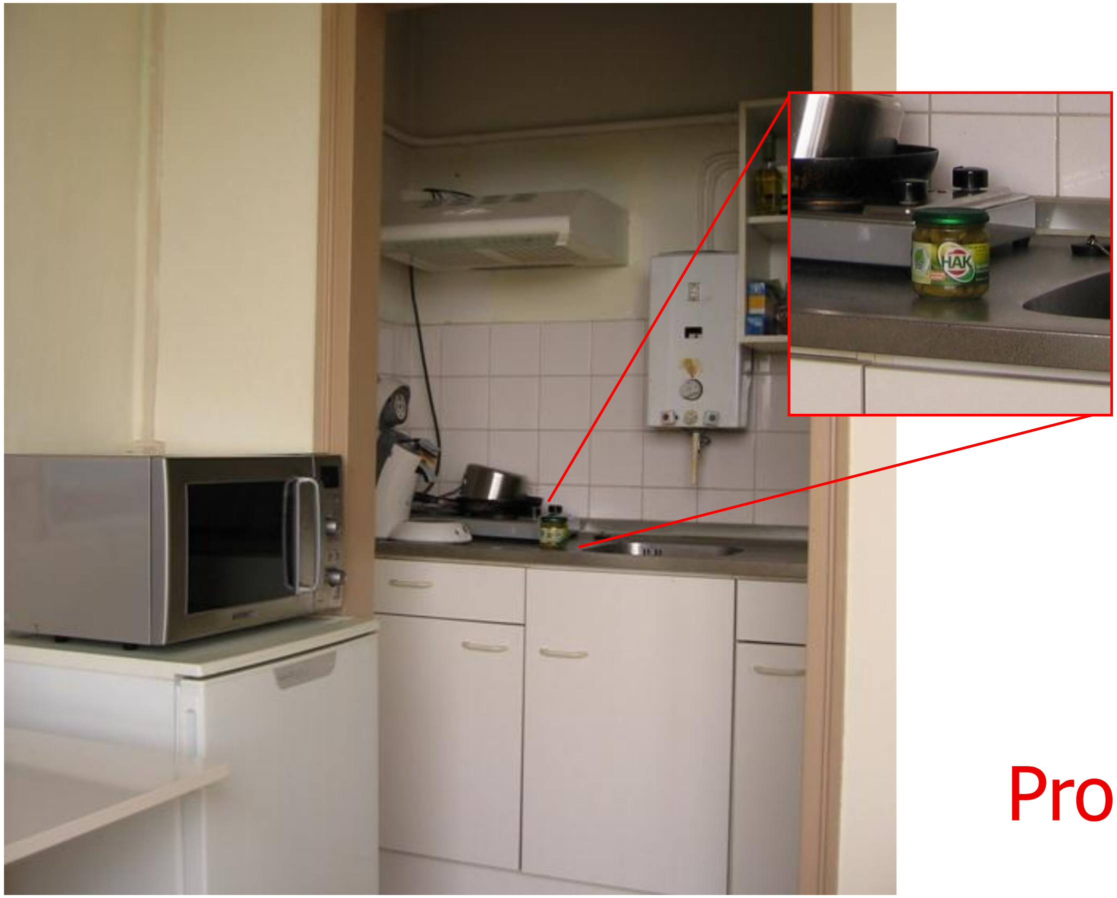
Step 1: define the problem

Analysis of the original plant design

- Chemistry (do not change), chemical kinetics
- Required operating conditions: temperatures, pressures, concentrations, flow rates/superficial velocities, residence times
- Process Flow Diagram (PFD)
- Rough dimensionalization
- Product specifications: purity, state (solute/crystallized/…)
- Weak spots in the design, hazards, bottlenecks

Detailed specification of the desired improvements: intensified and safer. This results in a set of **requirements for the new process design**

Example #1 – Cook a jar of beans



Process:

Heat the beans in this jar.

Step 1

Problem definition

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Example #1—Problem definition

“chemistry”

energy

$$\text{cold beans} \xrightarrow{\text{energy}} \text{hot beans}$$

thermodynamic requirements

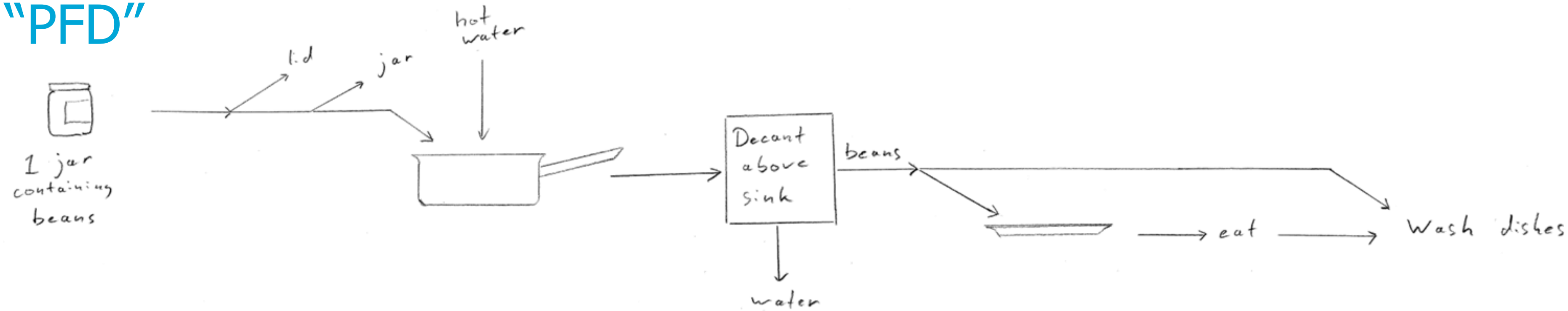
heat until close to boiling

additional processing requirements

- one jar of beans
- shortest possible residence time

Example #1—Problem definition

"PFD"



