Chemical Engineering Department Seminar
Carnegie Mellon University, Pittsburgh, 27 March 2012

Thermodynamics and Innovative Design for Energy Efficiency and Carbon Capture

by

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with important contributions from
***Audun Aspelund**, PhD, 20 March 2012*
***Chao Fu**, PhD, September 2012*
***Danahe Marmolejo Correa**, PhD, Spring 2013*

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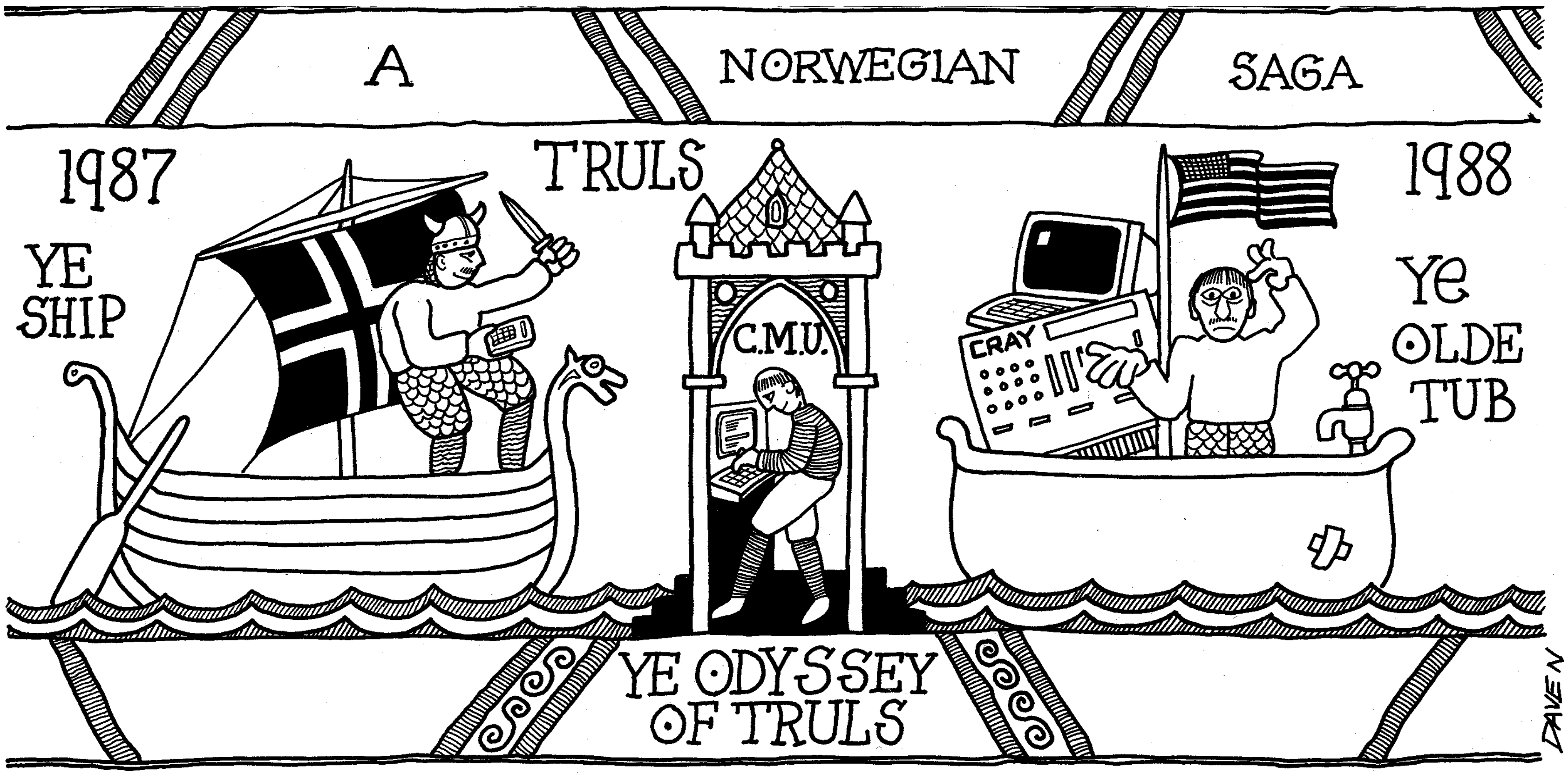
Comments from a "UK University" October 1988



Promoting Optimization (Math Programming) was quite challenging in those Days !

Thermodynamics and **Innovative Design** for Energy Efficiency and Carbon Capture

is <u>not</u> about Architecture (the Stata Center at MIT)

BIGCCS

International CCS Research Centre

Budget 80 MUSD over 8 years

> 20 PhDs and > 10 Post.docs

2009-2016

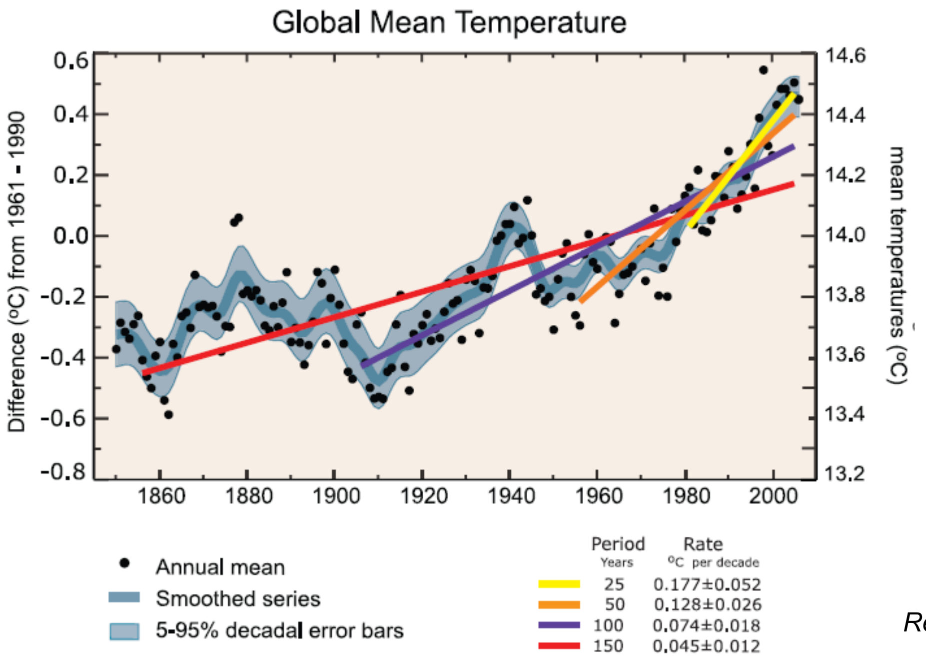
Objectives:

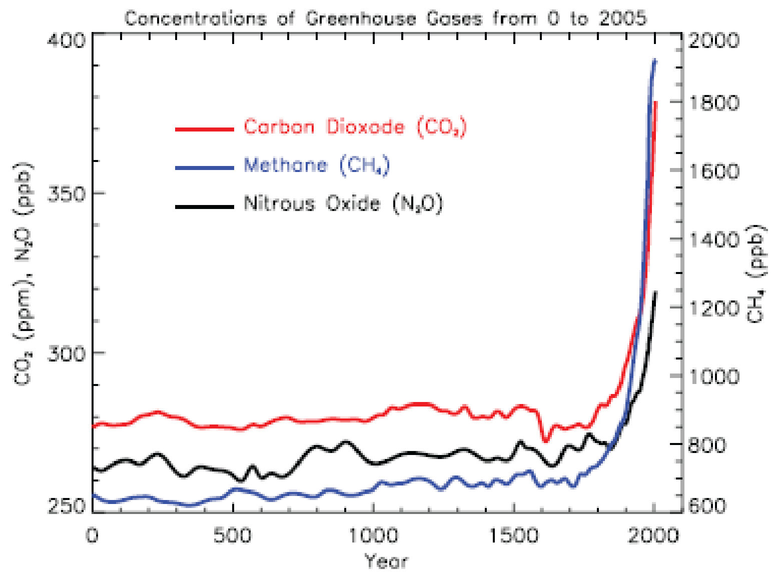
1. **Reduce CCS Cost by 50%**
2. **CO_2 Capture Rate of 90%**
3. **Fuel-to-Power Penalty ≤ 6 % pts**

Innovations are required

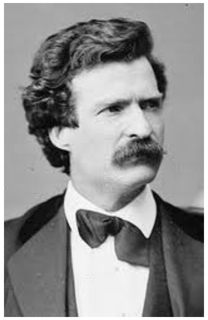
BIGCCS Director: Mona J. Mølnvik
BIGCCS Board Chair: Nils A. Røkke
SINTEF Energy Research
NTNU Coordinator: Truls Gundersen

Climate Change and CO_2 Emissions





Ref.: IPCC, Climate change 2007: The physical science basis



Mark Twain:

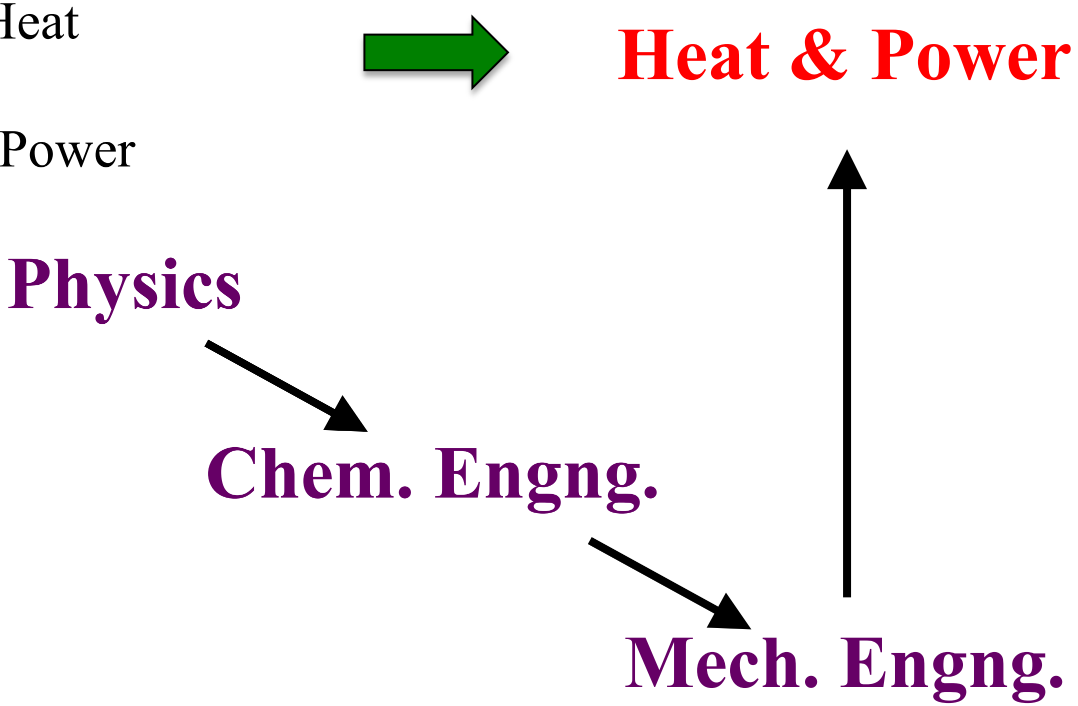
"Climate is what to expect, weather is what you get"

3 Main Options:

1. Energy Efficiency
2. CO_2 Capture & Storage
3. Renewable Energies

Thermodynamics and Innovative Design for Energy Efficiency and Carbon Capture

Greek-to-English:
Therme = Warm = Heat
(Thermie = Calorie)
Dynamis = Force = Power



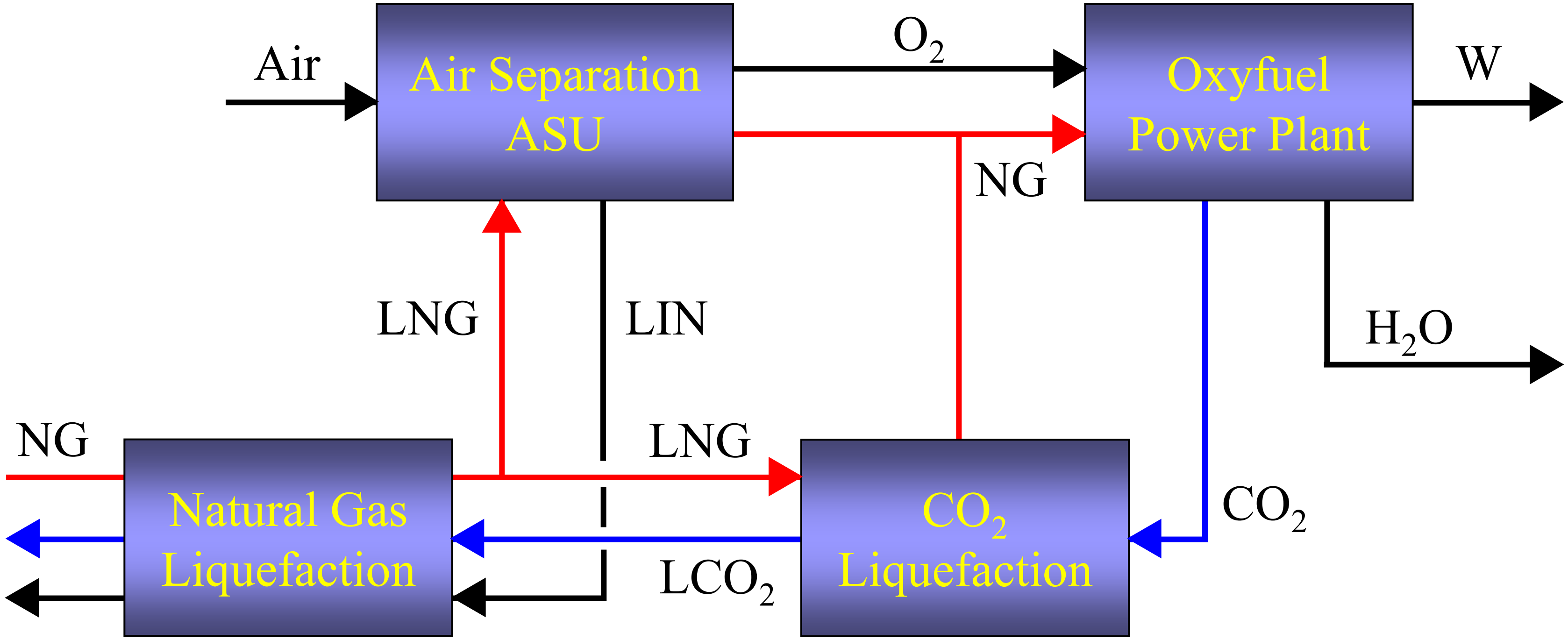
Obvious link: Thermodynamics & Energy Efficiency

Content of the Presentation

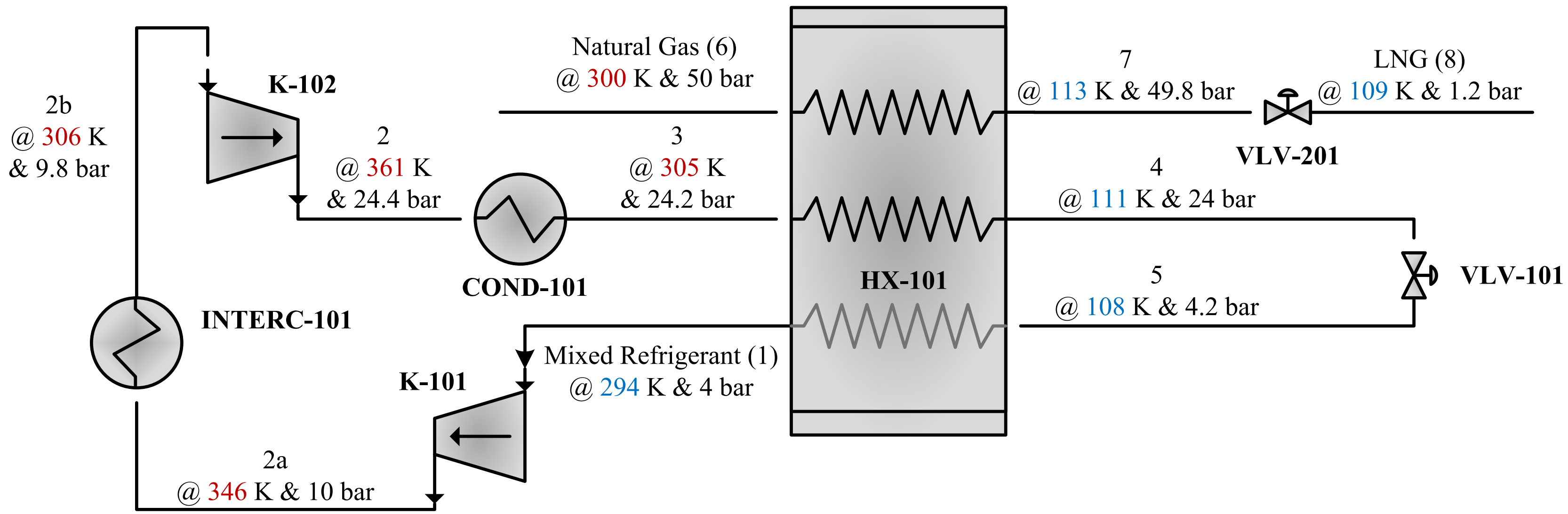
- 2 “subambient” Processes
  - ***LNG*** and ***ASU*** (Air Separation Units)
- Scenario: 2 types of Power Stations
  - Supercritical pulverized Coal based Plant
  - Combined Cycle Natural Gas based Plant
  - Both of the ***Oxy-combustion*** type for CO_2 Capture
- Design Methodologies
  - **Thermodynamics** based (Pinch & Exergy Analyses)
  - Optimization based (Math Programming & Superstructures)
- Examples will focus on **Energy Efficiency** and **CCS**
- **Innovations** will be discussed
  - Patent Application for new ASU cycles
  - Liquefied Energy Chain with offshore LNG
- Round up with a Summary

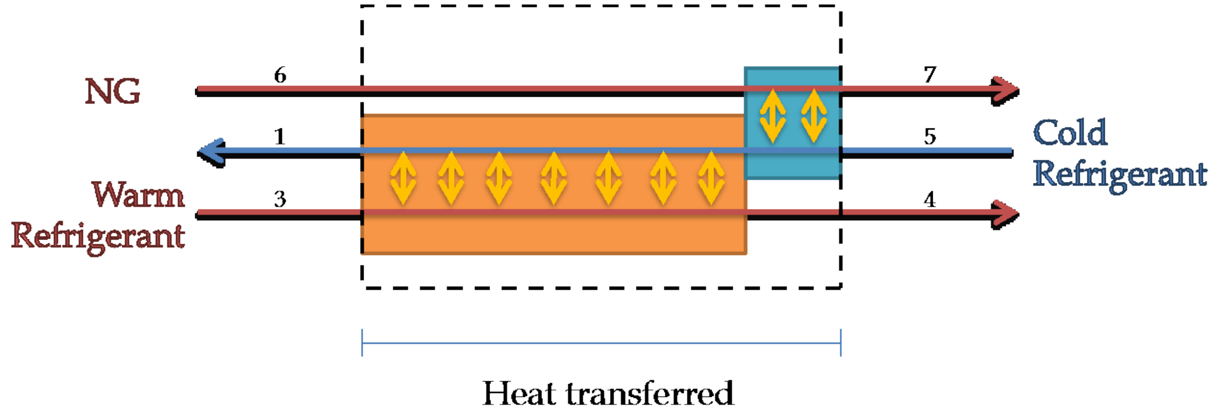
Audun Aspelund: **A Liquefied Energy Chain (LEC)**

Combined Transport of Natural Gas and CO_2



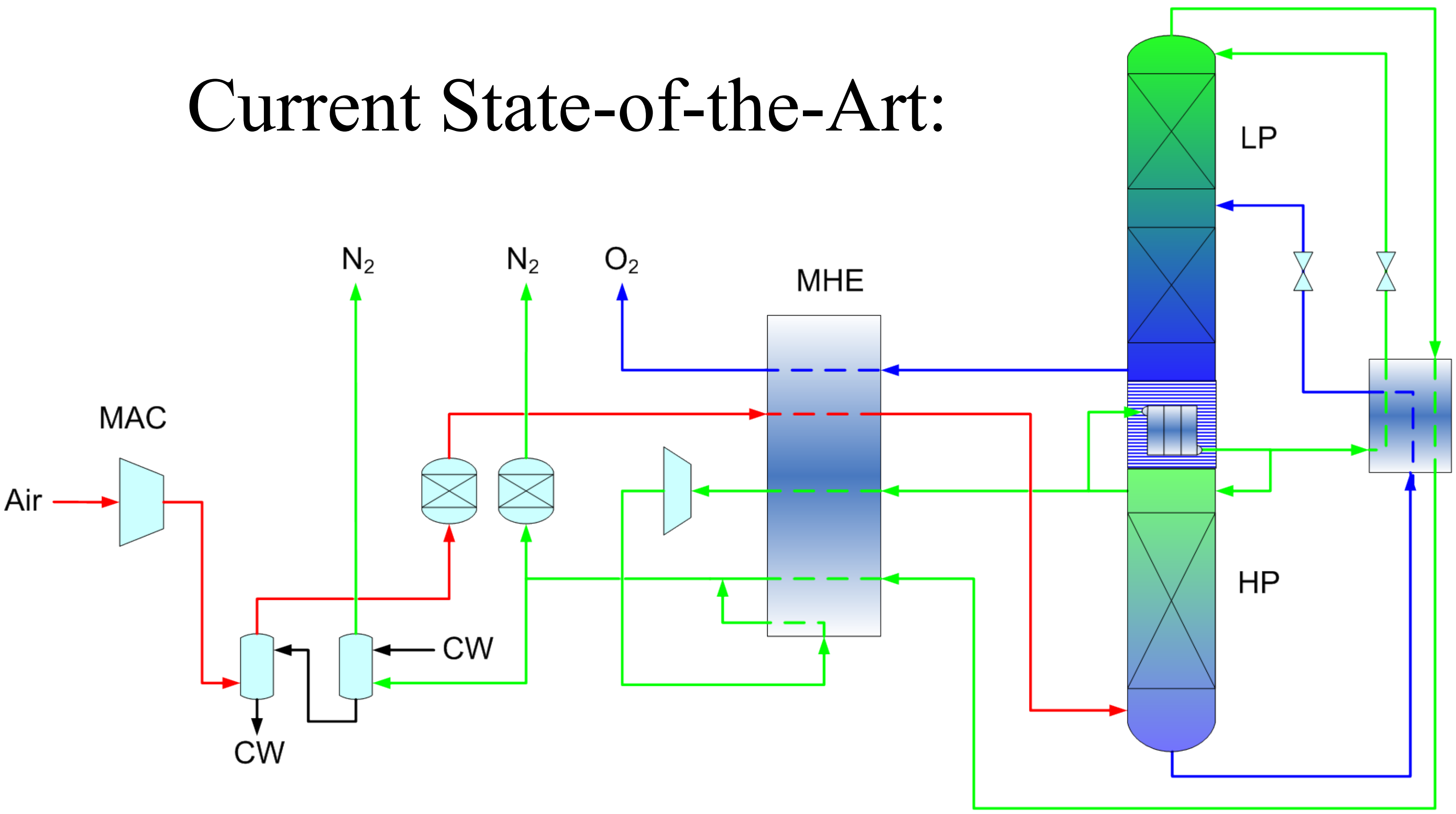
Why is the PRICO Process so inefficient?