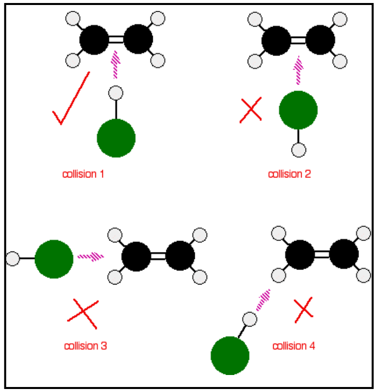
product requirements	hot beans, fast
bottleneck	limited heating rate (ratio power to thermal mass)
hazard	hot fluids
reliability	electric cooking plates are very reliable
side reactions	dry cooking

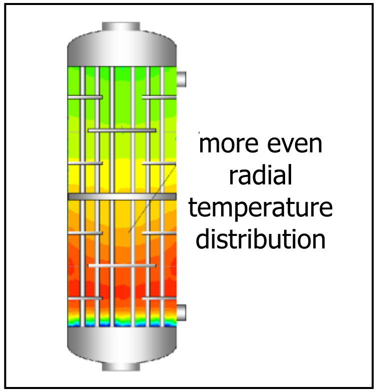
Step 2: Find solutions

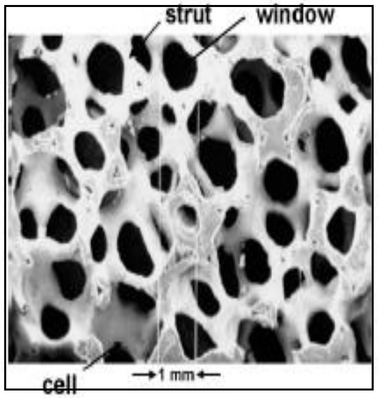
A. Identify the PI principles that can address the weak spots in the original design

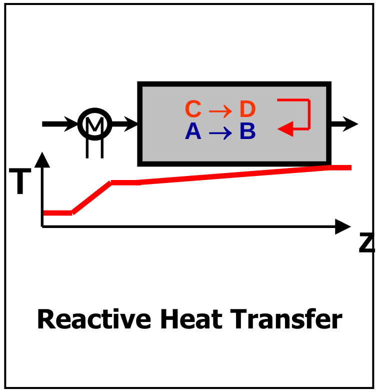
PRINCIPLES (GOALS)

maximizing the effectiveness of intra- and intermolecular events	giving each molecule the same processing experience	optimizing the driving forces and maximizing the specific surface areas to which these forces apply	maximizing synergistic effects from partial processes









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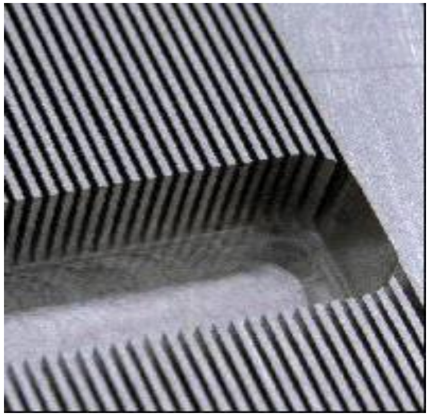
Step 2: Find solutions

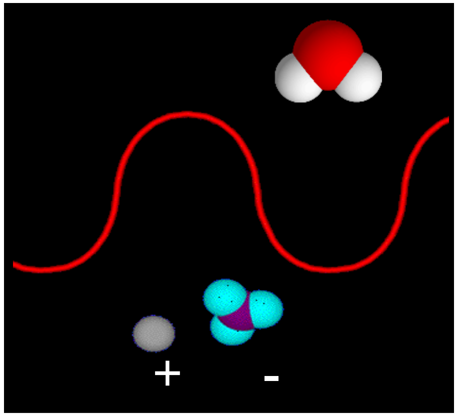
B. Select the technologies in the four domains of process intensification that satisfy the selected PI principles

APPROACHES

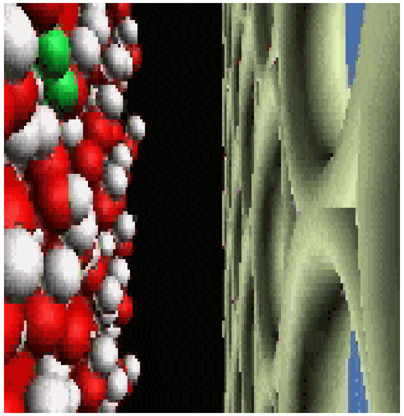
STRUCTURE	ENERGY	SYNERGY	TIME
(spatial domain)	(thermodynamic domain)	(functional domain)	(temporal domain)



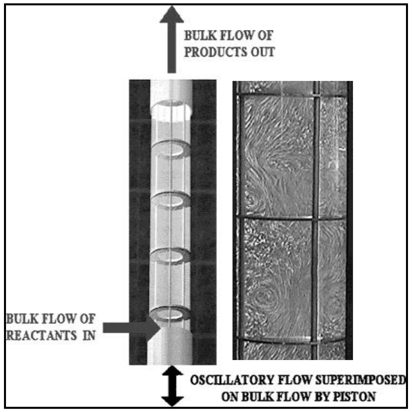
e.g. microreactors



e.g. electromagnetic energies



e.g. membrane reactors



e.g. Oscillatory flow reactors

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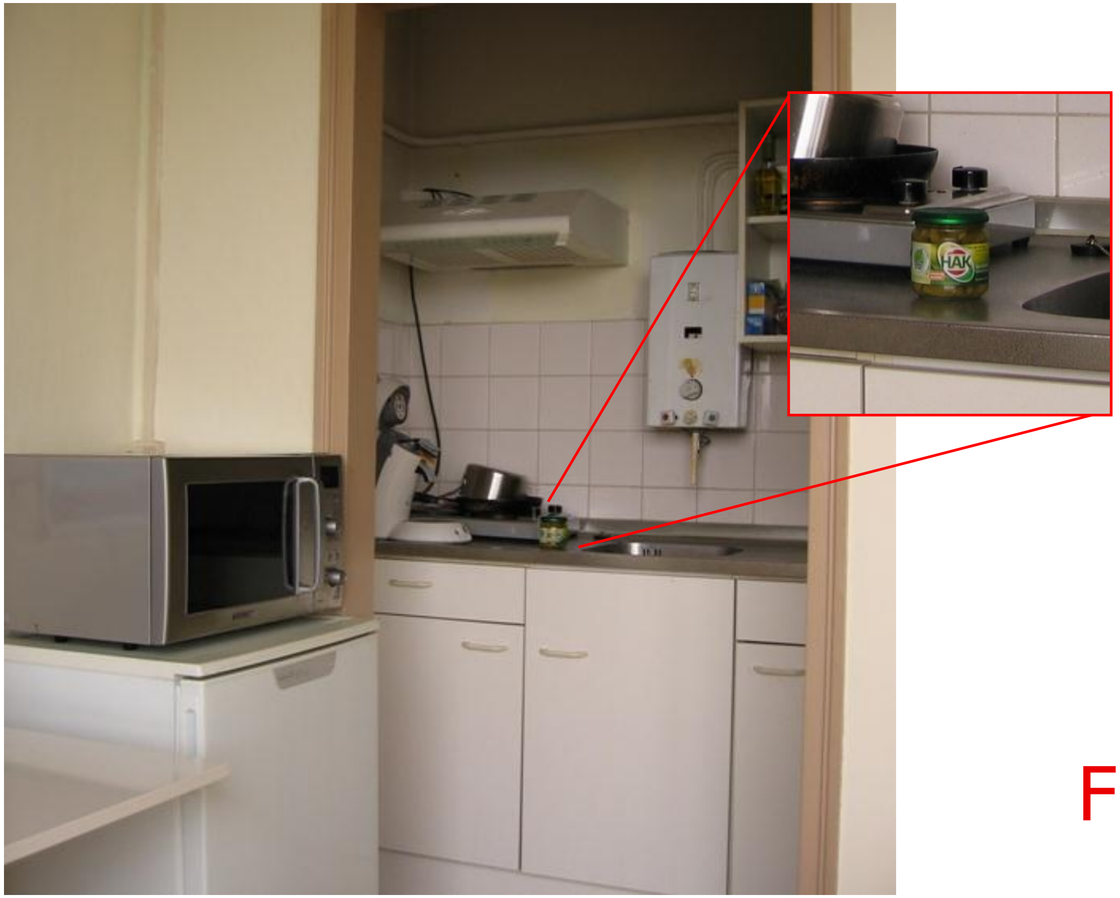
Example #1—Cook a jar of beans



Process:

Heat the beans in this jar.

Step 2

Find solutions

Example #1—Find solutions

Structure	smaller volume, add less or no water
Energy	gas heating or microwave
Synergy	use jar for multiple purposes
Time	change order of operations; remove jar later in the process

Step 3: evaluation and select solutions

Systematic selection chart

concepts	criteria 1	2	3	4	5	…
a	−	+	+	0	0	
b	0	+	−	0	+	
c	0	+	+	0	0	
d	+	+	0	−	−	
e	+	−	0	−	+	
⋮						