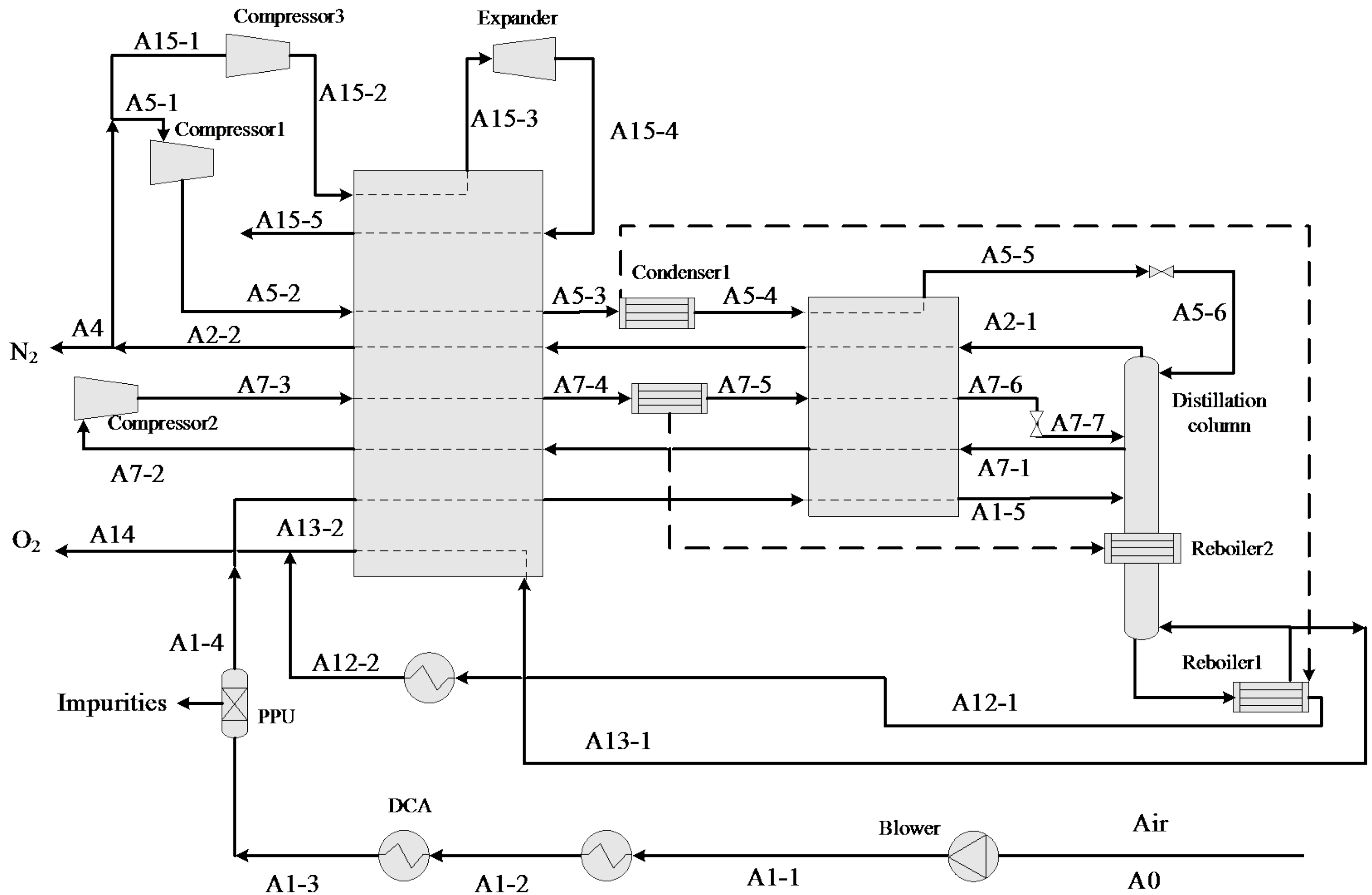
Chao Fu: **ASU Cycles with up to 20% Energy Savings**

Current State-of-the-Art:



Linde's Classical Coupled Column Design

Chao Fu: **ASU Cycles with up to 20% Energy Savings**

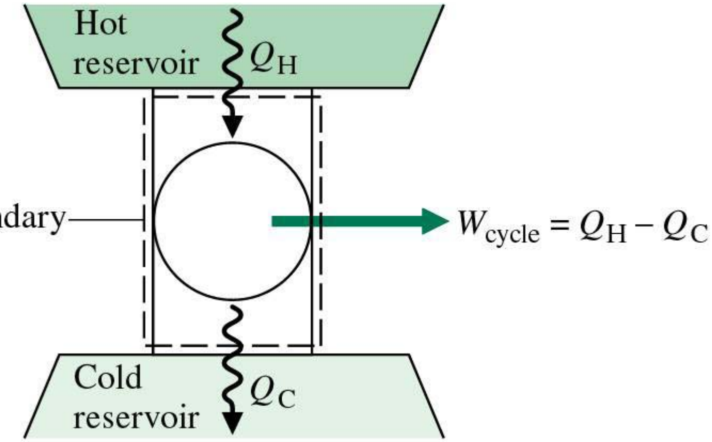


Recuperative Vapor Recompression Cycle - *Patented*

A short Tutorial on Exergy

- What is Exergy?
  - *"The **Maximum** Amount of **Work** that can be produced if a "System" is brought to **Equilibrium** with its natural Environment through **Reversible** Processes"*
  - Equilibrium here refers to Composition, ***Pressure***, ***Temperature***, Velocity, Gravitational Level, etc.
- Is Exergy related to Entropy?
  - They are "inverse" properties
  - Entropy is a measure of disorder (chaos)
  - Entropy Production in processes due to **Irreversibilities** is Equivalent to Exergy Losses (and Lost Work)
- Why use Exergy?
  - Energy Forms have different Qualities, i.e. Exergy
  - Subambient ➔ Refrigeration ➔ Compr. Work ➔ Exergy
  - But: Exergy and Cost are often (not always) in Conflict

The Exergy of Heat



Without **1**st Law Losses:

$$W_{cycle} = Q_H - Q_C$$

Without **2**nd Law Losses:

$$(Q_C/Q_H) = (Q_C/Q_H)_{rev} = T_C/T_H$$

Thermal Efficiency:

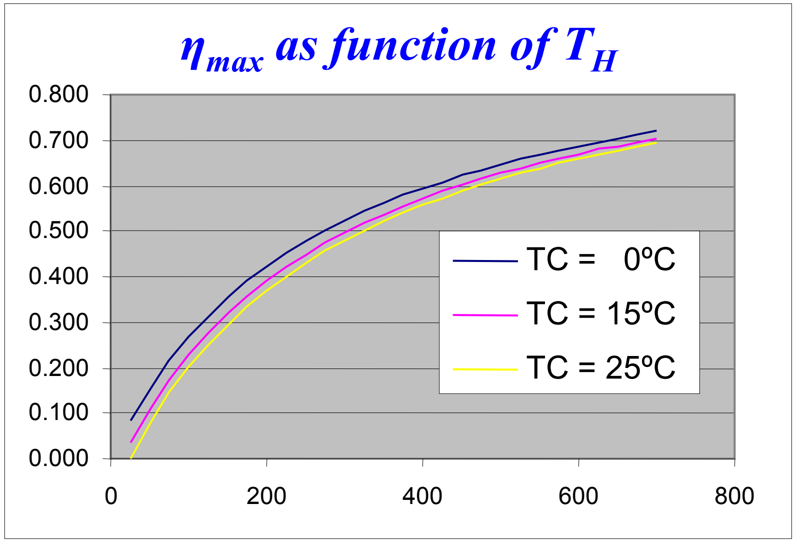
$$\eta = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H}$$

Carnot Efficiency:

$$\eta_C = \eta_{\max} = \frac{W_{\max}}{Q_H} = 1 - \frac{T_C}{T_H}$$

Exergy of Heat:

$$E_x(Q_H) = W_{\max} = Q_H \cdot \eta_{\max} = Q_H \cdot \left(1 - \frac{T_0}{T_H}\right)$$



Using Exergy in Subambient Processes?

Low Temperature Processes ⟷ Compression & Expansion

NG
@ 298 K (25°C) & 50~70 bar

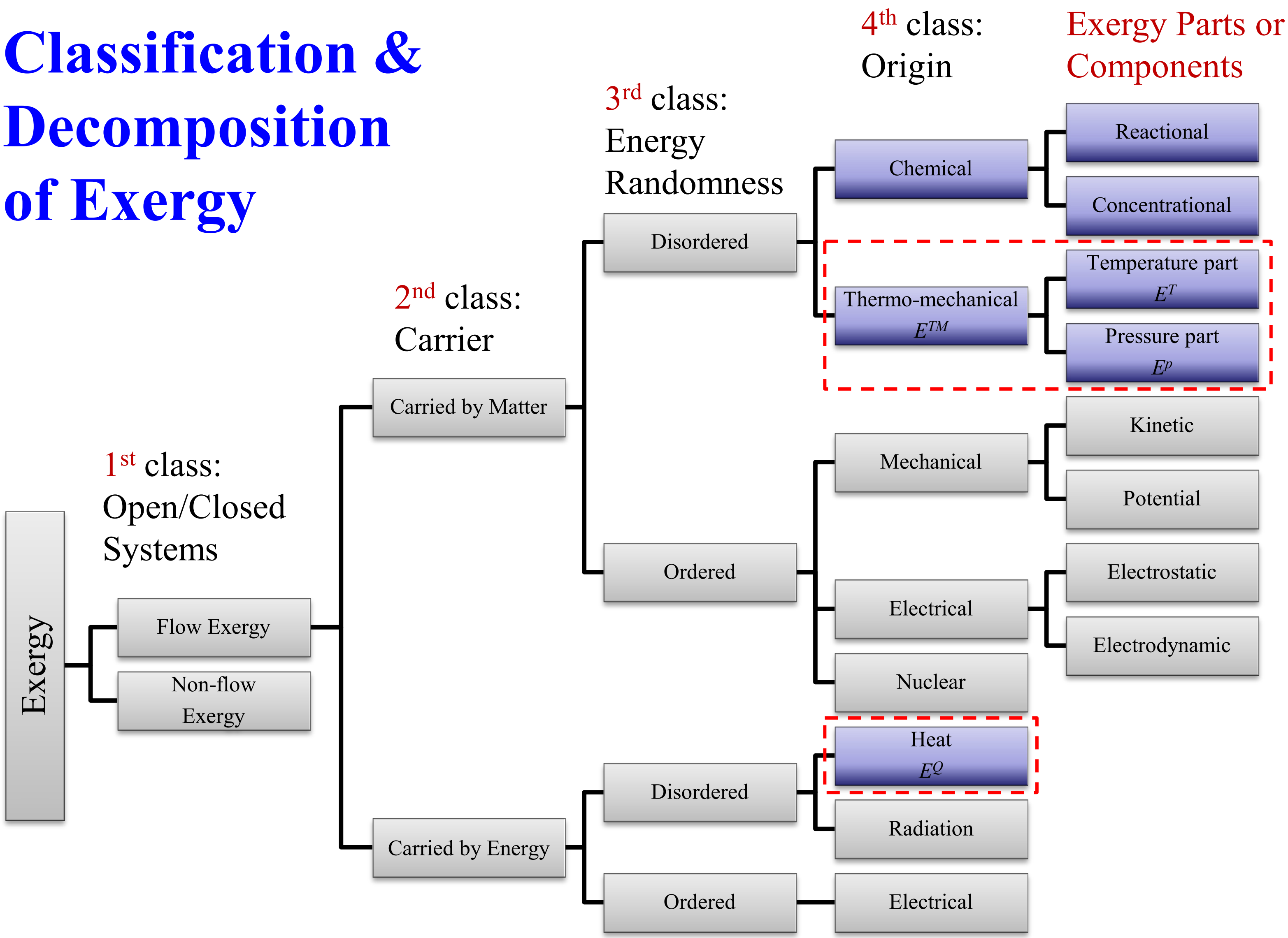
Liquefaction →

LNG
@ 109 K (-164°C) & 1 bar

↑

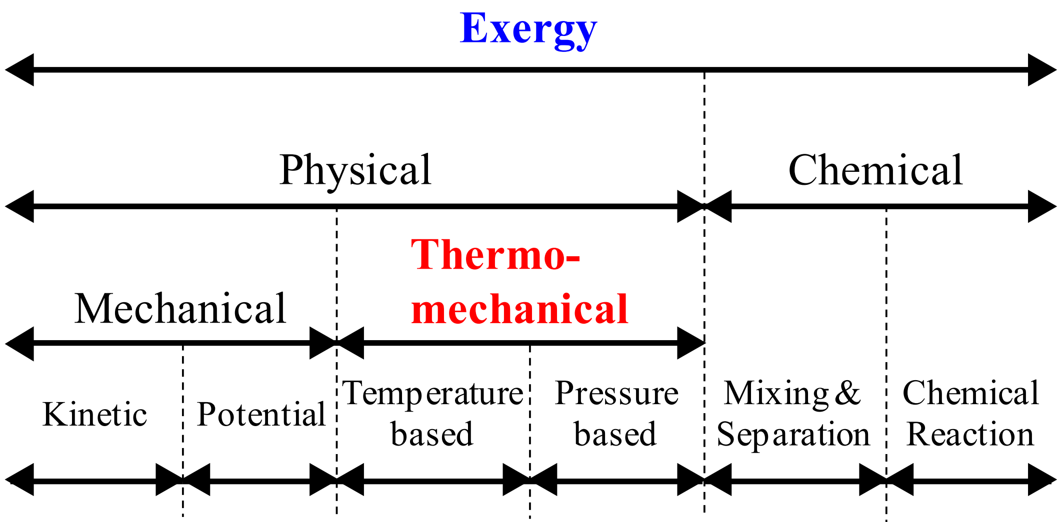
Work = Exergy

Classification & Decomposition of Exergy

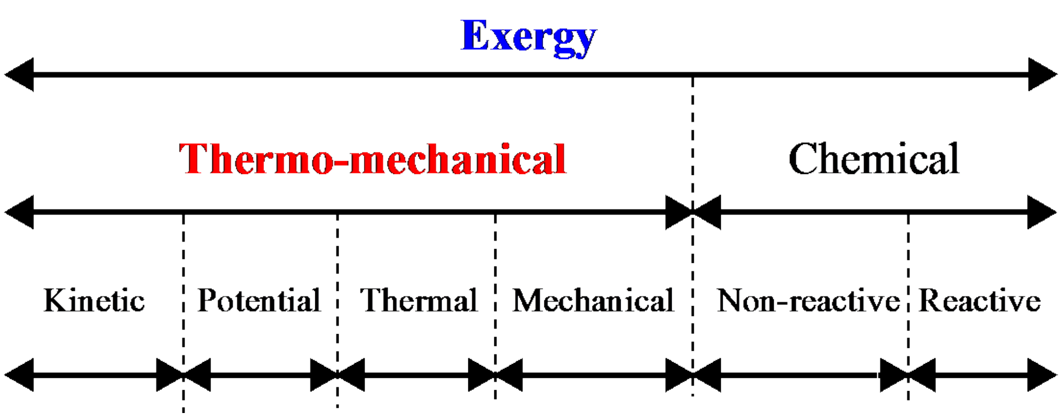


*D. Marmolejo-Correa, T. Gundersen, "A Comparison of Exergy Efficiency Definitions with focus on Low Temperature Processes", submitted to **Energy**, October 2011.*

Classification of Exergy Types



Kotas T.J., The exergy method of thermal plant analysis, Krieger Publishing Company, Florida, USA, 1995.



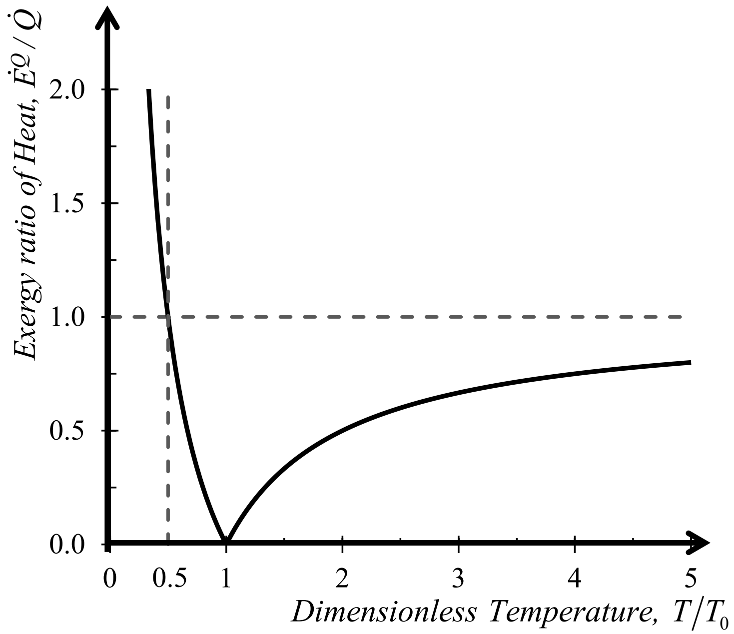
Bejan A., Tsatsaronis G. and Moran M., Thermal design and optimization, Wiley, New York City, 1996.