Adapt from step 1: problem definition and requirements

From step 2: intensified solutions found

Select the technology that scores best

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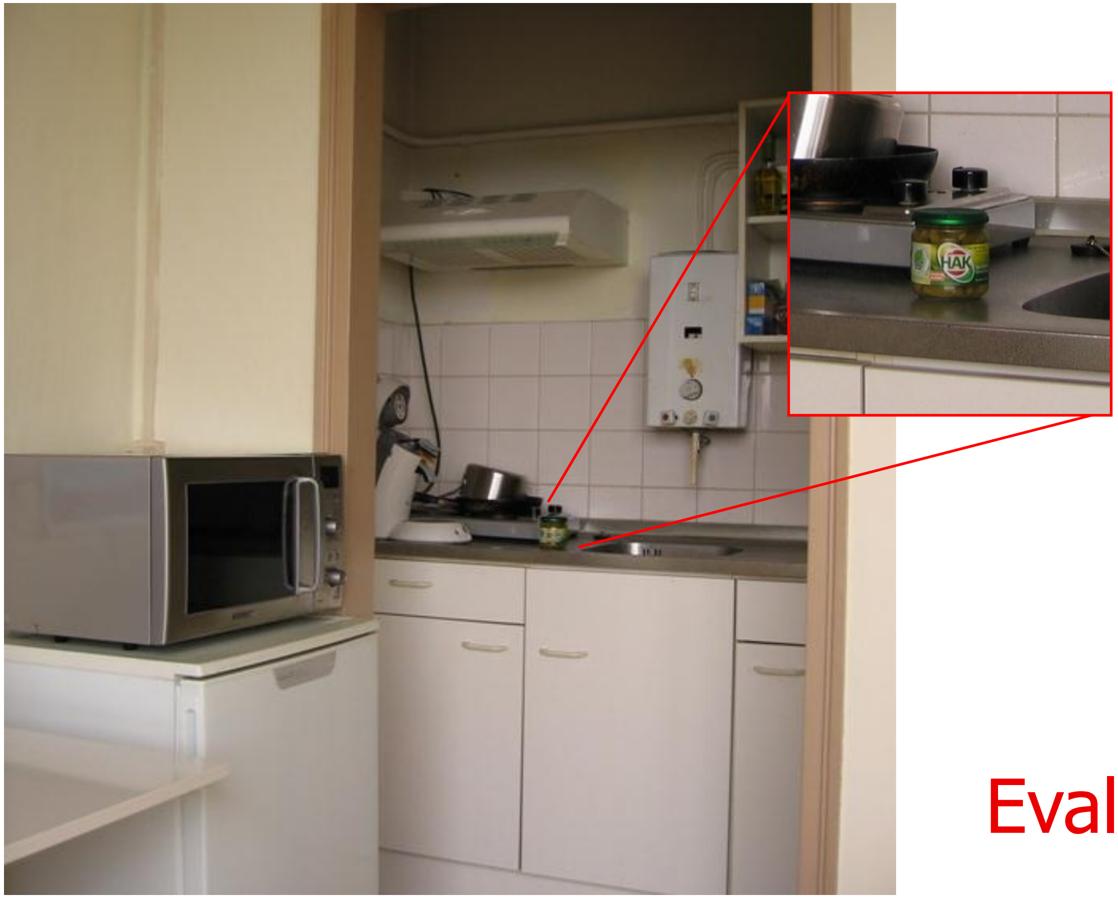
Example #1—Cook a jar of beans



Process:

Heat the beans in this jar.

Step 3

Evaluate and select solutions

Example #1—Evaluate and select

	low thermal stresses on jar	no dry cooking	low energy consumption	low time requirement	reduced complexity	low investment cost
add no or less water	0	–	+	+	0	0
heat beans in jar	–[a]	0	0[b]	+	+	0
eat beans from jar	–[a]	0	0[b]	+	++	0
gas heater	0	–	++[c]	+	0	– –
microwave heating	0	–	+[c]	++	0	0

[a]not applicable with electric or gas stove

[b]energy consumption evaluated as for microwave heating, see [a]

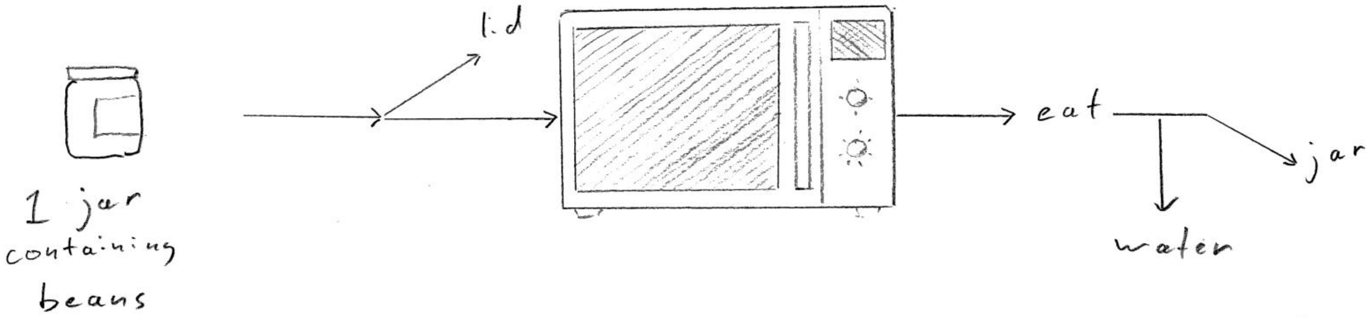
[c]compared to electric stove

Example #1—Evaluate and select

gas heating	+ 0
microwave heating	+ 2
gas heating, less water	+ 1
microwave heating, less water	+ 3
microwave heating, less water, heat in jar	+ 4
microwave heating, less water, eat from jar	+ 5

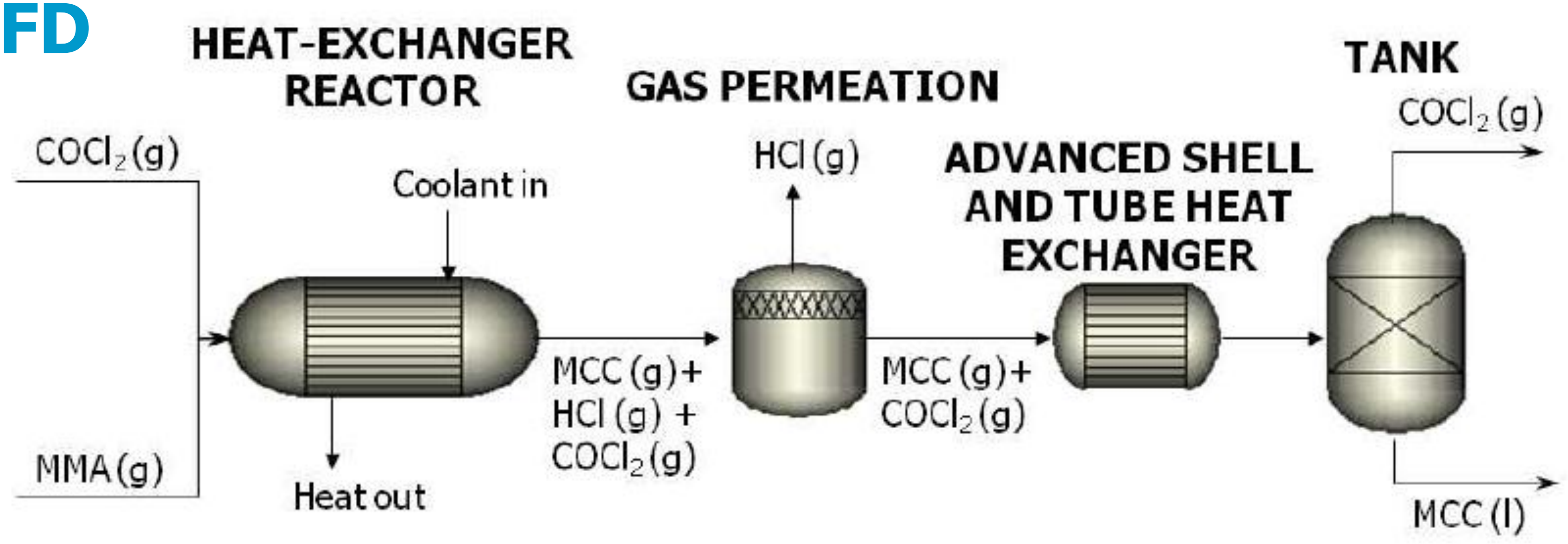
Example #1—Evaluate and select

Intensified PFD



Step 4: Implementation

PFD



Calculate main process characteristics: rough dimensionalization (volumes heat & mass transfer areas, residence times), energy consumption, cost, intensification factors.

Not all data is known: make assumptions and look at the big picture.

Example #2: making assumptions

Your roomate is a moonshiner. He illegally distils alcoholic spirits. An for his enterprise *he stole the pages on ethanol out of chemistry book*. Also Wikipedia is down.

Your report on a bioethanol process is due tomorrow. *You need to know the boiling point.* What do you do?

You make assumptions.

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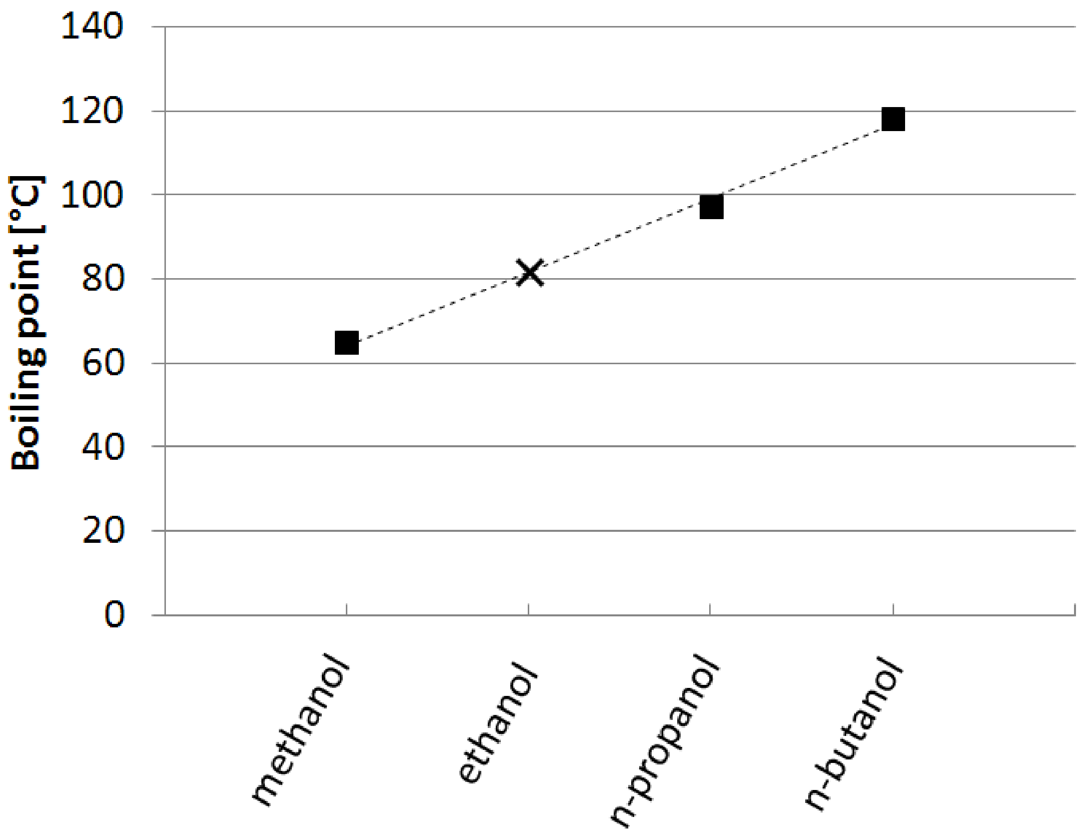
Example #2: making assumptions