Our Modest Contributions to Exergy

- Discussed the Various **Classifications**
  - OK, it is only a matter of words, but?
- Looked for Ways to **Standardize** Terms and Definitions
- Illustrated the importance of **Decomposition**
  - Explains behavior of Compressors/Expanders above/below T_0
  - Results in Exergy Efficiencies that measure Design Quality
- Discussed various **Exergy Efficiencies**
  - Compared existing ones applied to LNG Processes
  - Proposed a new Exergy Efficiency based on Sources & Sinks
- New **"Exergetic" Temperatures** (beyond Scope here)
- New Graphical Diagrams and Representations
- New **Targeting** Procedure for Exergy

Special Behavior of Temperature based Exergy

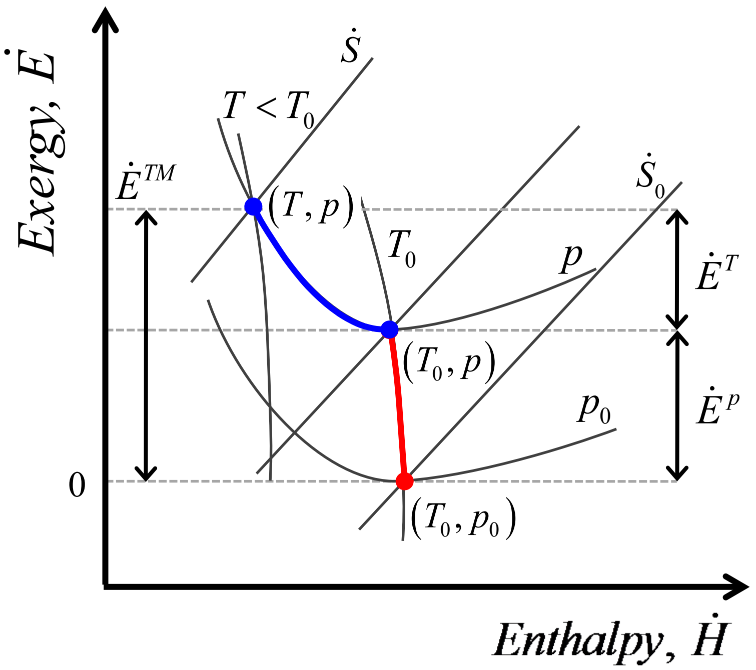
Exergy of Heat



$$\dot{E} = \dot{Q} \cdot \left(1 - \frac{T_0}{T}\right) \quad \text{for} \quad T \geq T_0$$

$$\dot{E} = \dot{Q} \cdot \left(\frac{T}{T_0} - 1\right) \quad \text{for} \quad T \leq T_0$$

Thermo-mechanical Exergy of a Stream



$$\dot{E} = \dot{E}^T + \dot{E}^p$$

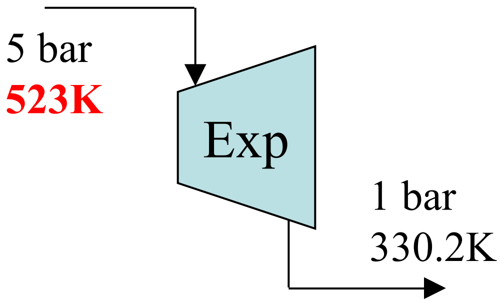
Consider Expansion above/below Ambient

Thermo-mechanical Exergy: $e^{TM} = e^{T} + e^{P}$

$$e^{T} = C_p \left[T - T_0 \left(1 + \ln \frac{T}{T_0} \right) \right]$$

Assume Isentropic Expansion of Ideal Gas, with C_p = 1.0 kJ/kgK and $k = C_p / C_v$ = 1.4

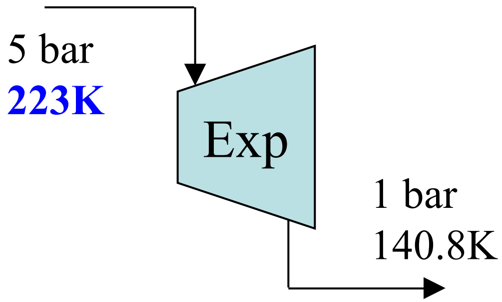
$$e^{P} = T_0 R \ln \frac{P}{P_0} = \frac{k-1}{k} C_p T_0 \ln \frac{P}{P_0}$$



$$\frac{\dot{W}}{\dot{m}} = 137.65 + 55.76 = \underline{\underline{193.41 \text{ kJ/kg}}}$$

Ambient T_0=298 K

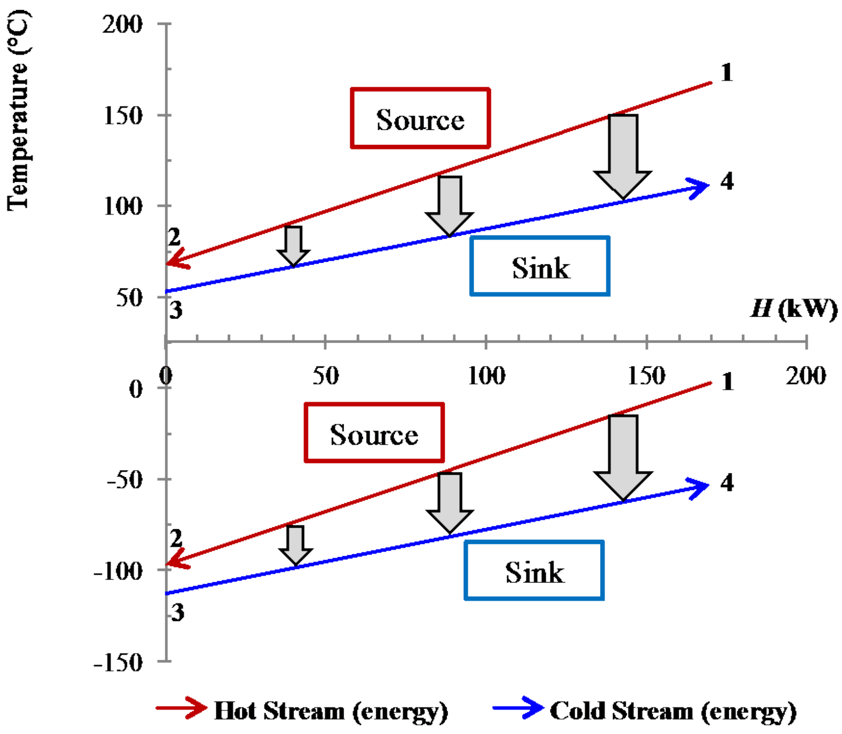
$$\dot{W}_{max} = -\Delta \dot{E} = -\dot{m} \cdot (\Delta e^{P} + \Delta e^{T})$$



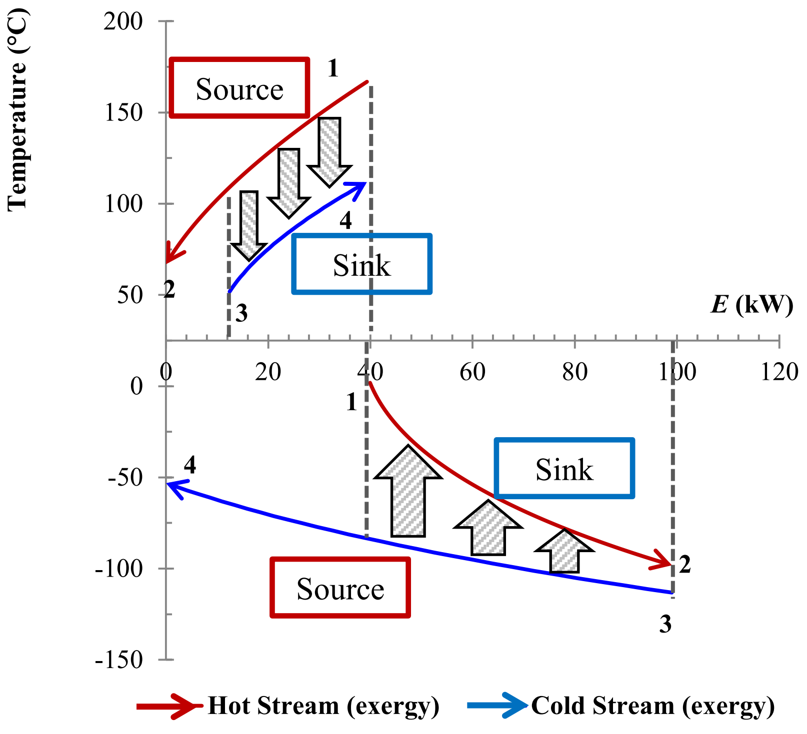
$$\frac{\dot{W}}{\dot{m}} = 137.65 - 54.83 = \underline{\underline{82.82 \text{ kJ/kg}}}$$

Consider Heat and Exergy Transfer above/below Ambient Temperature

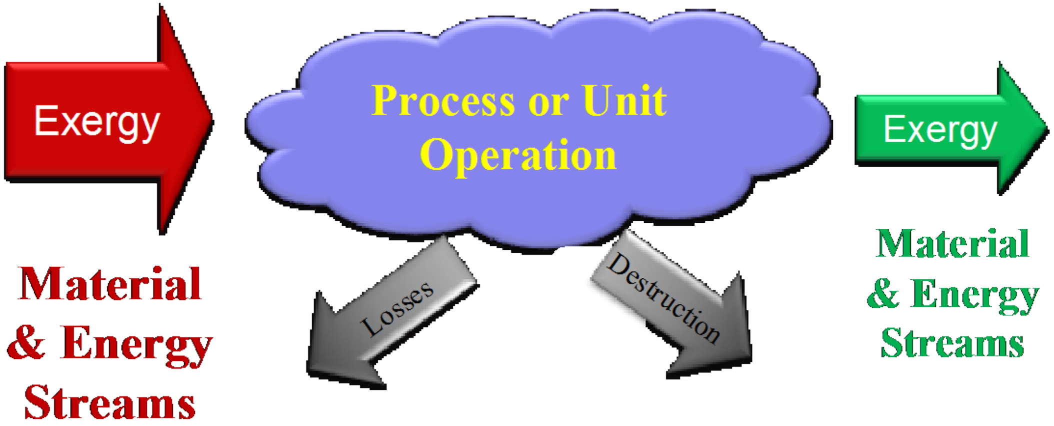
Heat Transfer

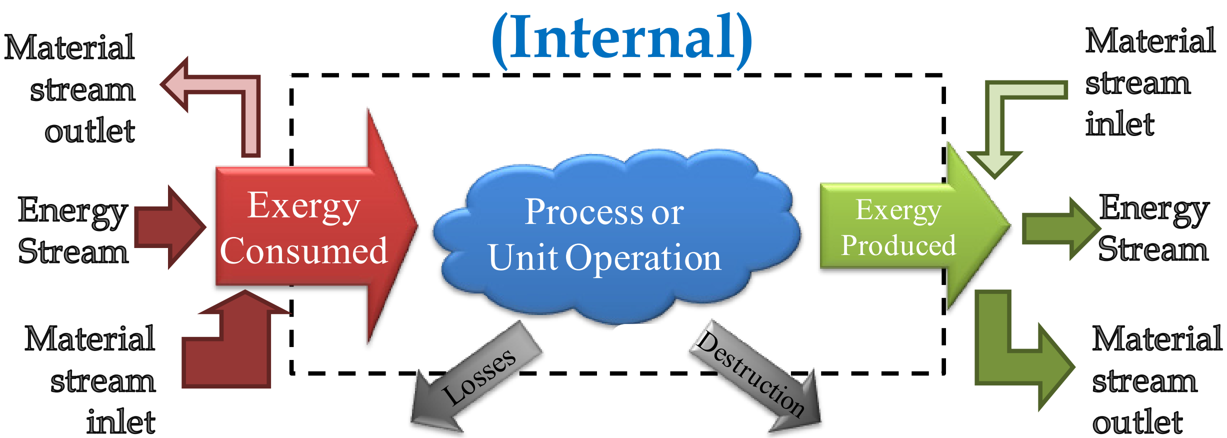


Exergy Transfer



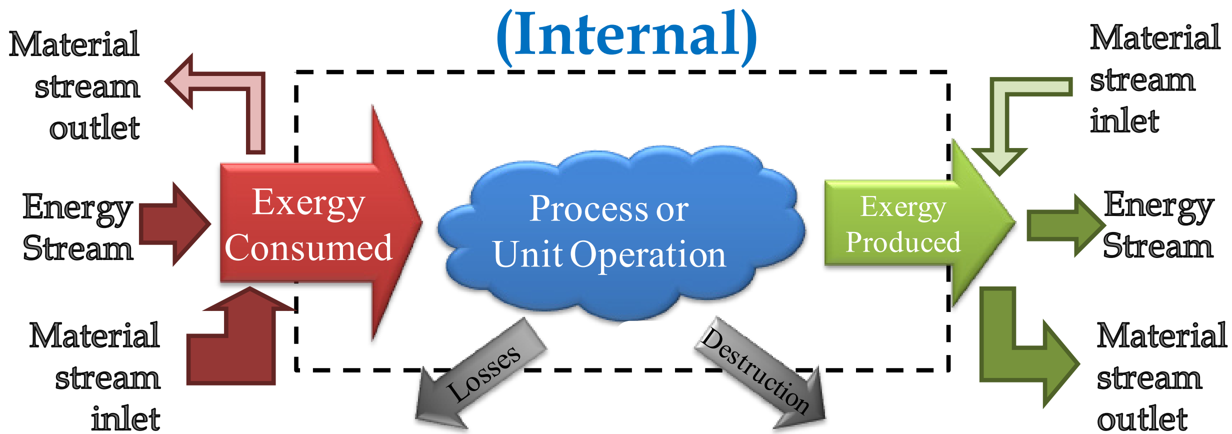
What is Exergy Efficiency?





*D. Marmolejo-Correa, T. Gundersen, "Challenges in Low Temperature Process Design and Optimization – Using Exergy as the Objective?", **AIChE Mtg.**, Salt Lake City, November, 2010.*

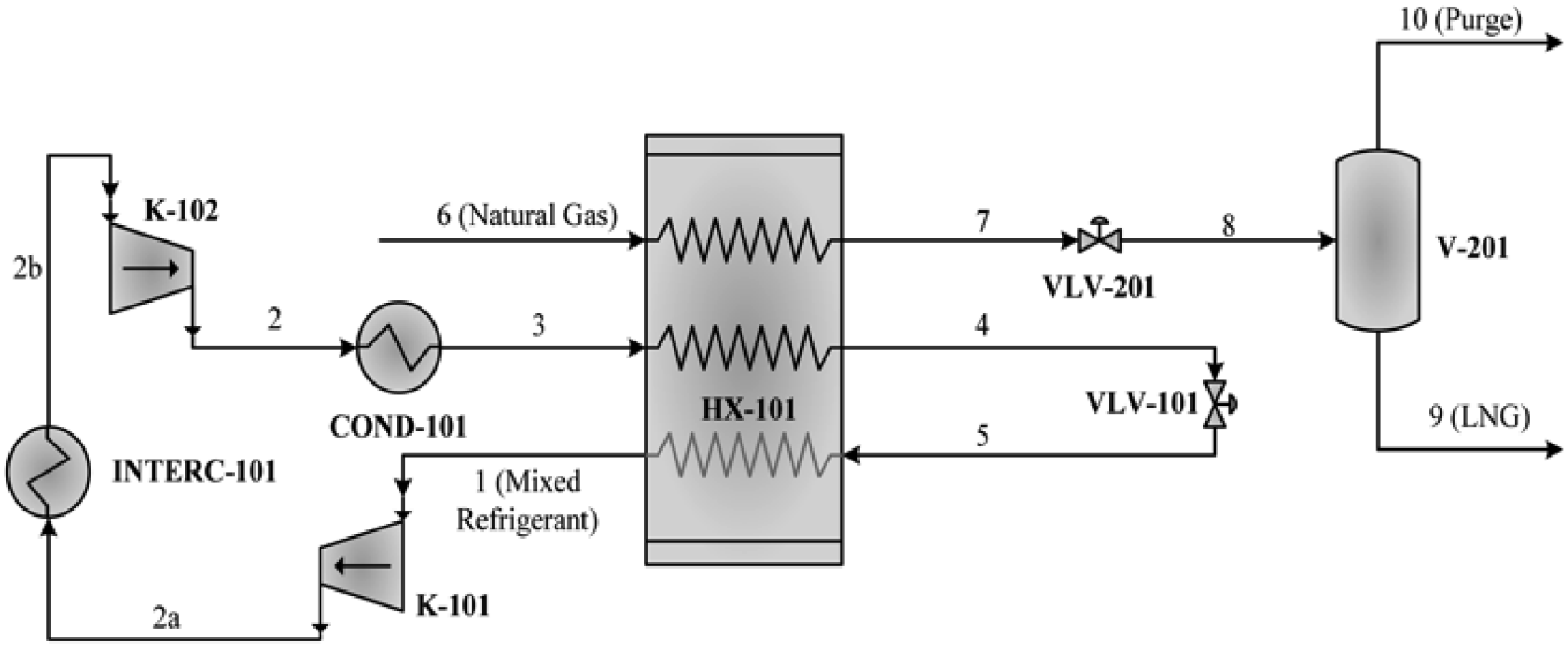
Exergy Efficiency Definitions



Brodyansky et al. (1994)	Bejan et al. (1996)	Kotas (1995)	Marmolejo-Correa and Gundersen (2012)
"Exergy Efficiency"	***"Exergetic Efficiency"***	***"Rational Efficiency"***	***"Exergy Transfer Effectiveness (ETE)"***
$\eta_e = \frac{\dot{E}_{out} - \dot{E}_{transit}}{\dot{E}_{in} - \dot{E}_{transit}}$	$\varepsilon = \frac{\dot{E}_{products}}{\dot{E}_{fuels}}$	$\psi = \frac{\dot{E}_{out,\,desired}}{\dot{E}_{in,\,necessary}}$	$\varepsilon_{tr} = \frac{\dot{E}_{sinks}}{\dot{E}_{sources}}$

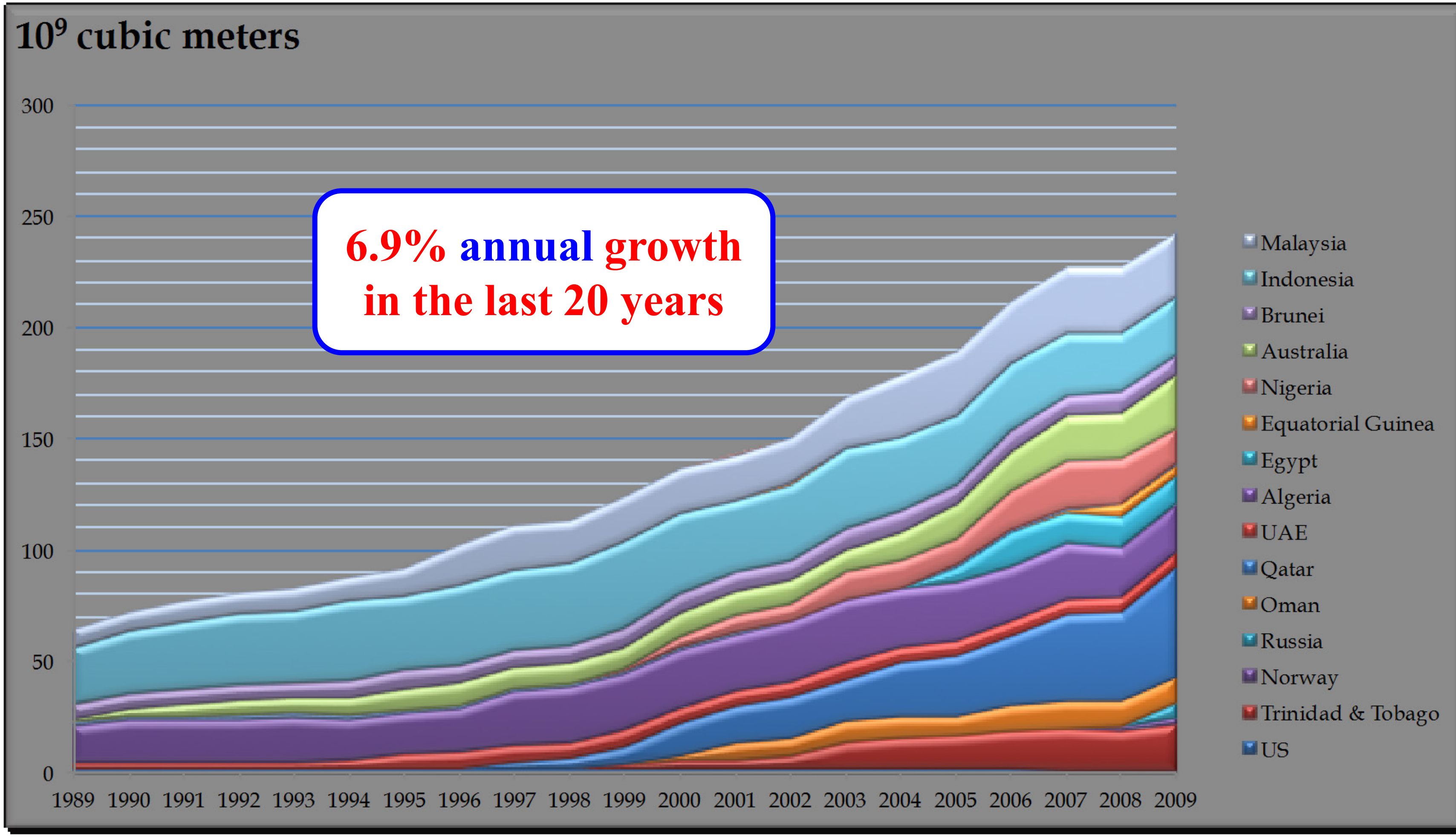
D. Marmolejo-Correa, T. Gundersen, "Exergy Transfer Effectiveness for Low Temperature Processes", to be submitted to ***Intl. Jl. of Thermodynamics****, 2012.*