Interpolating the boiling point of ethanol gives you a value of 81.5 °C, slightly to high (vs. 78.4 °C).

But for a rough assumption it surely is good enough.

It does not have to be exact.



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Example #3: the big picture

Case system

$$A + B \xrightarrow{\text{catalyst}} C$$ mildly exothermic

$$B + B \xrightarrow{\text{catalyst}} D$$ side reaction

An excess of A is fed and cooling controls temperature

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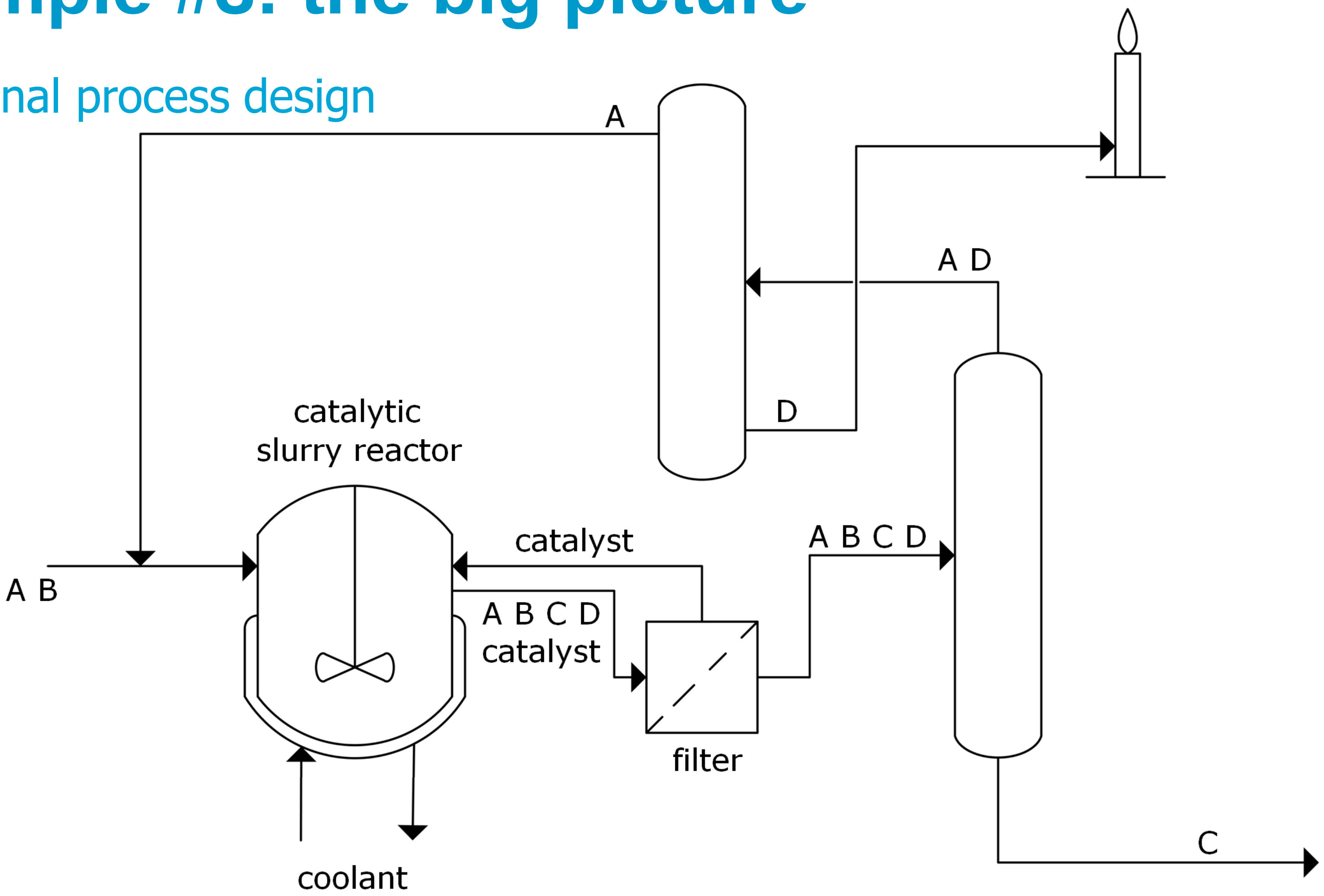
Example #3: the big picture