Applied to the simple PRICO Process



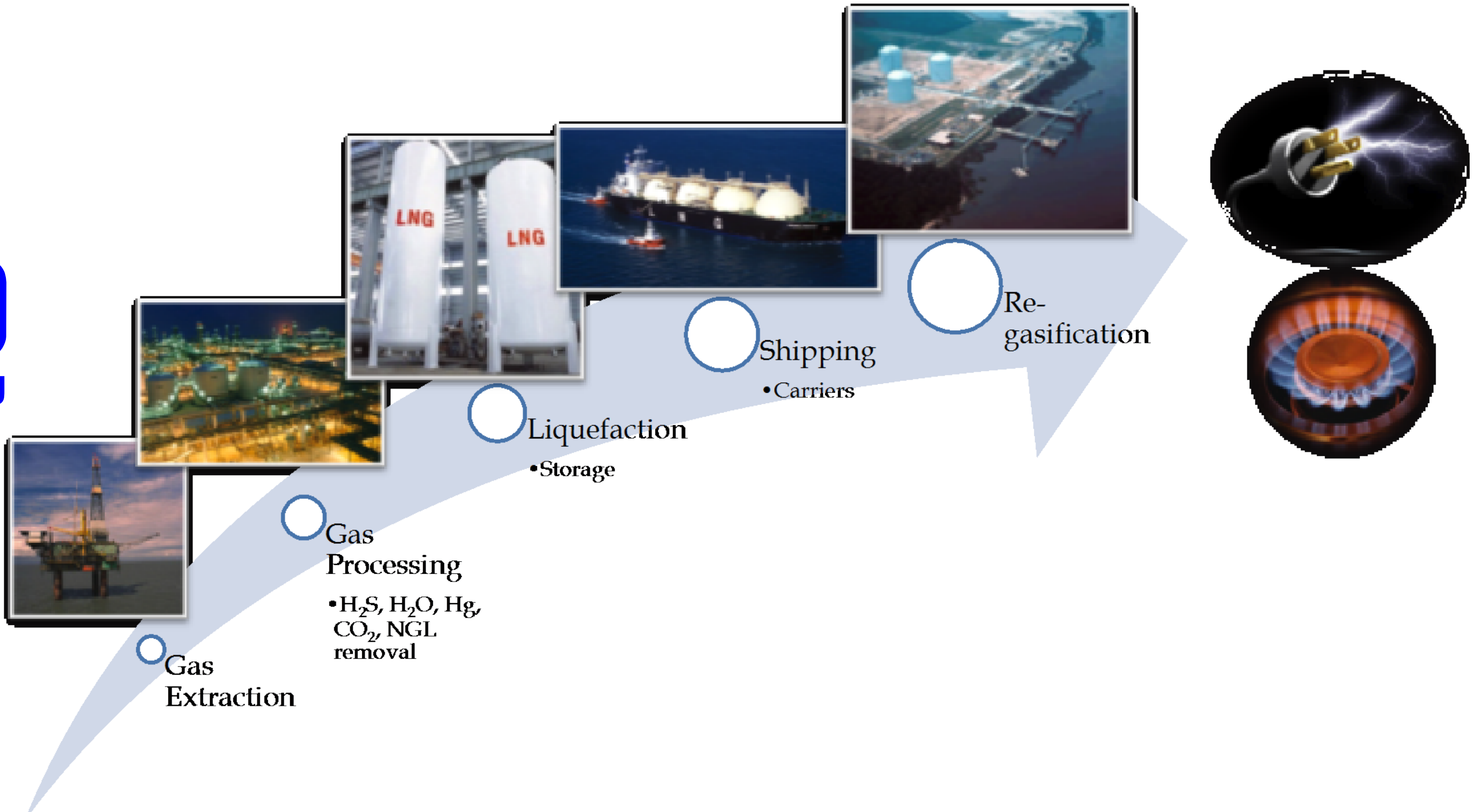
Brodyansky et al. (1994)	Bejan et al. (1996)	Kotas (1995)	Marmolejo-Correa and Gundersen (2012)
$\eta_e = \dfrac{\dot{E}_8^T}{\dot{E}_6^T + \Delta\dot{E}_{6-8}^p + \dot{W}_{tot}} = \mathbf{0.508}$	$\varepsilon = \dfrac{\Delta\dot{E}_{6-8}^{TM}}{\dot{W}_{tot}} = \mathbf{0.323}$	$\psi = \dfrac{\Delta\dot{E}_{6-8}^T}{\Delta\dot{E}_{6-8}^p + \dot{W}_{tot}} = \mathbf{0.500}$	$\varepsilon_{tr} = \dfrac{\dot{E}_8^T}{\dot{E}_6^T + \Delta\dot{E}_{6-8}^p + \dot{W}_{tot}} = \mathbf{0.508}$

LNG as energy carrier: International Trade

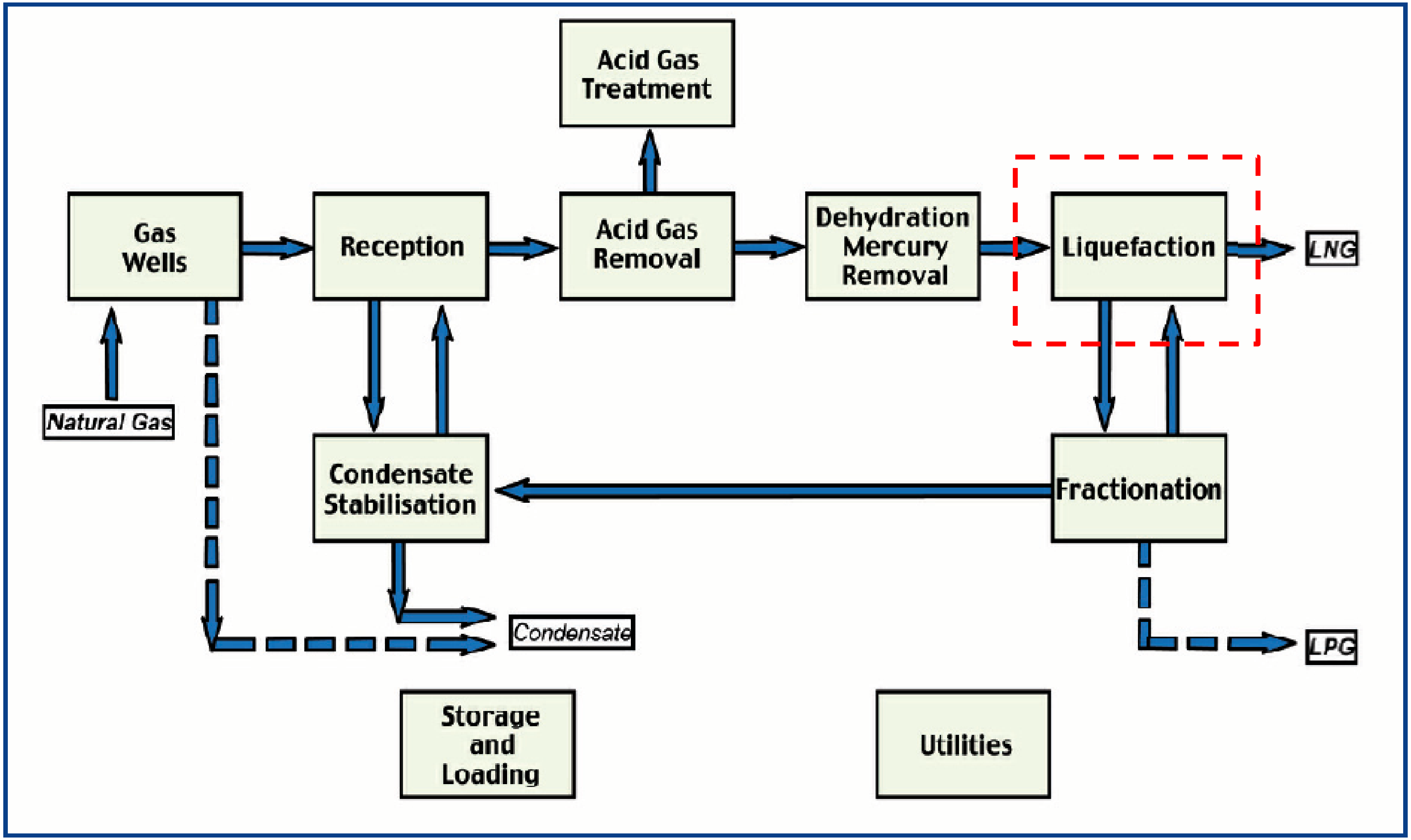


Source: BP Statistical Review of World Energy 1990-2010

Liquefied Natural Gas Value Chain

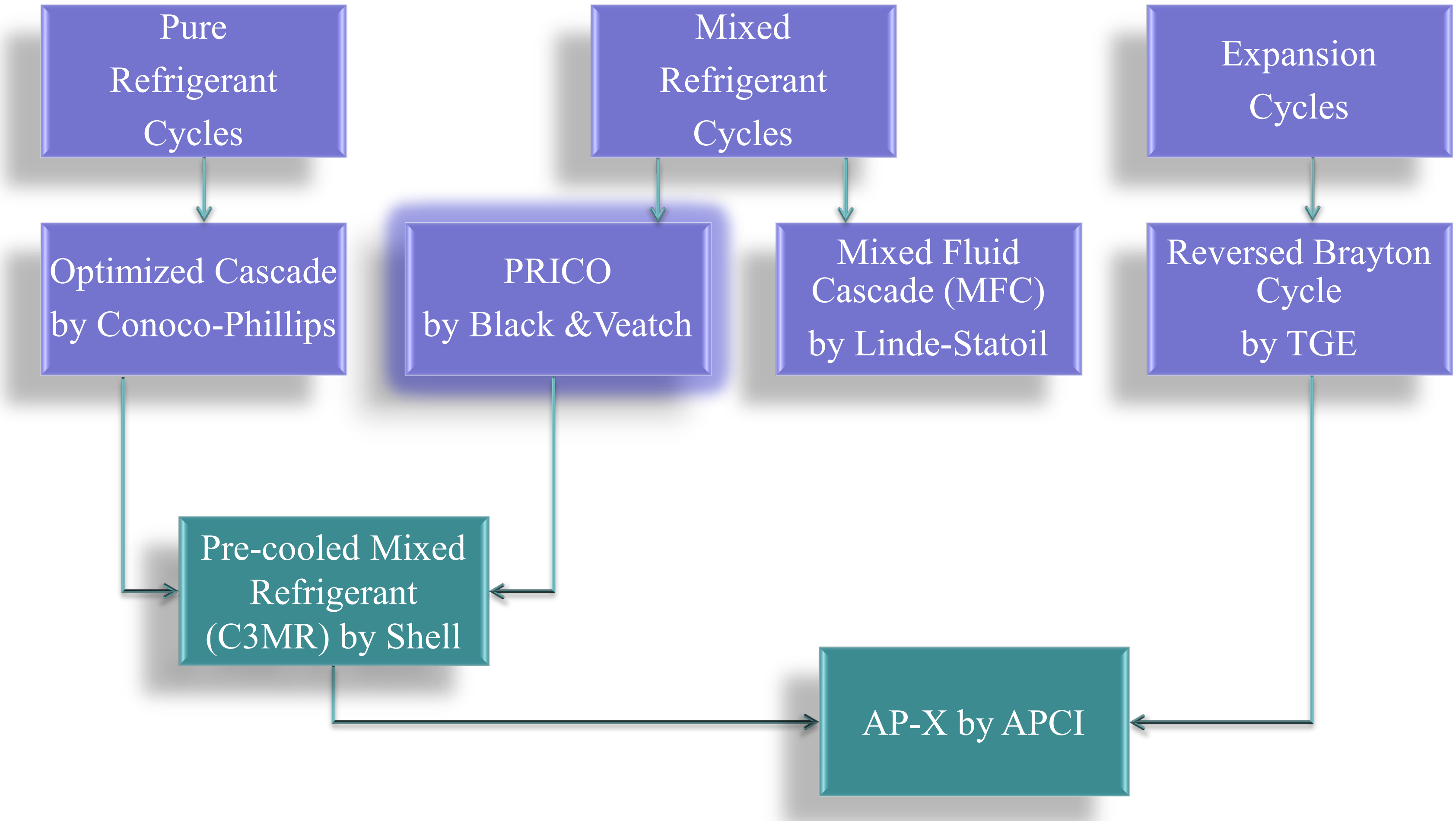


Liquefaction of Natural Gas

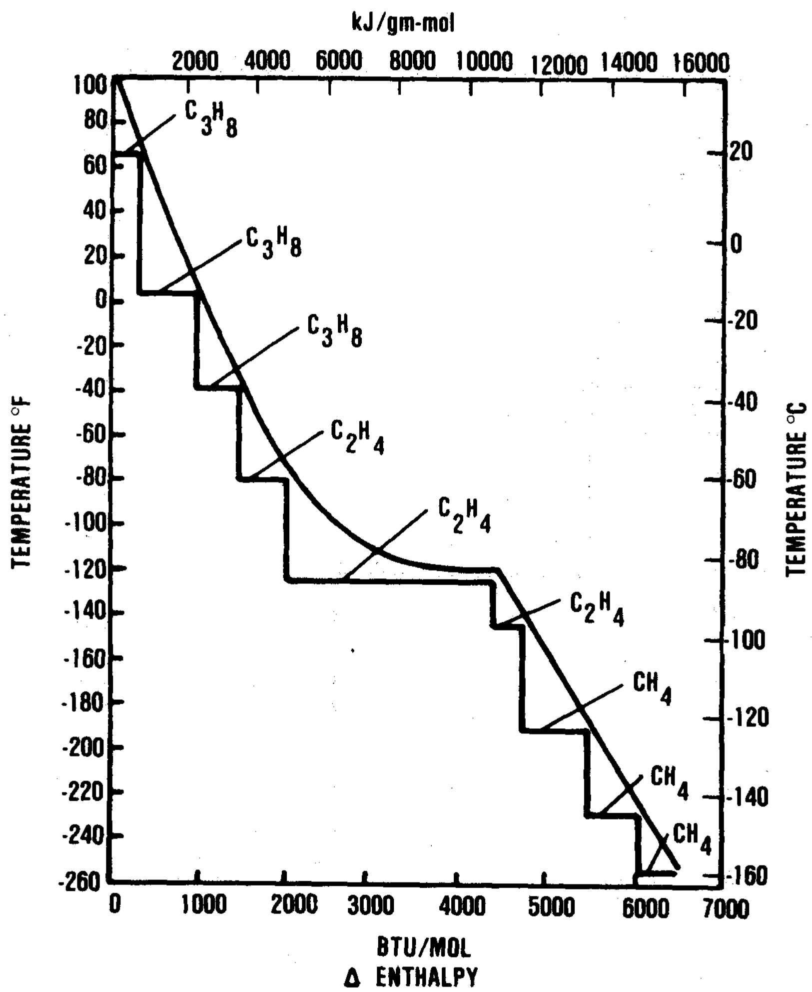


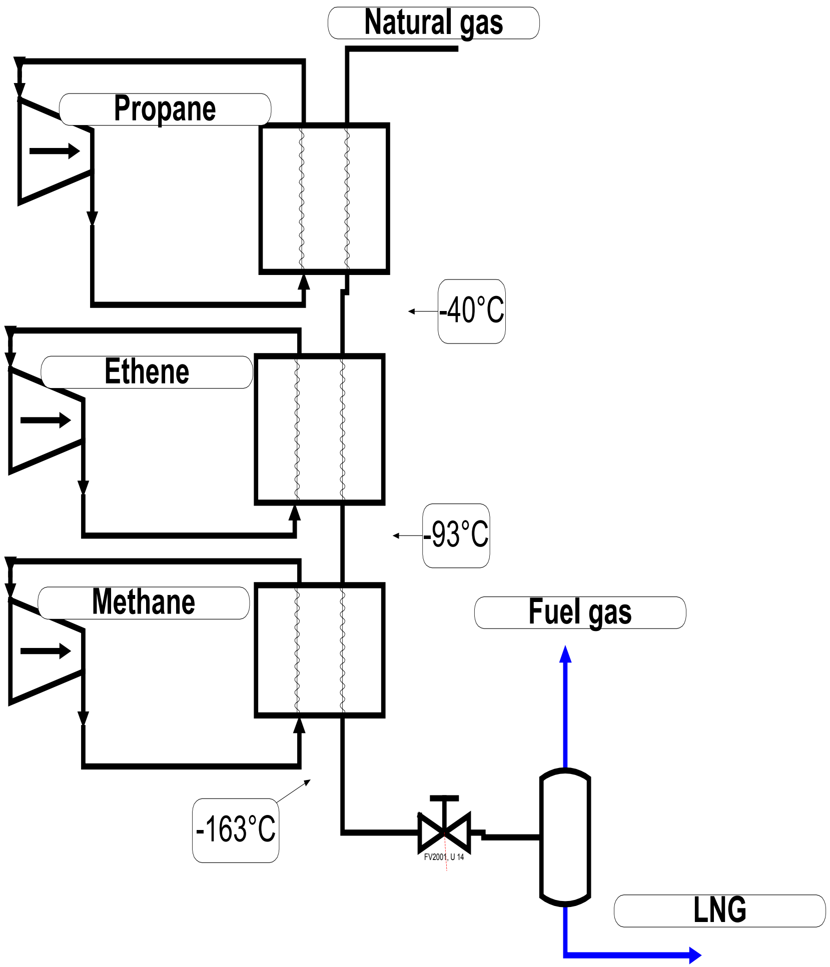
T. Shukri (Poster Wheeler, UK), "LNG Technology Selection", Hydrocarbon Engineering, February 2004

Some LNG Processes

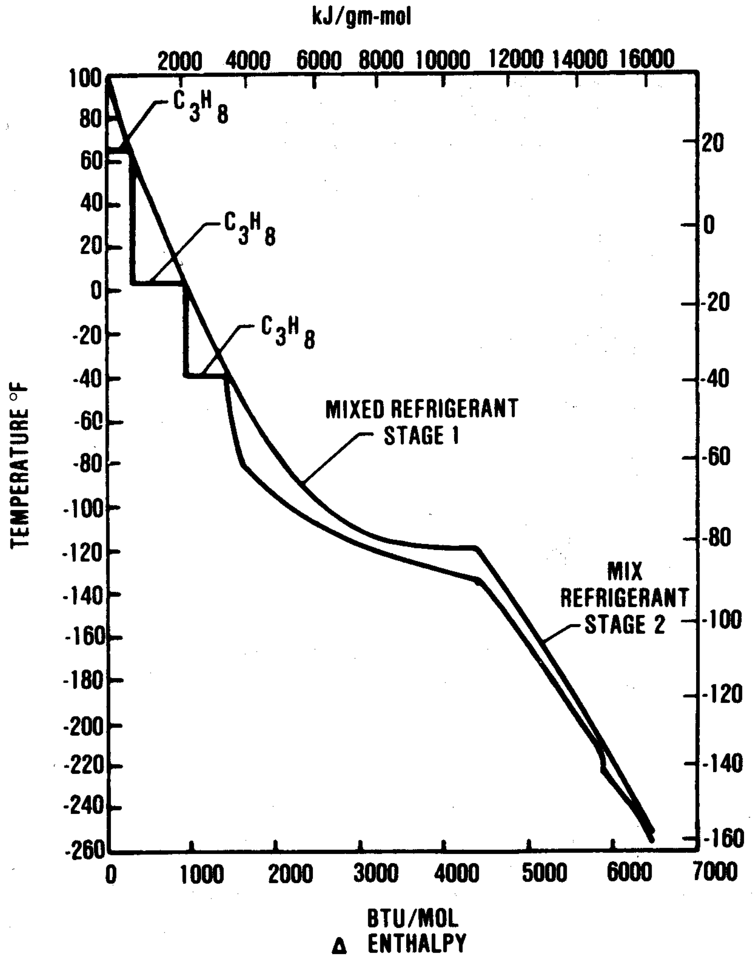


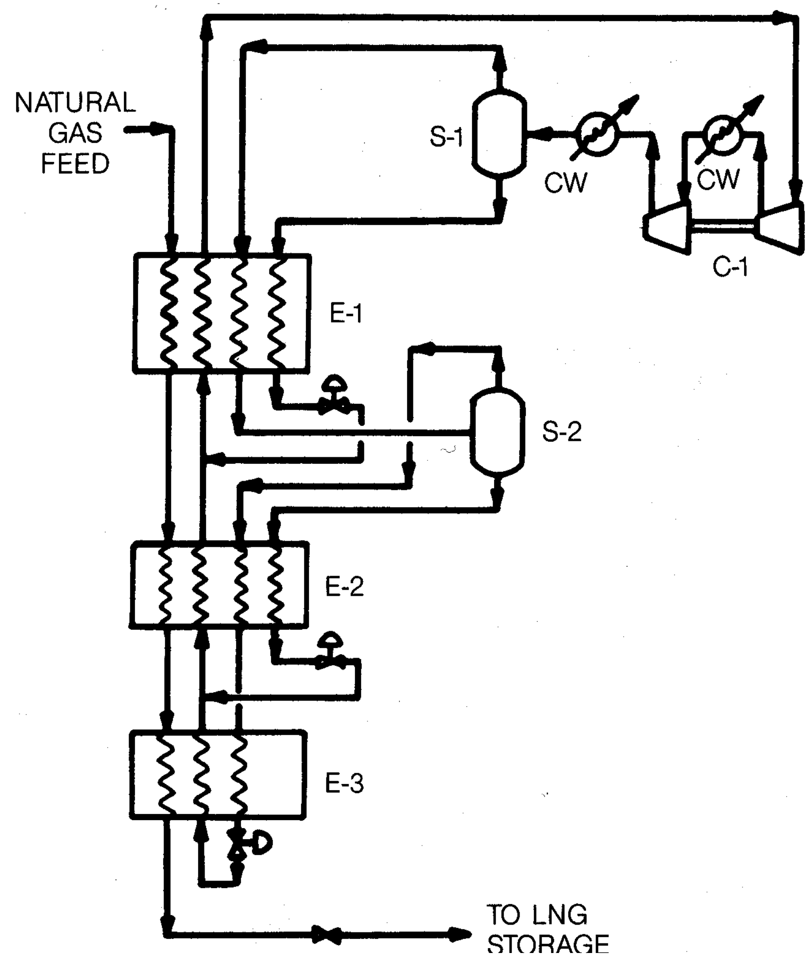
Cascade Liquefaction Process





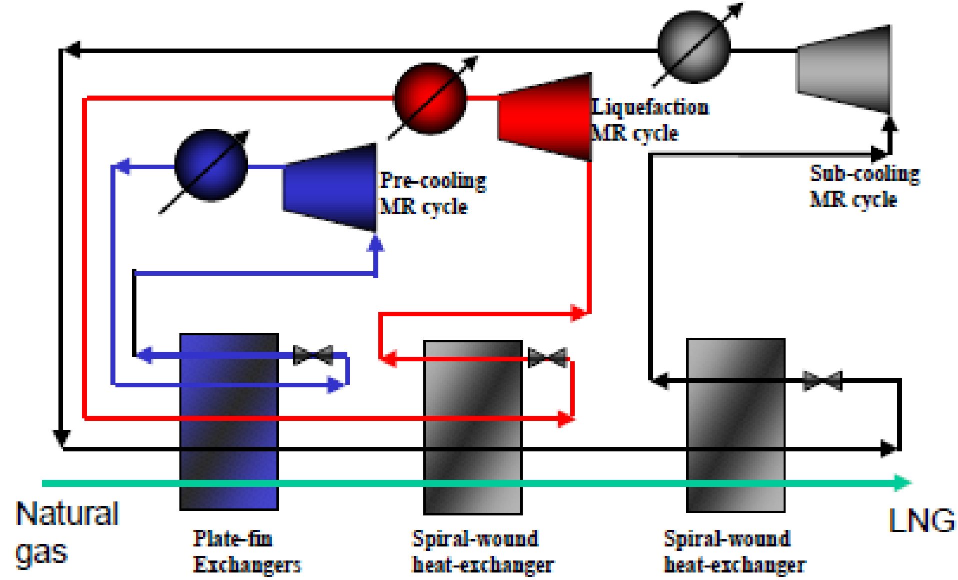
Liquefaction using Multicomponent Mixtures

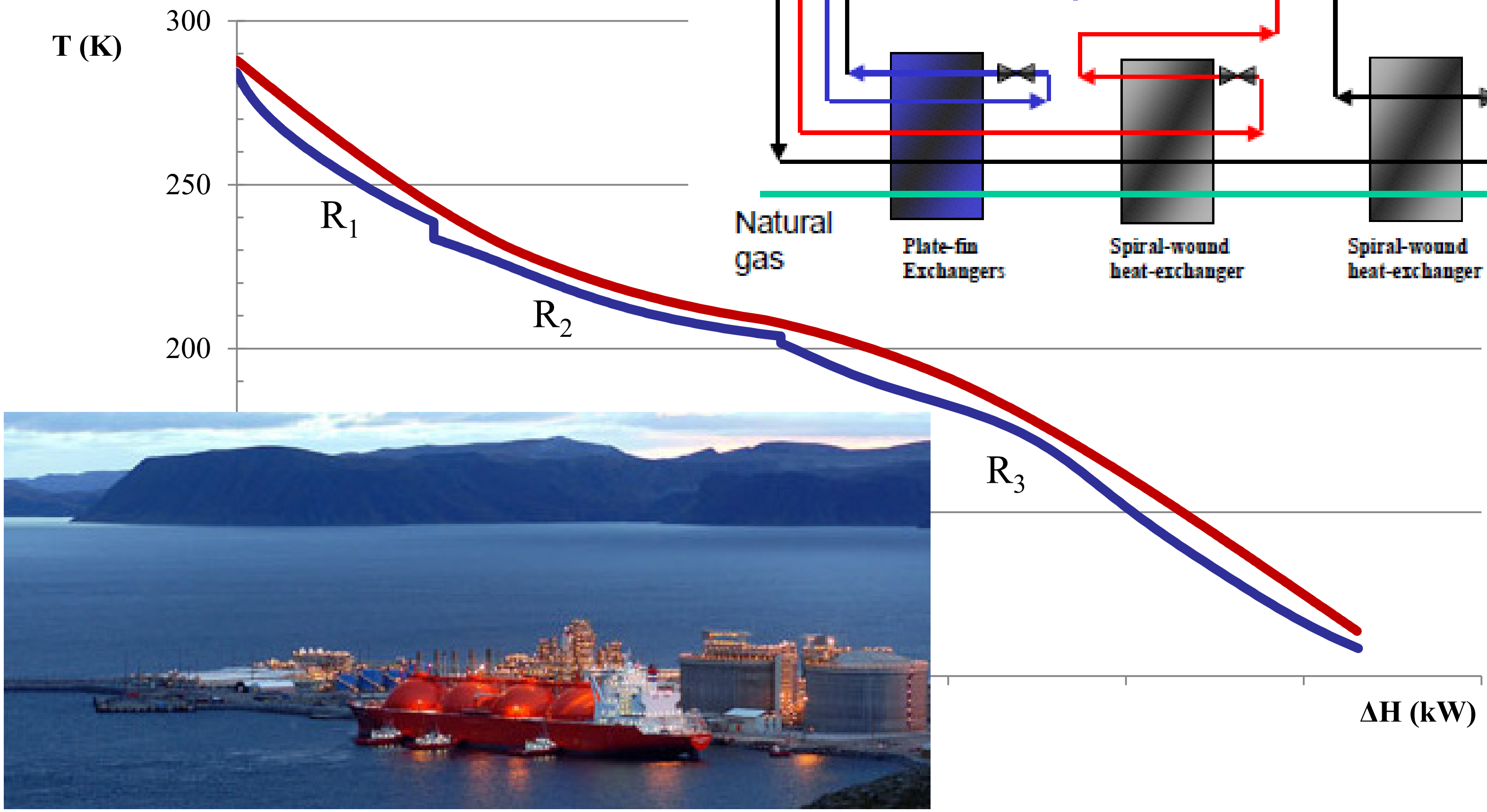




Linde and Statoil: Mixed Fluid Cascade

3 Mixed Refrigerants





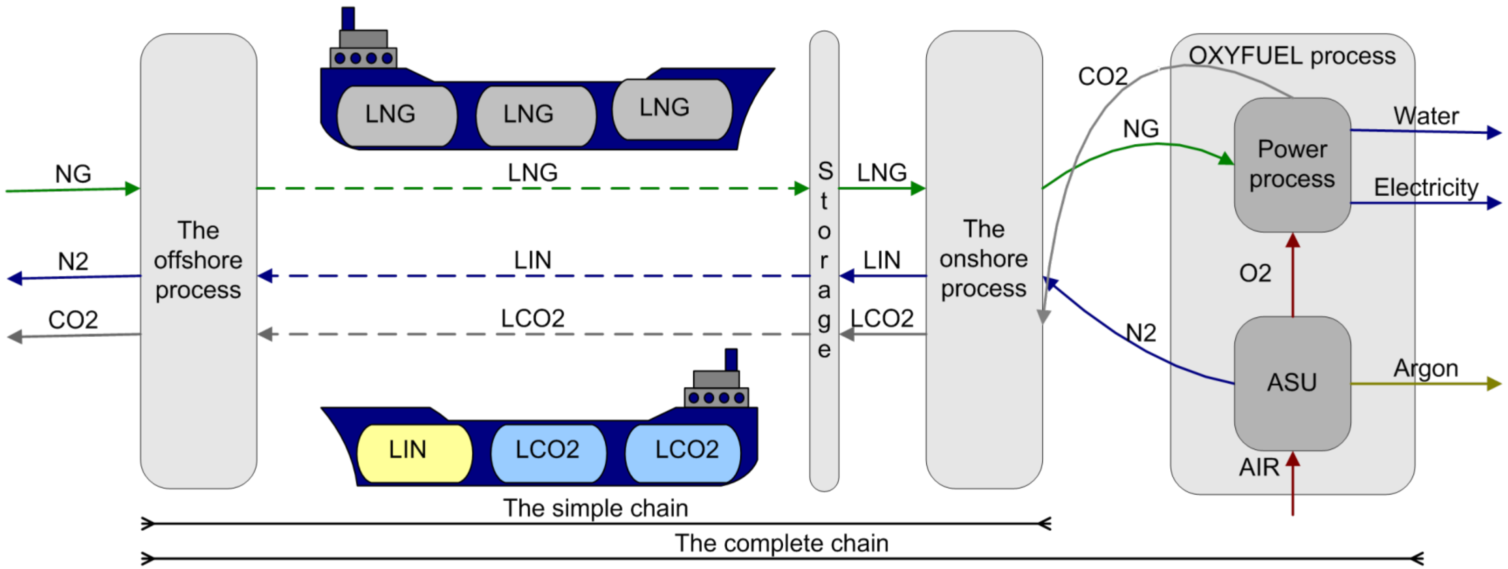
A new Process Synthesis Methodology utilizing Pressure based Exergy in Subambient Processes

ExPAnD = Extended Pinch Analysis and Design

- The Classical Heat Recovery Problem was redefined
  - *"Given a Set of Process Streams with a Supply and Target State (Temperature, Pressure and the resulting Phase), as well as Utilities for Heating and Cooling ➔ Design a System of Heat Exchangers, Expanders, Pumps and Compressors in such a way that the Irreversibilities (or Costs) are minimized"*
- 10 Heuristic Rules were developed
- Automated by new Superstructure and Math Programming

*Aspelund A., Berstad D.O. and Gundersen T. "An Extended Pinch Analysis and Design Procedure utilizing Pressure based Exergy for Subambient Cooling", **Applied Thermal Engineering**, vol. 27, No. 16, pp. 2633-2649, November 2007.*

Application: A Liquefied Energy Chain (LEC)



- **Key Features of the "LEC" Concept**
  - Utilization of **Stranded** Natural Gas for Power Production
  - High **Exergy Efficiency** of 46.4% (vs. 42.0% for traditional)
  - **Innovative** and Cost Effective solution to the **CCS** Problem
  - CO_2 replaces Natural Gas injection for **EOR**
  - **Combined** Transport Chain for Energy (LNG) and CO_2

*Aspelund A. and Gundersen T. "A Liquefied Energy Chain for Transport and Utilization of Natural Gas for Power Production with CO_2 Capture and Storage – Part 1", **Journal of Applied Energy**, vol. 86, pp. 781-792, 2009.*

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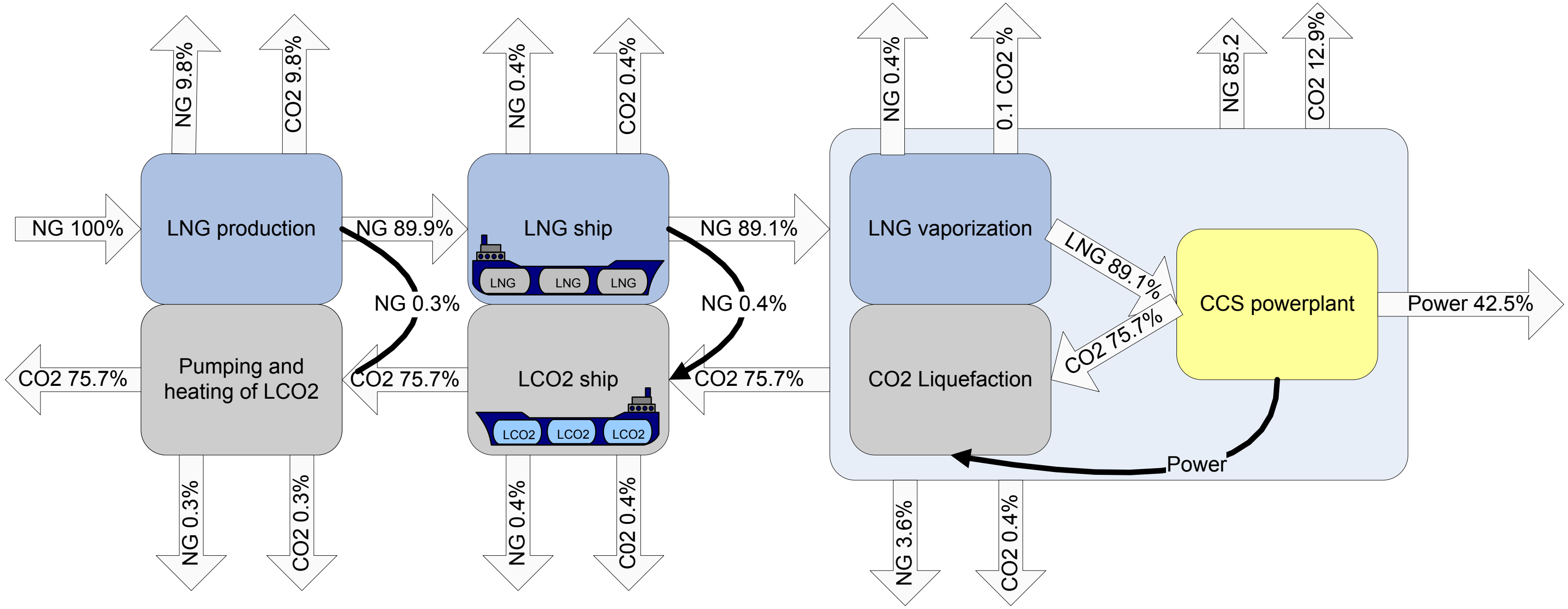
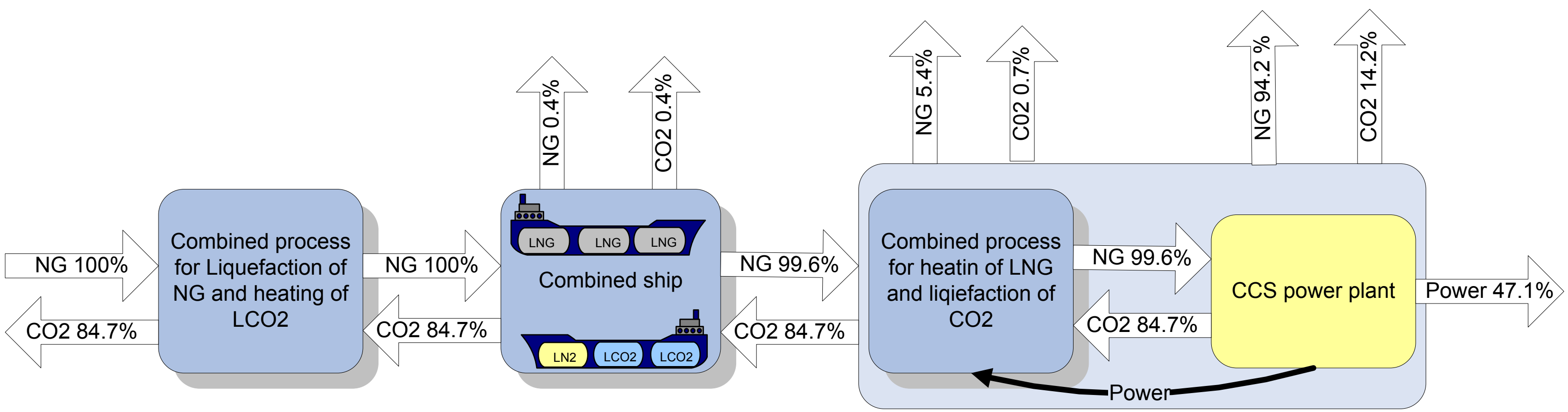


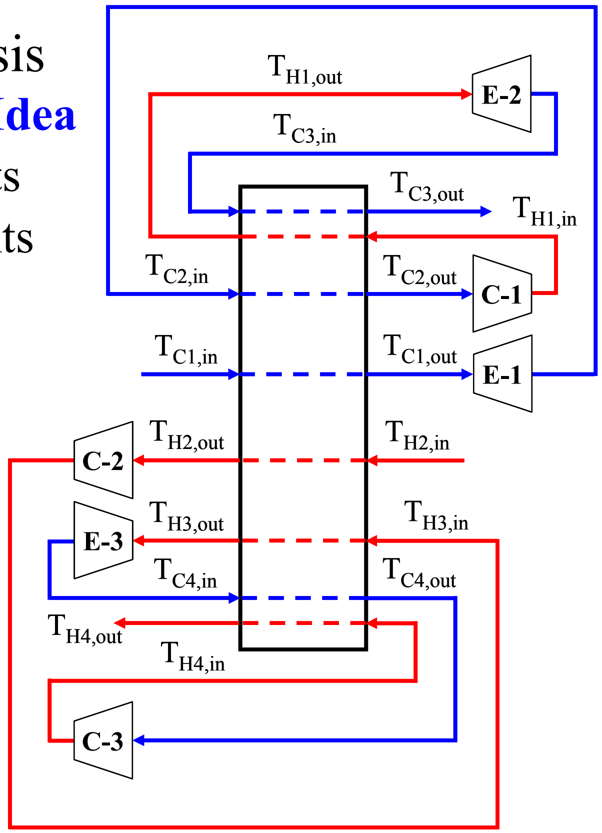
”Conventional” ship-based energychain: Loss NG during transport 14%, CO2 emissions 24.3%, Efficiency 42.5%



New combined energy-chain: Loss NG during transport 5.8%, CO2 emissions 15.3%, Efficiency 47.1%

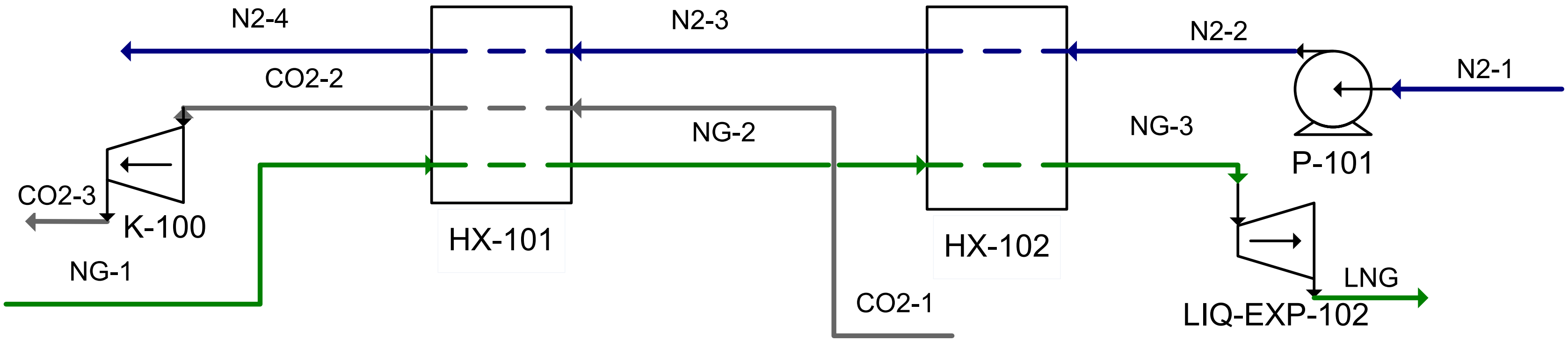
Developing the Liquefied Energy Chain
– Manual and Automated Design Procedures

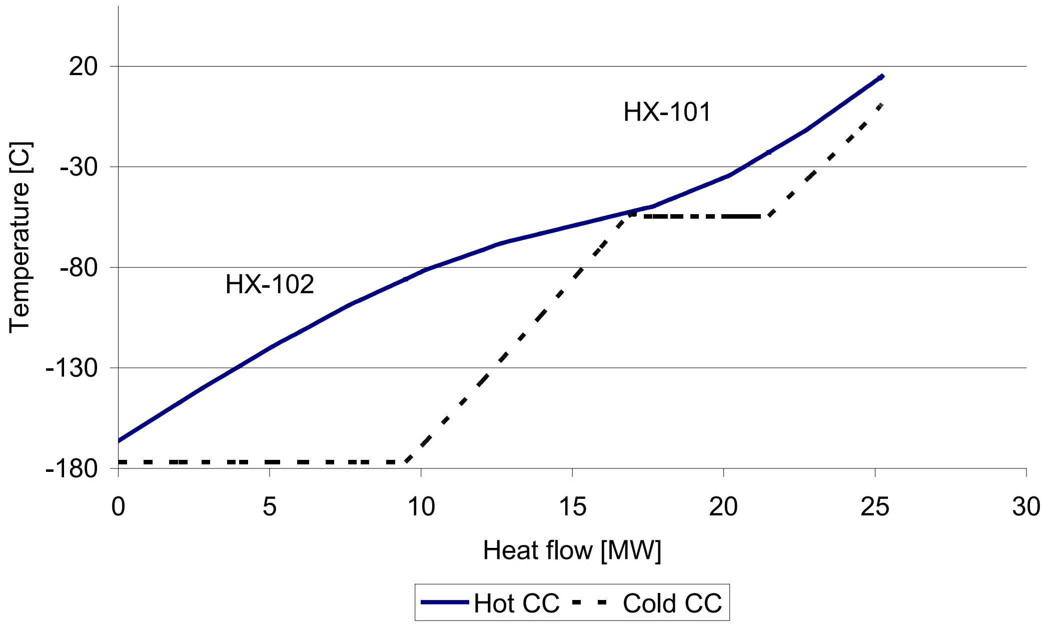
- **The ExPAnD Methodology was used**
  - Original version uses 10 Heuristic Rules
  - Combines Pinch Analysis & Exergy Analysis
    - Composite & Grand Composite Curves for **Idea Generation** related to Process Improvements
    - Exergy Efficiency to **Quantify** Improvements
  - Optimization has also been included
    - New Superstructure allows **Simultaneous** Optimization of Networks with Heat Exchangers, Pumps, Compressors and Expanders using Math Programming