Original process design



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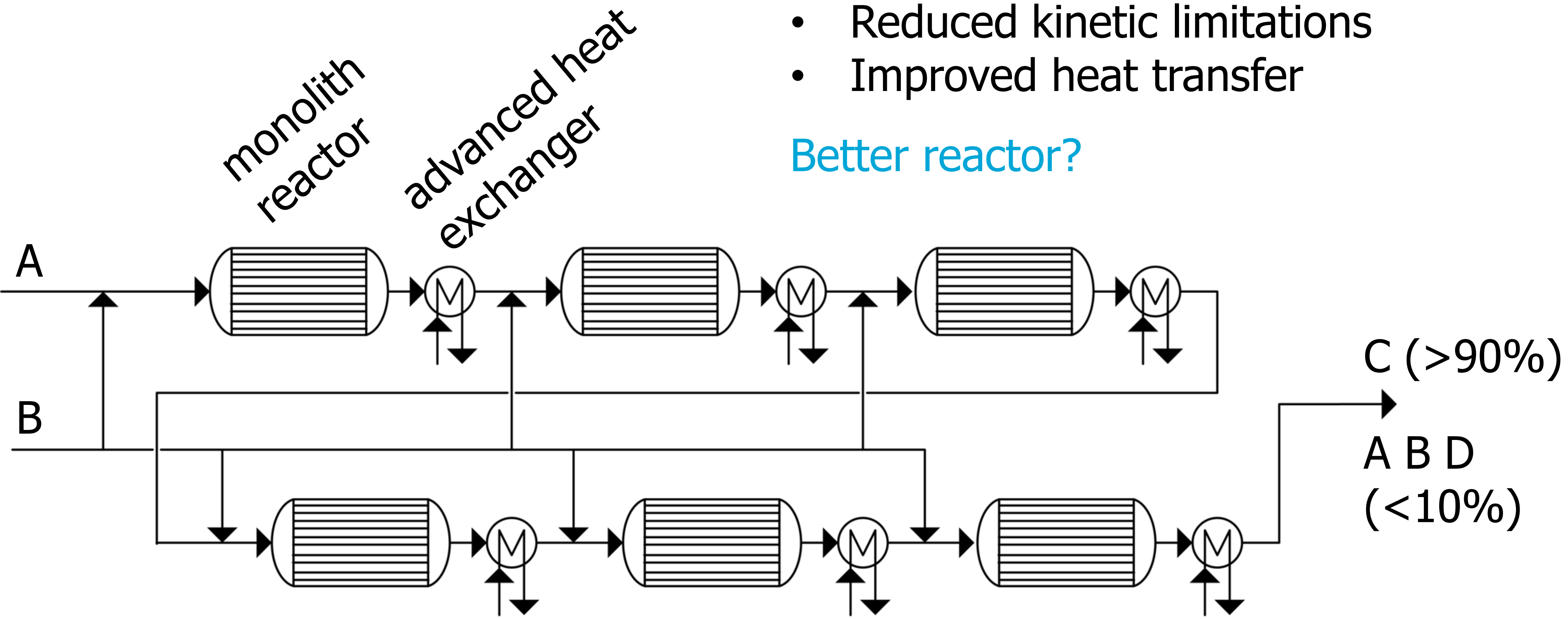
Example #3: the big picture

New reactor design

- More ideal plug flow
- Distributed feed of B
- Reduced kinetic limitations
- Improved heat transfer

Better reactor?



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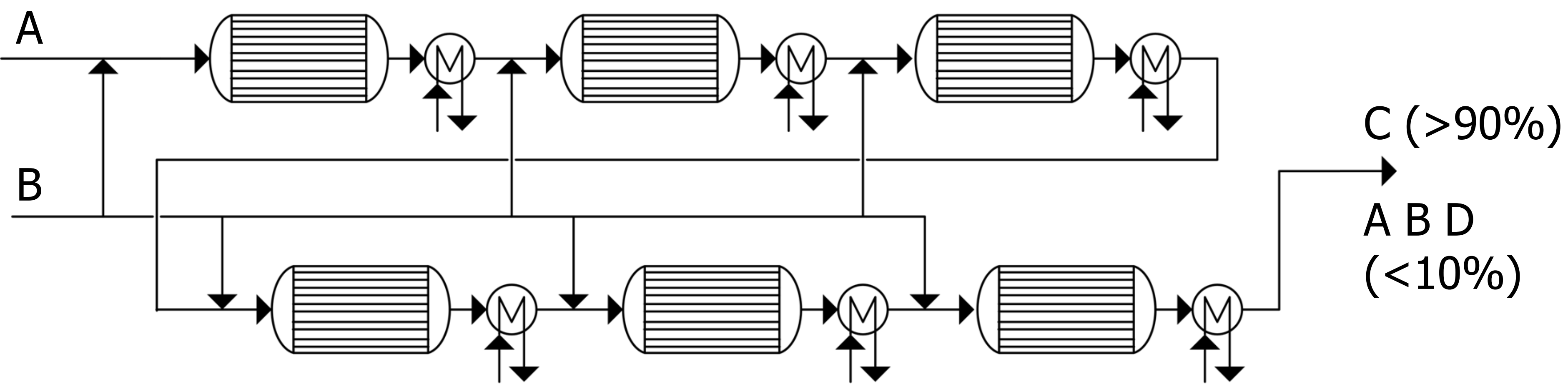
Example #3: the big picture

Look at big picture

- New bottleneck: mass transfer at catalytic surface, reactor volume needs to be 3 times larger!
- Much more complex design; control, maintenance

Better reactor?