*A. Wechsung, A. Aspelund, T. Gundersen and P.I. Barton, "Synthesis of Heat Exchanger Networks at Sub-Ambient Conditions with Compression and Expansion of Process Streams", **AIChE Jl.**, vol. 57, no. 8, pp. 2090-2108, 2011.*

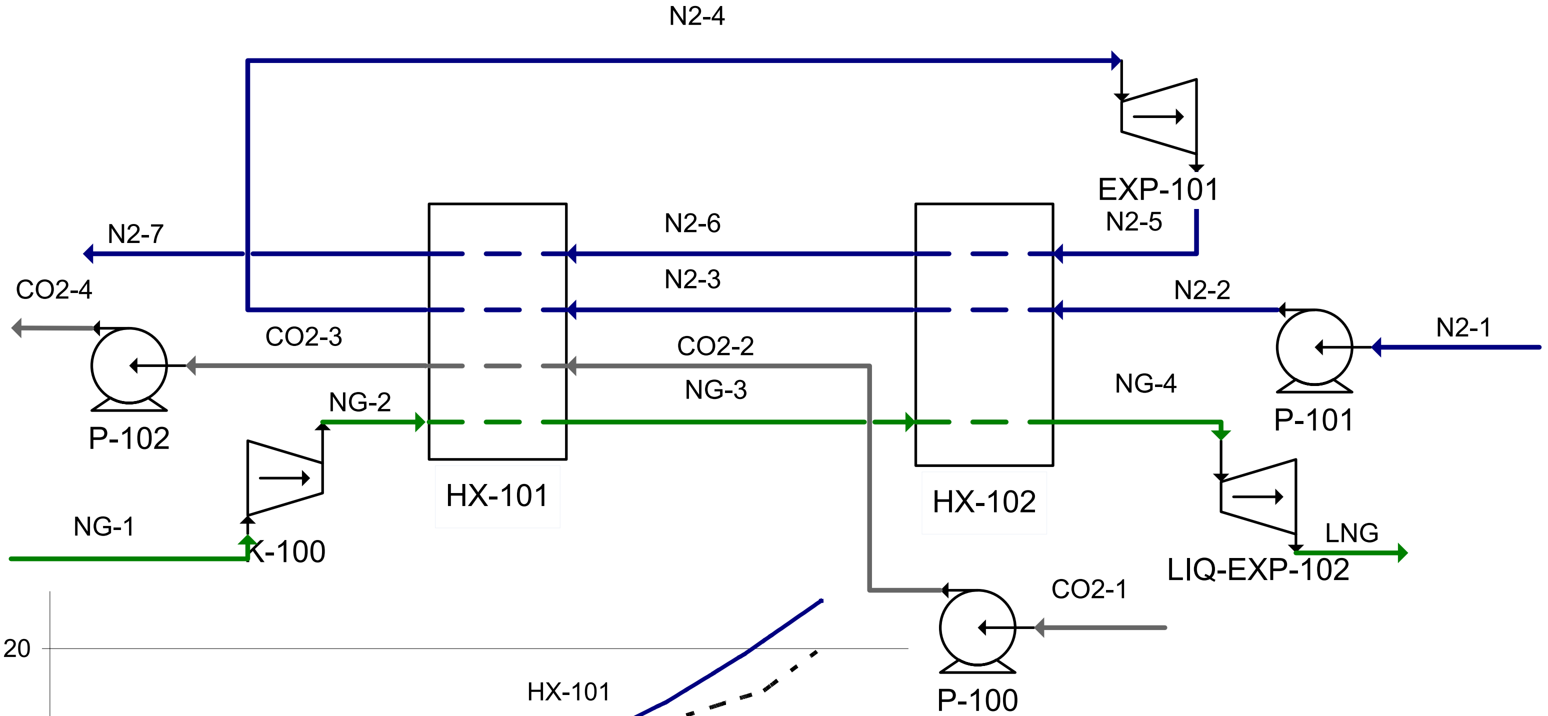
Offshore Process **without** Pressure Manipulations

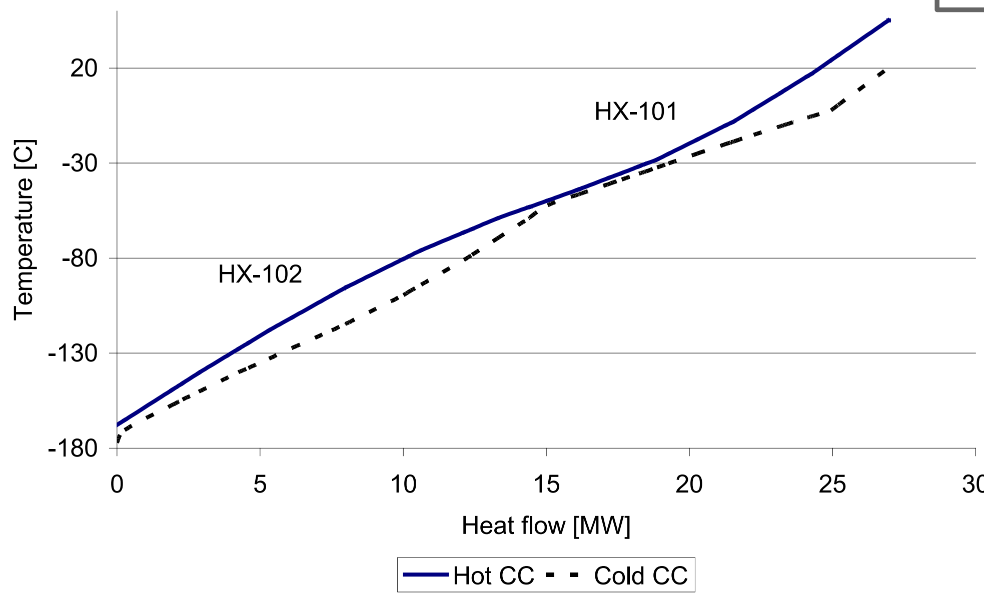




- LIN: 1.75 kg/kgLNG
- LCO_2: 0.41 kg/kgLNG
- Power Deficit
- Exergy Efficiency: **55.7%**

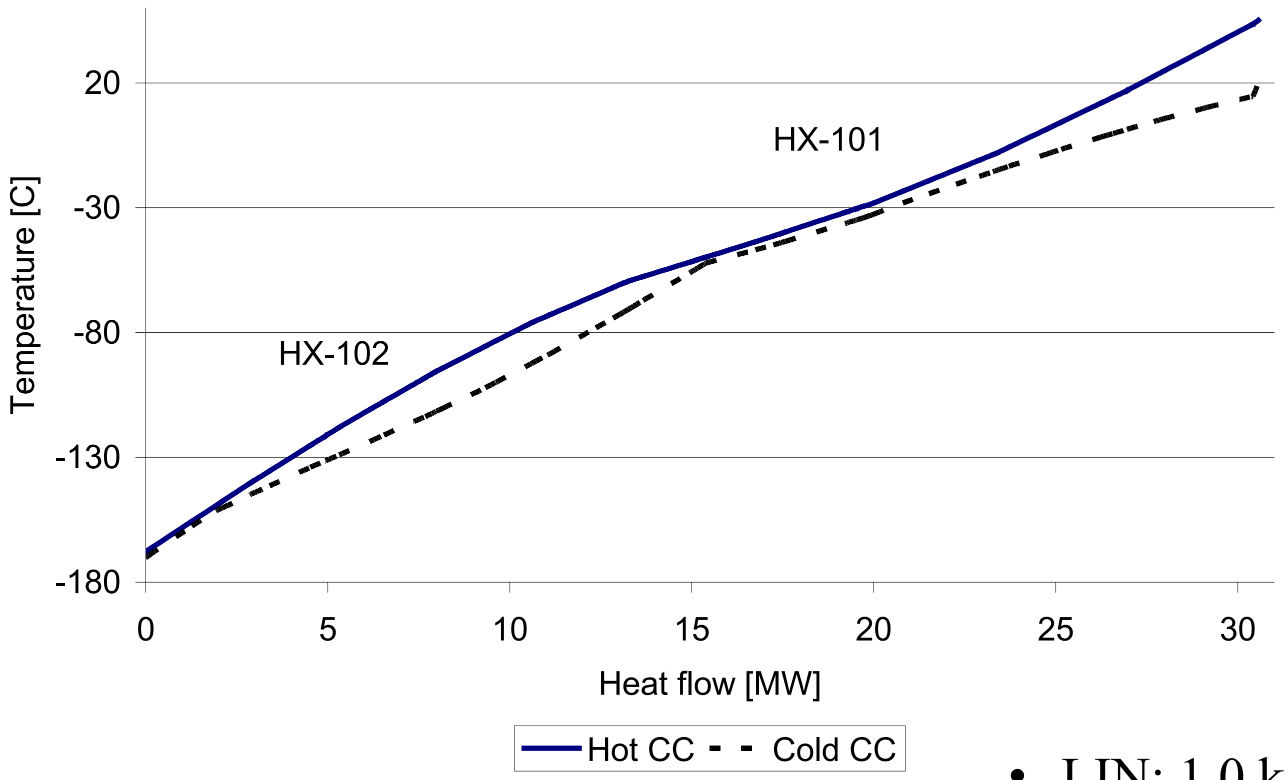
Offshore Process with Pressure Manipulations





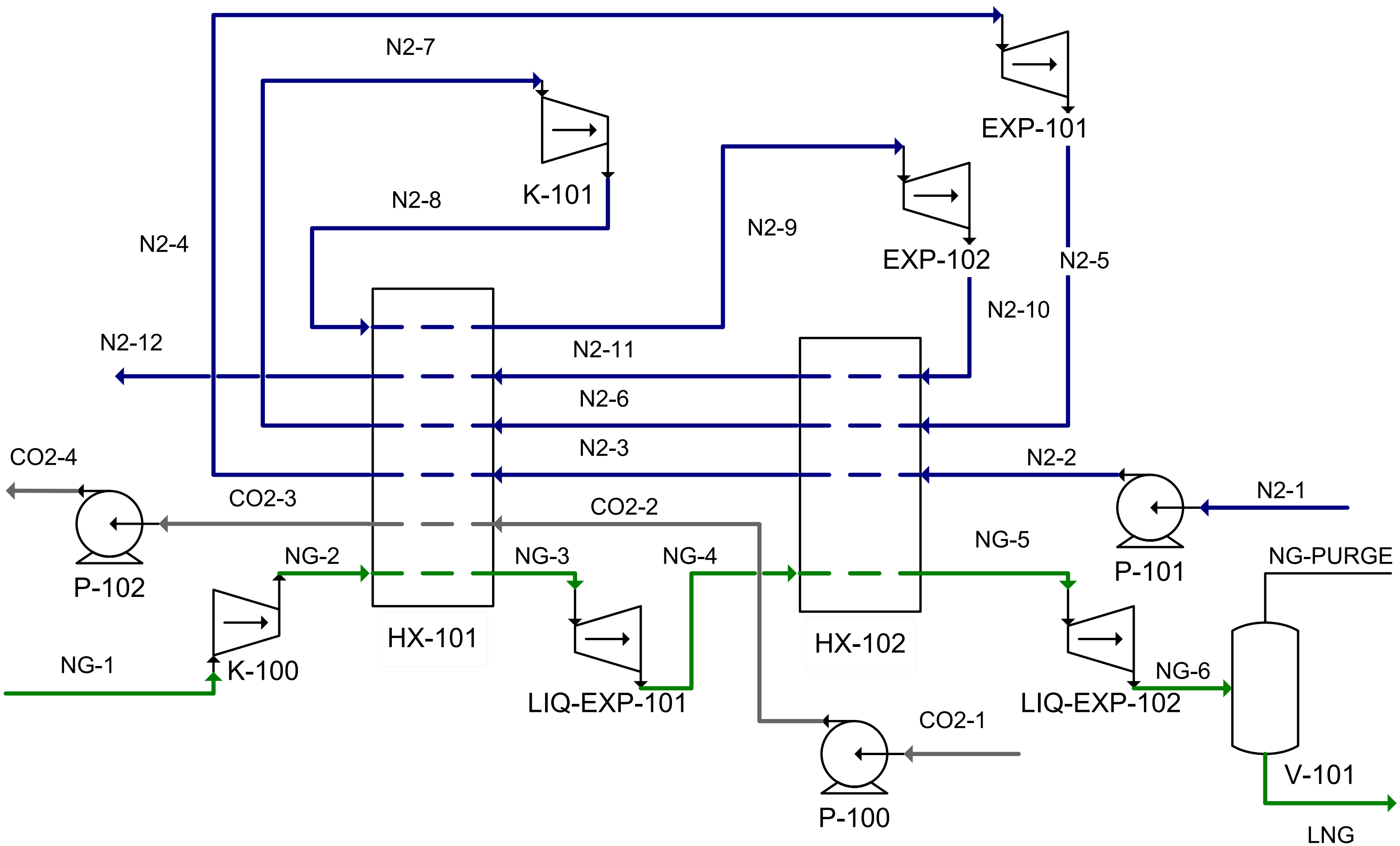
- LIN: 1.25 kg/kgLNG
- LCO_2: 1.50 kg/kgLNG
- Power ***Surplus***
- Exergy Efficiency: **84.1%**
- No Power Export: **76.3%**

Offshore Process in Balance with respect to Thermal and Mechanical Energy



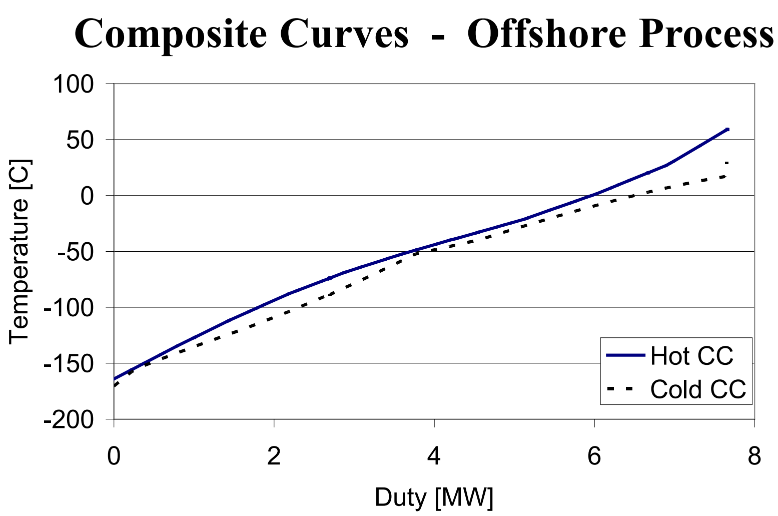
- LIN: 1.0 kg/kgLNG
- LCO_2: 2.2 kg/kgLNG
- Power ***Balance***
- Exergy Efficiency: **85.7%**

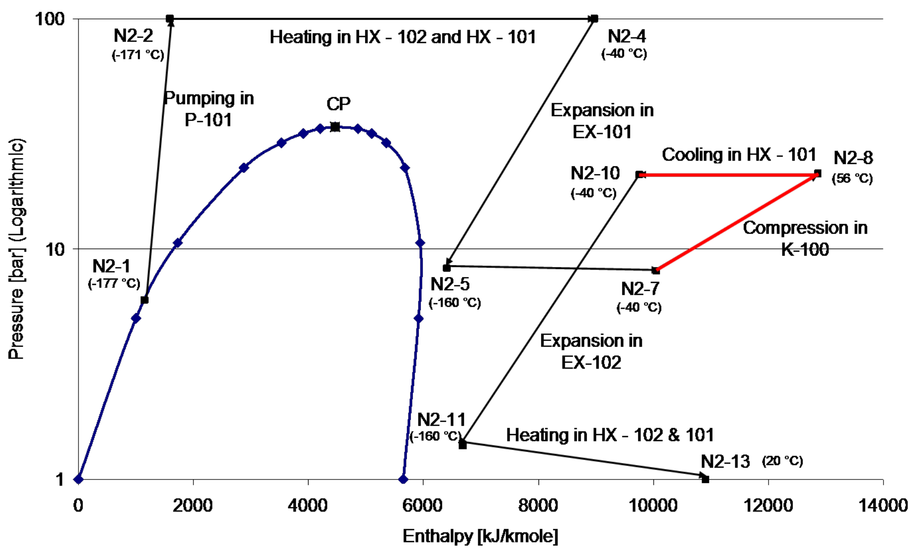
The Offshore Process in the LEC



No flammable Refrigerants and no Gas Turbines !!

Detailed Features of the Offshore Process

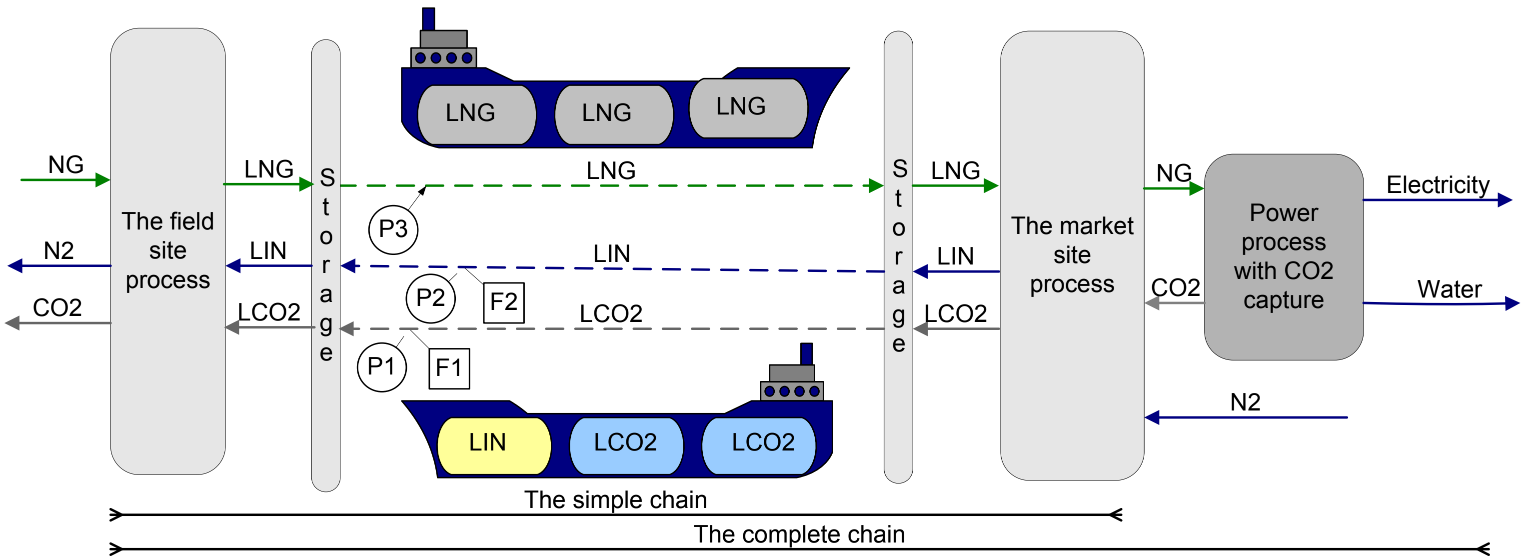


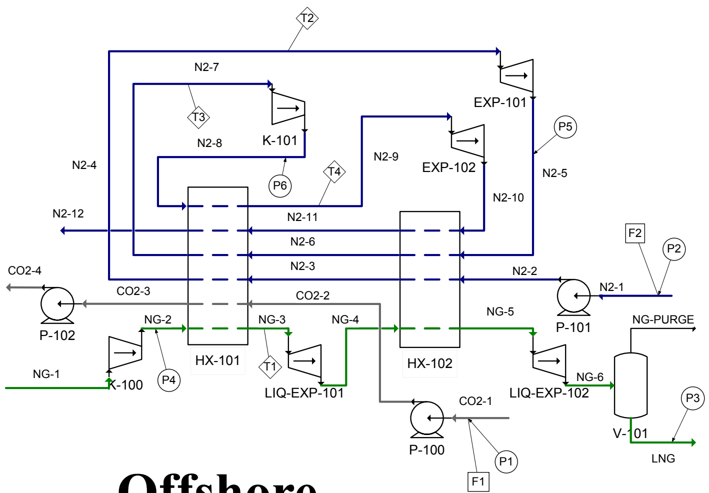


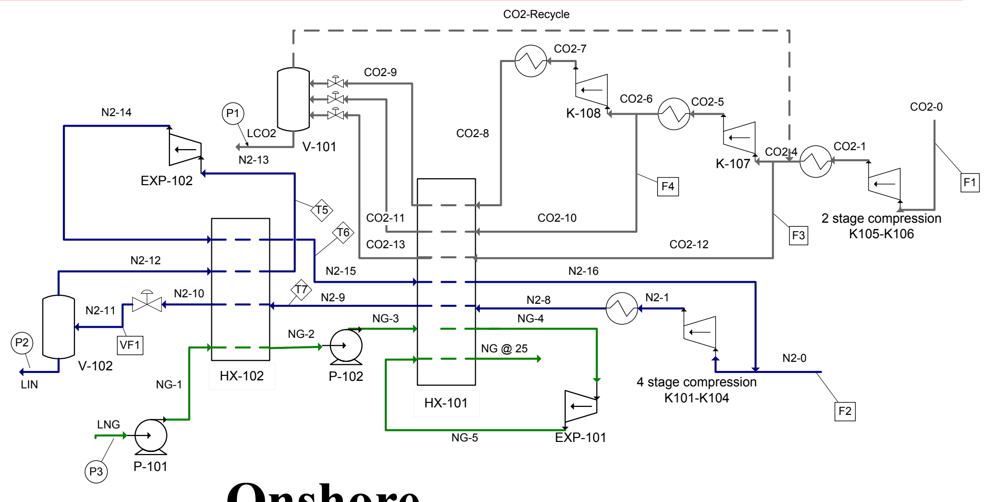
Single Components (here CO_2 and N_2) exhibit Multi-component Behavior by Expansion and Compression

*Aspelund A. and Gundersen T. "A Liquefied Energy Chain for Transport and Utilization of Natural Gas for Power Production with CO_2 Capture and Storage – Part 2, The Offshore and the Onshore Processes", **Journal of Applied Energy**, vol. 86, pp. 793-804, 2009.*

Simulation-Optimization of the entire LEC







Optimization Variables

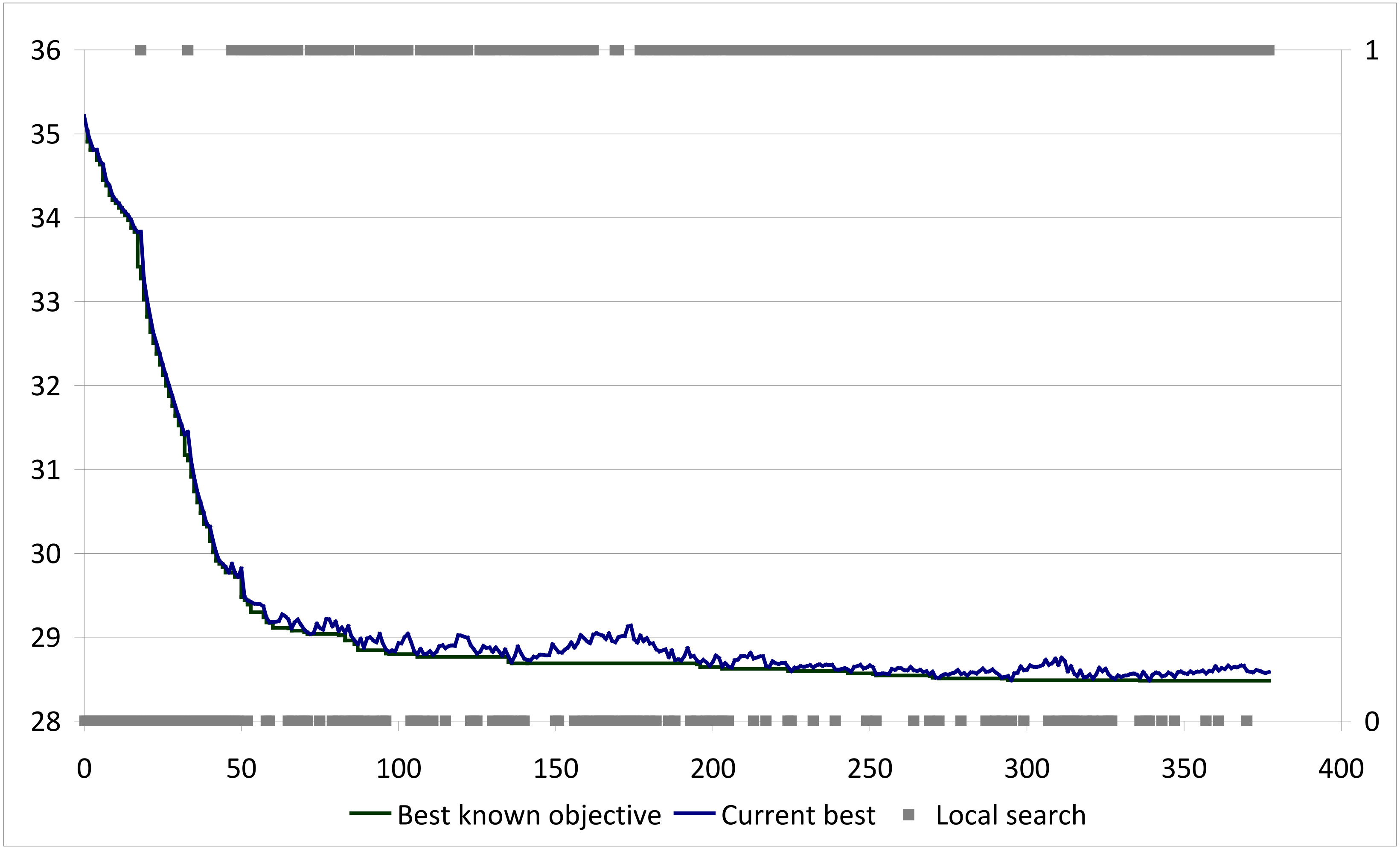
Field Site Process (offshore)

Stream	Type I	Type II	Name	Unit	Initial value	Lower bound	Upper bound
CO2-1	Global	Pressure	P1	kPa	600	550	1000
CO2-1	Global	Flow rate	F1	kg/h	80000	60000	150000
N2-1	Global	Pressure	P2	kPa	400	400	1000
N2-1	Global	Flow rate	F2	kg/h	65000	55000	65000
LNG	Global	Pressure	P3	kPa	110	100	300
NG-2	Global	Pressure	P4	kPa	9000	8000	10000
NG-3	Local	Temperature	T1	°C	-61	-70	-50
N2-4	Local	Temperature	T2	°C	-40	-60	0
N2-5	Global	Pressure	P5	kPa	600	400	1000
N2-7	Local	Temperature	T3	°C	-40	-60	20
N2-8	Gobal	Pressure	P6	kPa	2800	1500	3500
N2-9	Local	Temperature	T4	°C	-40	-60	20

Market Site Process (onshore)

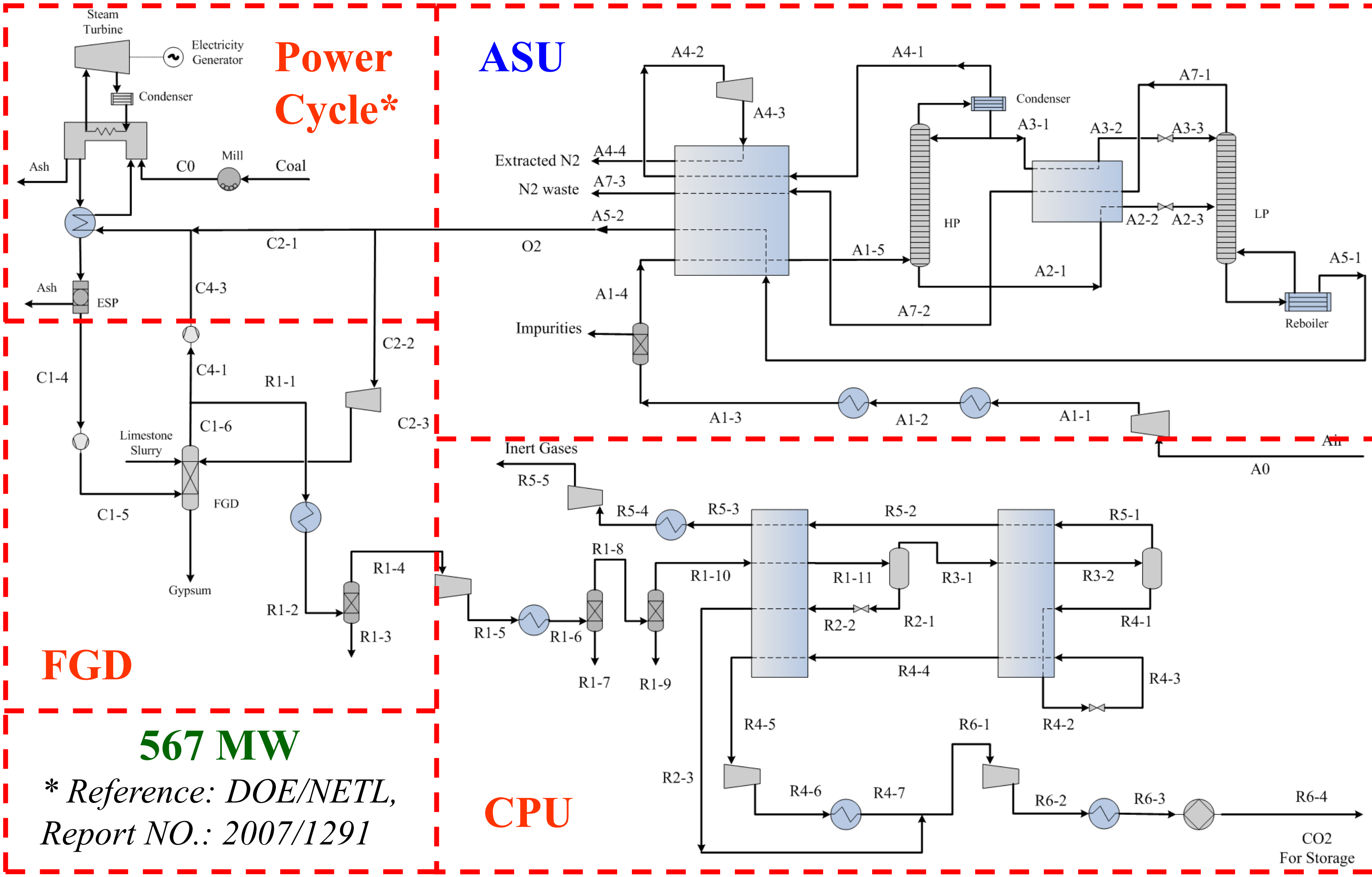
Stream	Type I	Type II	Name	Unit	Initial value	Lower bound	Upper bound
LCO2	Global	Pressure	P1	kPa	600	550	1000
CO2-0	Global	Flow rate	F1	kg/h	80000	60000	150000
LIN	Global	Pressure	P2	kPa	400	400	1000
N2-0	Global	Flow rate	F2	kg/h	65000	55000	65000
LNG	Global	Pressure	P3	kPa	110	100	300
CO2-12	Local	Flow rate	F3	kg/h	10500	9000	25000
CO2-6	Local	Flow rate	F4	kg/h	35000	30000	55000
N2-9	Local	Temperature	T7	°C	-96	-115	-80
N2-11	Global	Void fraction	VF1	-	0.4	0.1	0.5
N2-13	Local	Temperature	T5	°C	-101	-115	-80
N2-15	Local	Temperature	T6	°C	-115	-132	-92

Progress of the Optimization



*Myklebust J., Aspelund A., Tomasgard, A., Nowak M. and Gundersen T., "An Optimization-Simulation Model of a Combined Liquefied Natural Gas and CO2 Value Chain", **INFORMS Annual Meeting**, Seattle, November 2007.*

Supercritical Oxy-Combustion Pulverized Coal-based Power Plant

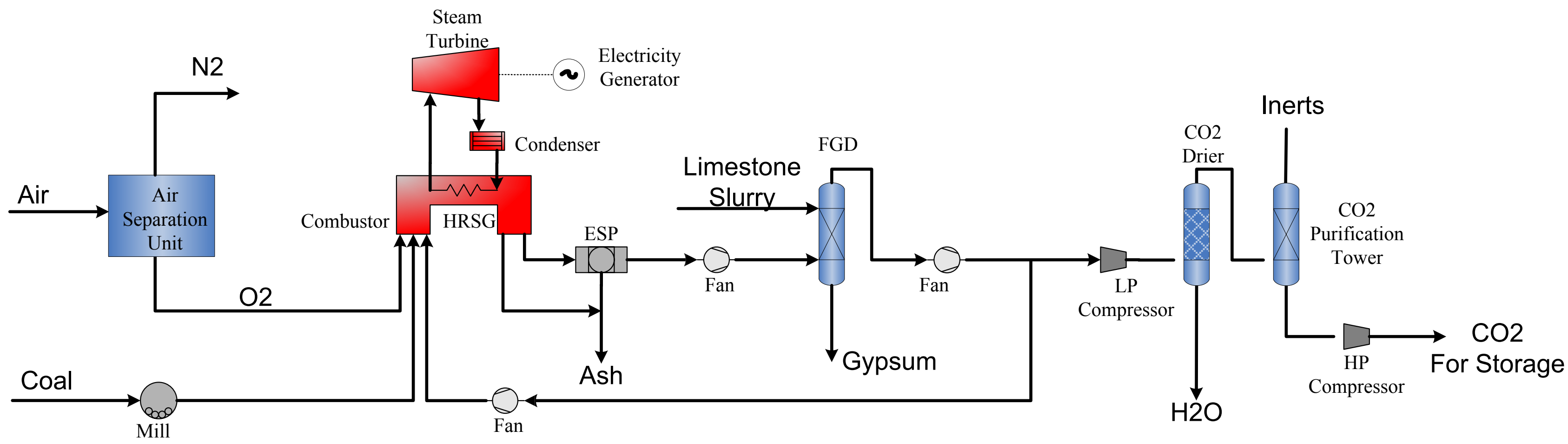


567 MW

** Reference: DOE/NETL, Report NO.: 2007/1291*

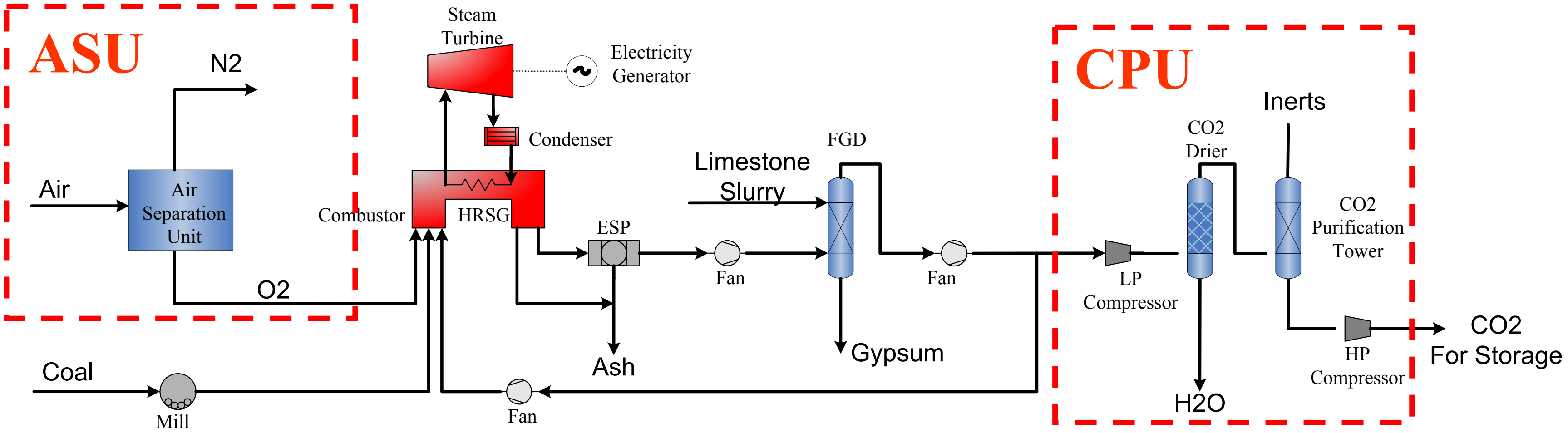
C. Fu and T. Gundersen, "Exergy Analysis of an Oxy-Combustion Process for Coal-fired Power Plants with CO_2 Capture", ECI, CO_2 Summit: Technology and Opportunity, Vail, Colorado, USA, 6-10 June, 2010.

Some key Production Figures



- **Net power output: 567 MW**
- **Coal feed: 69 kg/s = 5 962 tons/day**
- **O_2 feed: 161 kg/s (excess O_2: 10%) = 13 910 tons/day**
- **Efficiency penalty related to CO_2 capture: 10.3% points (ASU: 6.6% points)**
- **Power to produce O_2 (95 mol%): 124 MW**

Efficiency Penalties for CO_2 Capture



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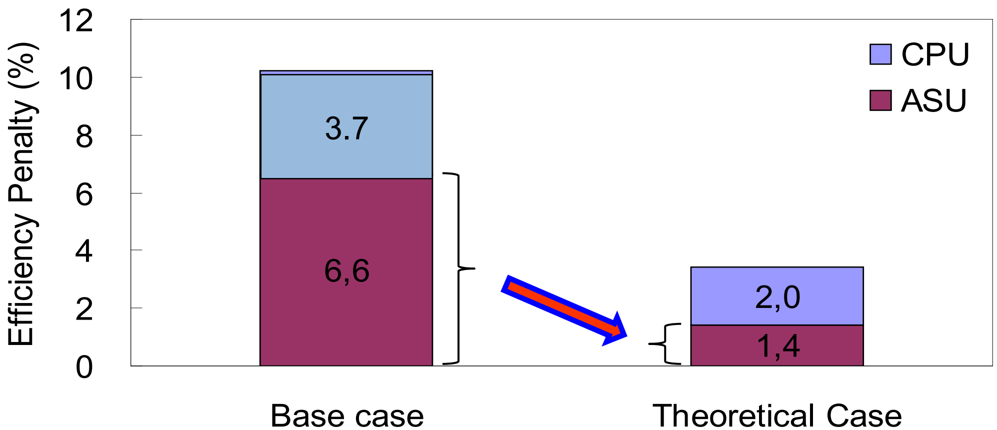
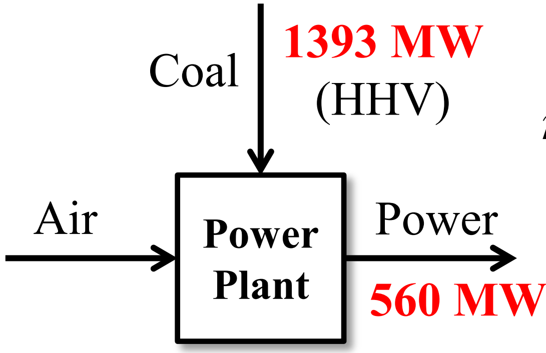
Specs on Oxygen:

~ 95 mol%, 1.25 bar

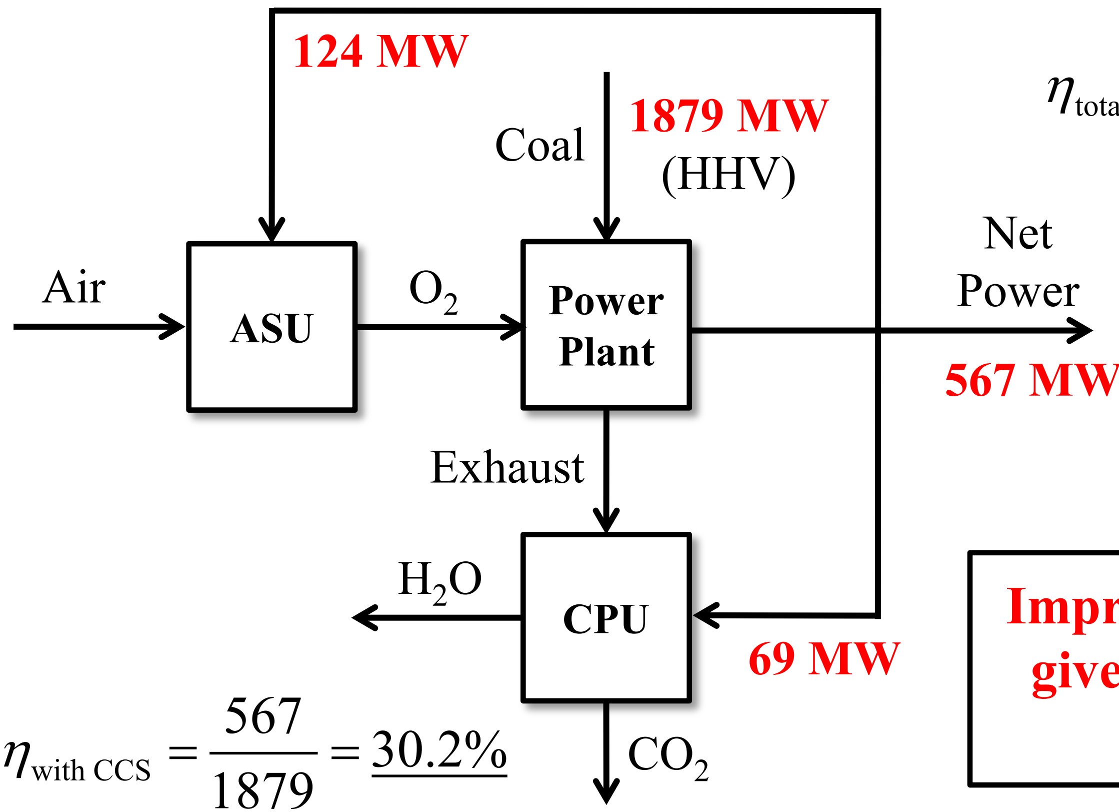


*Fu C. and Gundersen T., "Exergy Analysis of an Oxy-combustion Process for Coal-fired Power Plants with CO_2 Capture", submitted to **Fuel**, June 2011*