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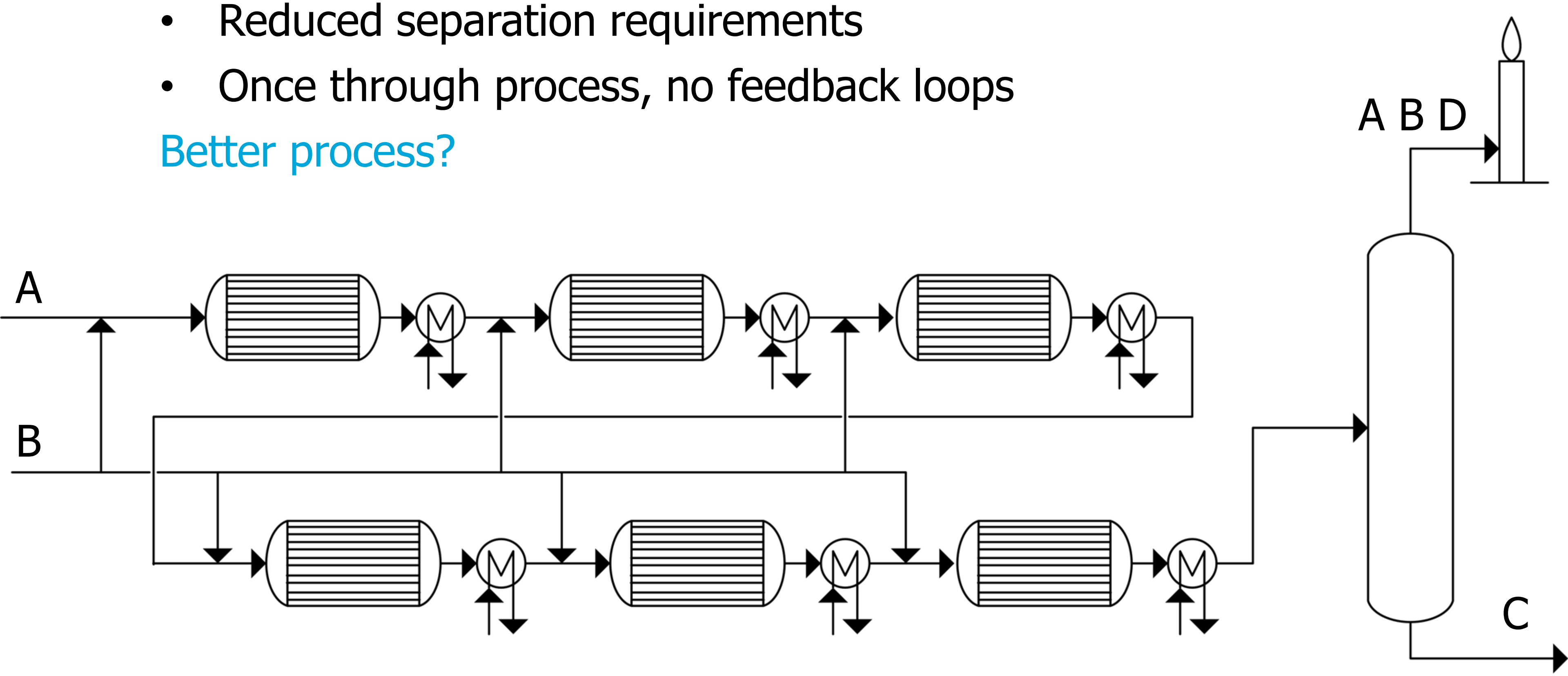
Example #3: the big picture

Look at *bigger* picture

- Reduced separation requirements
- Once through process, no feedback loops

Better process?



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Closing remarks

- Design a safer alternative for the Bhopal plant
- Same chemistry, same throughput
- Different, intensified equipment and methods
- Start by defining what the requirements are for the new process
- There is no best answer, you are graded for your argumentation to the answer

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YOUR TIMELINE

Nov. 5: Start of the PI course (G. Stefanidis)

Nov. 8: Presentation of PI assignments (G. Stefanidis, G. Sturm)

Nov. 8-15: **Form and e-mail your project groups** (3-4 members). You will be assigned a teaching assistant (TA) as project supervisor. G. Krintiras is coordinating.

Nov. 19-Nov. 30: First meeting with the TAs. Discuss your ideas on steps 1-2 of the working approach; ask questions; receive feedback.

Dec. 13 & 17: Mid-term presentations by the project teams. You are expected to present your work on steps 1-2 of the working approach. You will receive feedback on your choices by the course instructors (G. Stefanidis and A. Stankiewicz). 15 min presentation + 10 min discussion per team.

January: Work by the project teams on steps 3-4 of the working approach (i.e. finalization of the design of the intensified chemical plant) and writing of the project report. Contact the course instructors for any questions you may have!

Jan. 23: Written exam

February: Final presentations by the project teams and assessment. Exact dates will be fixed during the course. You are expected to submit the project report at least one week before the final presentation. Final meeting: 30 min presentation + 30 min discussion.