Our Research Motivation



$$\eta_{\text{without CCS}} = \frac{560}{1393} = \underline{40.2\%}$$



$$\eta_{\text{total}} = \frac{567+124+69}{1879} = \underline{40.5\%}$$

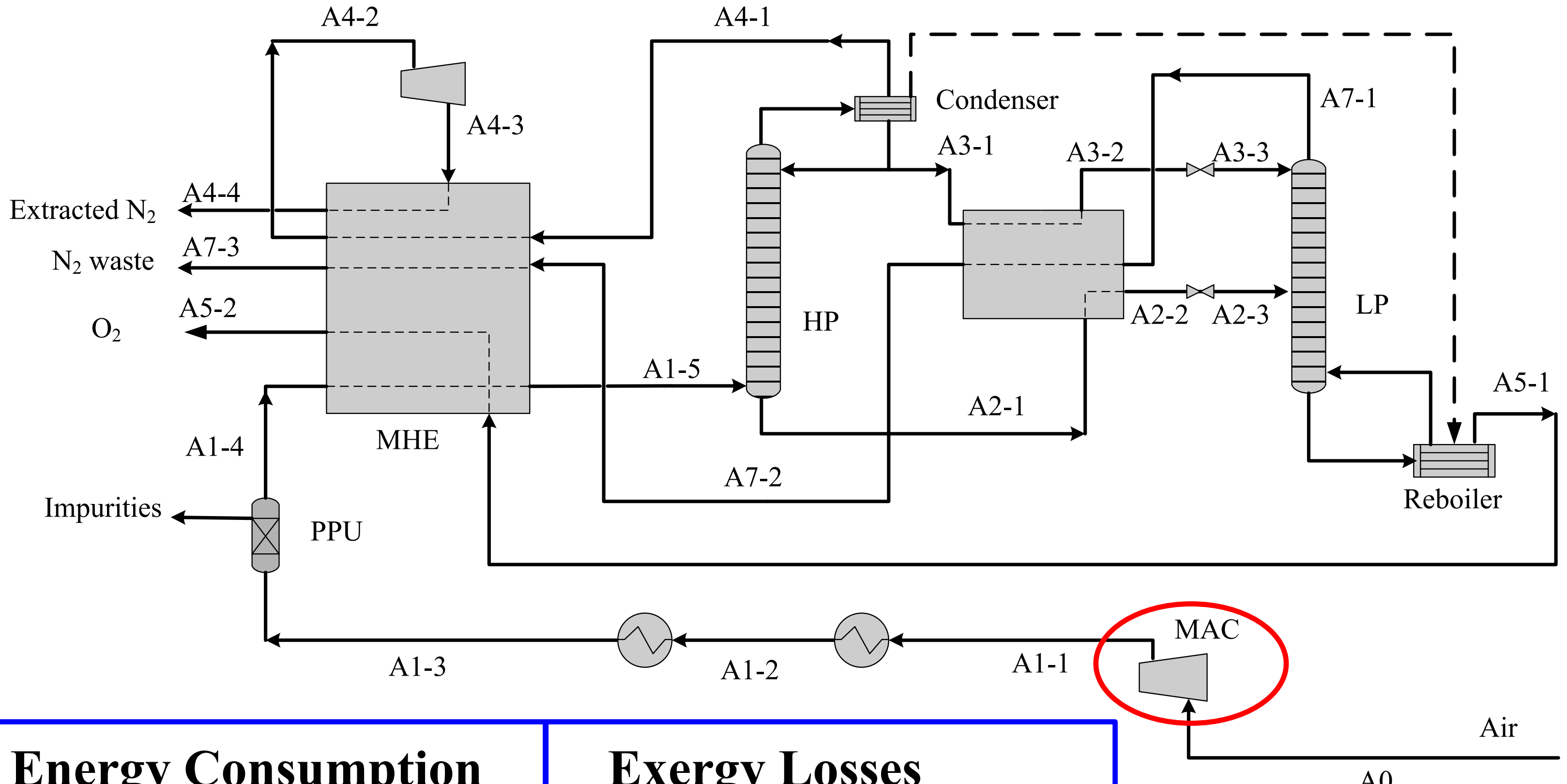
$$\Delta\eta^{1}_{\text{ASU}} = \frac{124}{1879} = \underline{6.6\%\ \text{pts}}$$

$$\Delta\eta^{1}_{\text{CPU}} = \frac{69}{1879} = \underline{3.7\%\ \text{pts}}$$

$$\eta_{\text{with CCS}} = \frac{567}{1879} = \underline{30.2\%}$$

Improving the ASU by 20% gives 4.4% more Power !! or 1.32% points

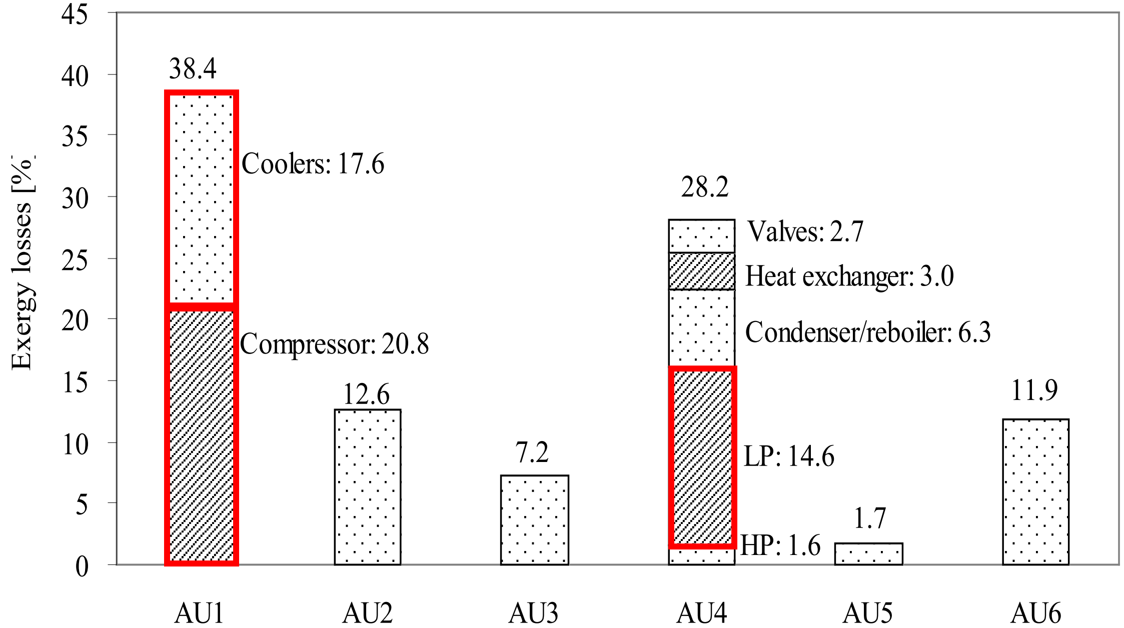
Conventional ASU – here producing 95% O_2



Energy Consumption	Exergy Losses	Our Goal:
♦ Actual: **0.193** kWh/kgO_2	♦ Air Compressor: 38%	♦ Save 10-20%
♦ Ideal: 0.049 kWh/kgO_2	♦ Distillation Cols.: 28%	

Fu C. and Gundersen T., "Using Exergy Analysis to reduce Power Consumption in Air Separation Units for Oxy-combustion Processes, ***Energy***, available on-line, http://dx.doi.org/10.1016/j.energy.2012.01.065, February, 2012

Distribution of Exergy Losses



AU1: The main air compressor

AU2: The pre-purification unit

AU3: The main heat exchanger

AU4:The air distillation system

AU5: The tail N_2 turbine

AU6: The waste N_2

- **Largest Sources of Exergy Losses**
  - Distillation System (28.2%)
    - LP Column
  - Main Air Compressor (38.4%)
    - Interstage Coolers
    - Compression Process itself

How to reduce Compressor Work?

$$\dot{W}_C = \frac{1}{\eta_{is}} \cdot \dot{m} \cdot c_p \cdot T_{in} \cdot \left[\left(\frac{p_{out}}{p_{in}} \right)^{\frac{\kappa-1}{\kappa}} - 1 \right]$$

- **Simplified Equation for Ideal Gas indicates:**
  - Increase Compressor Efficiency
    - Responsibility of the Manufacturers
  - Reduce Inlet Temperature
    - Beyond CW requires Refrigeration, thus more Work
  - Reduce Pressure Ratio
    - Limited by Condenser/Reboiler Match, but there are ways around it …. !!
  - Reduce Mass Flowrate through the Compressor
    - Do we really need to compress the Oxygen?
- **Our Inventions are based on the last two:**
  - Reducing Compressor Flowrate and Pressure Ratio

Fu C. and Gundersen T. "Power Reduction in Air Separation Units for Oxy-Combustion Processes based on Exergy Analysis", in E.N. Pistikopoulos et al. (eds.), 21st European Symposium on Computer Aided Process Engineering (ESCAPE 21), Elsevier B.V., vol. 29, Part B, pp. 1794-1798, June 2011.

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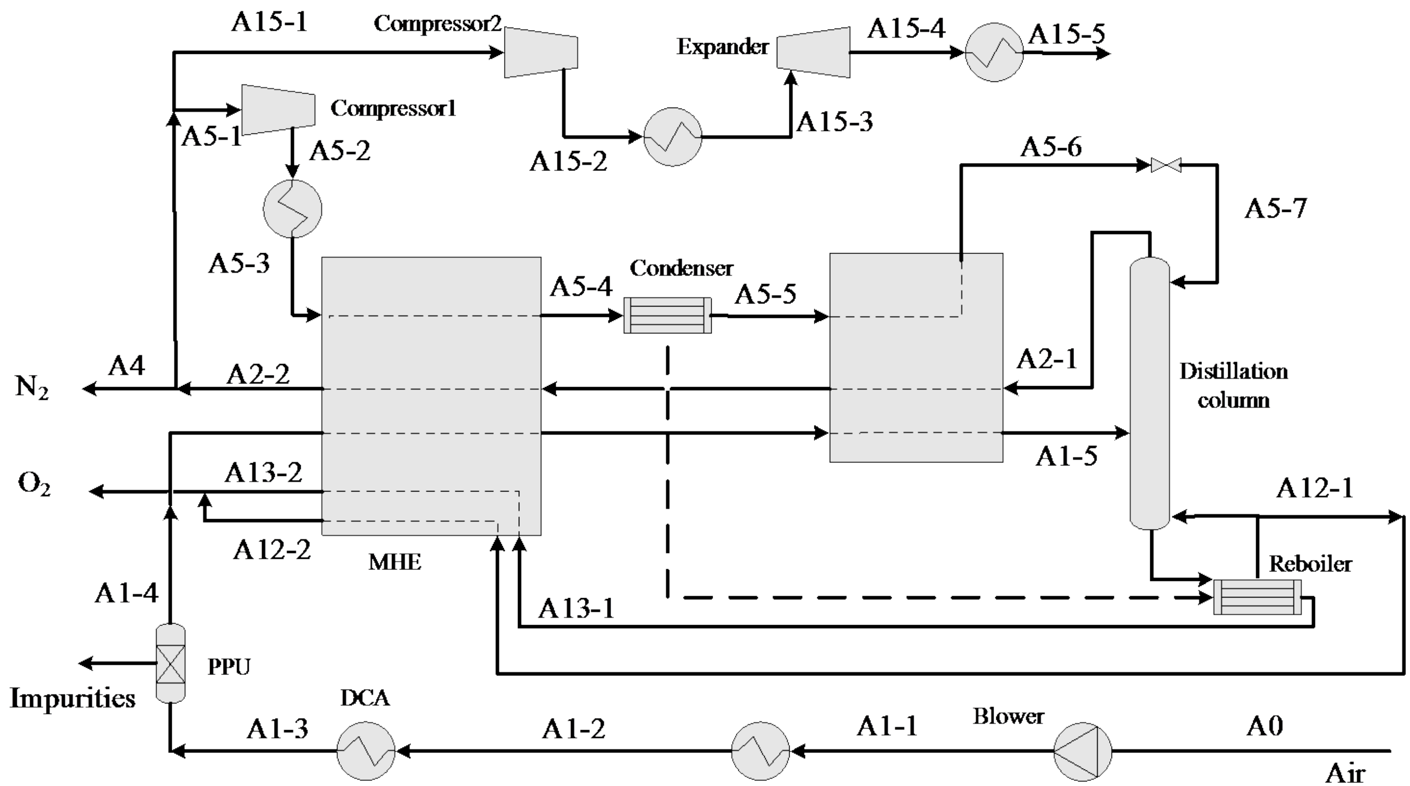
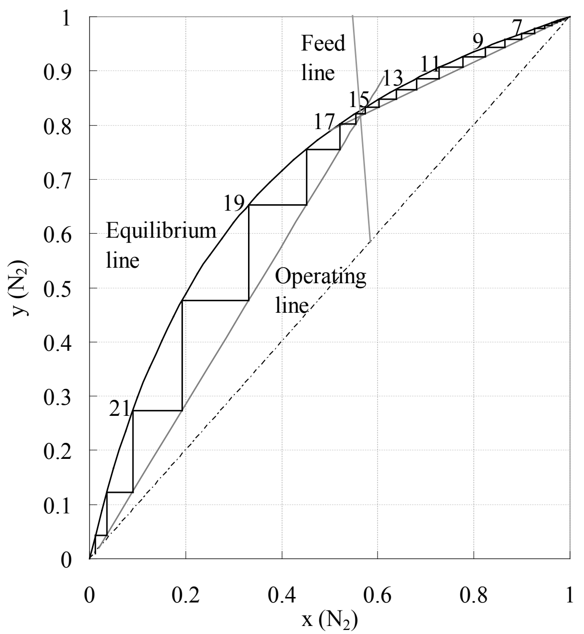
Recuperative Vapor Recompression Cycle

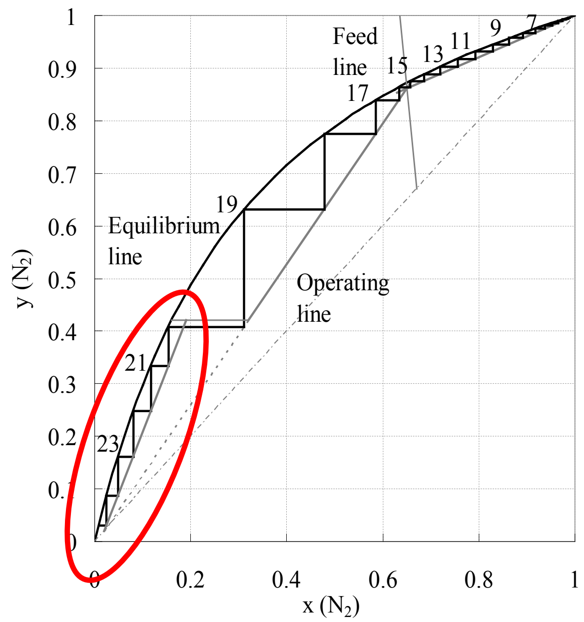


Specific Shaftwork for Separation: **0.178** kWh/kgO_2

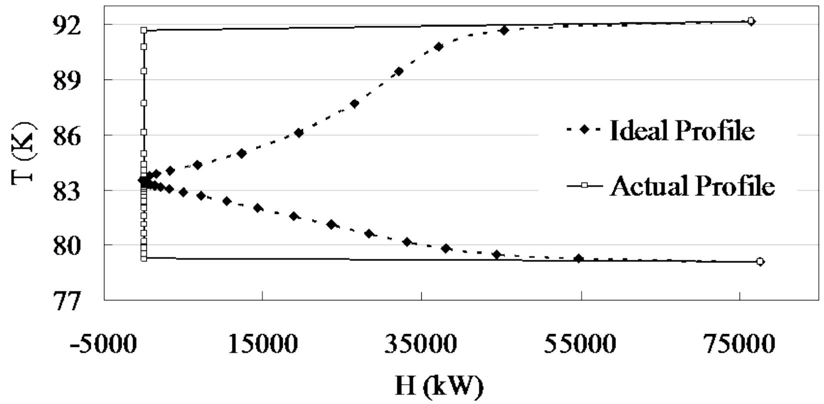
Fu C. and Gundersen T. "Innovative air separation processes for Oxy-Combustion plants", 2nd International Oxy-fuel Combustion Conference, Yeppoon, Australia, September 2011.

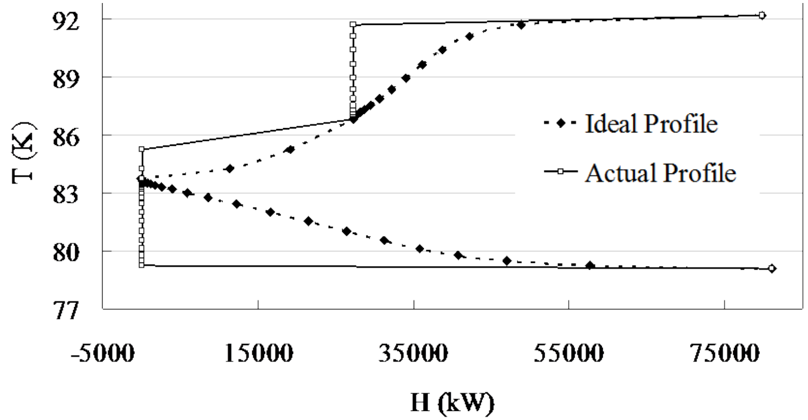
McCabe-Thiele Diagram for Distributed Reboiling



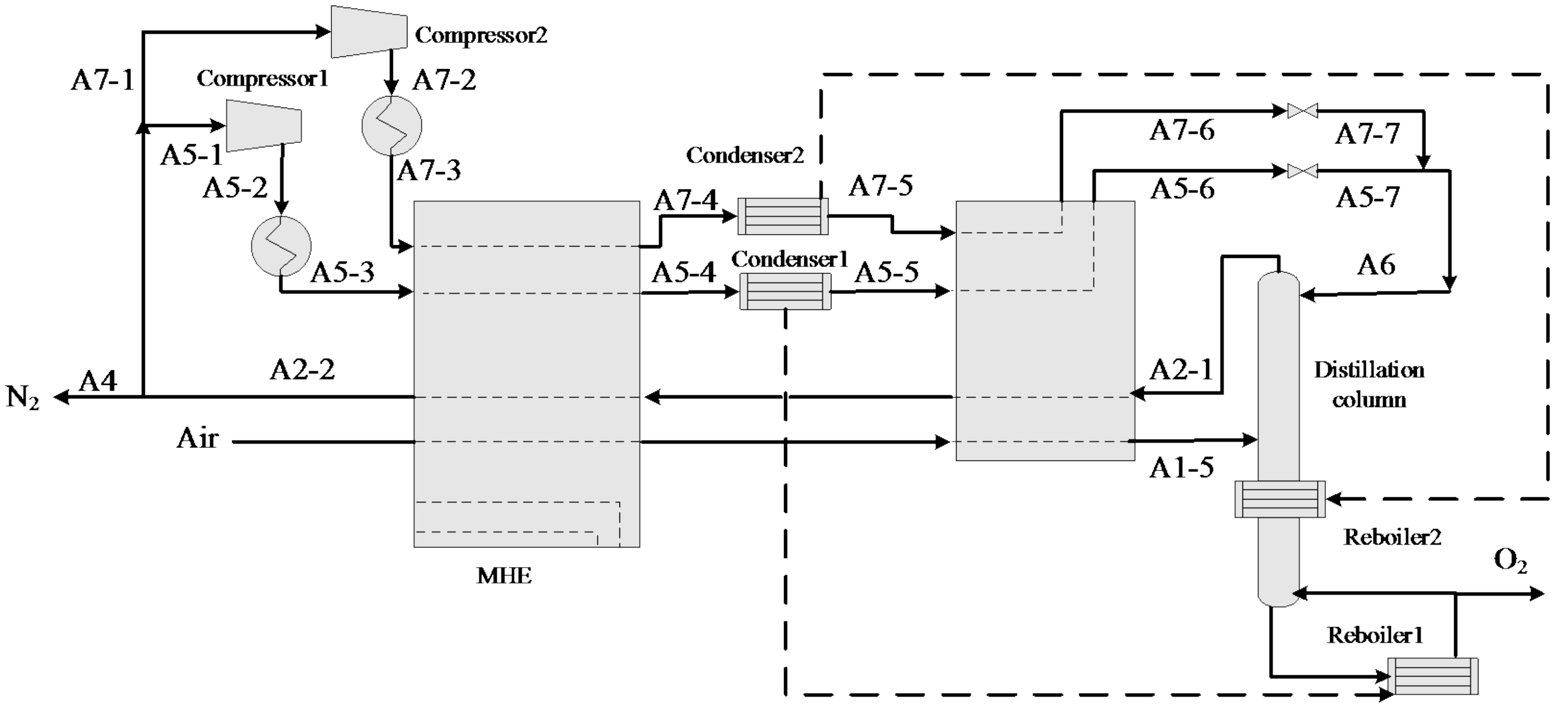


Column Grand Composite Curve for Distributed Reboiling





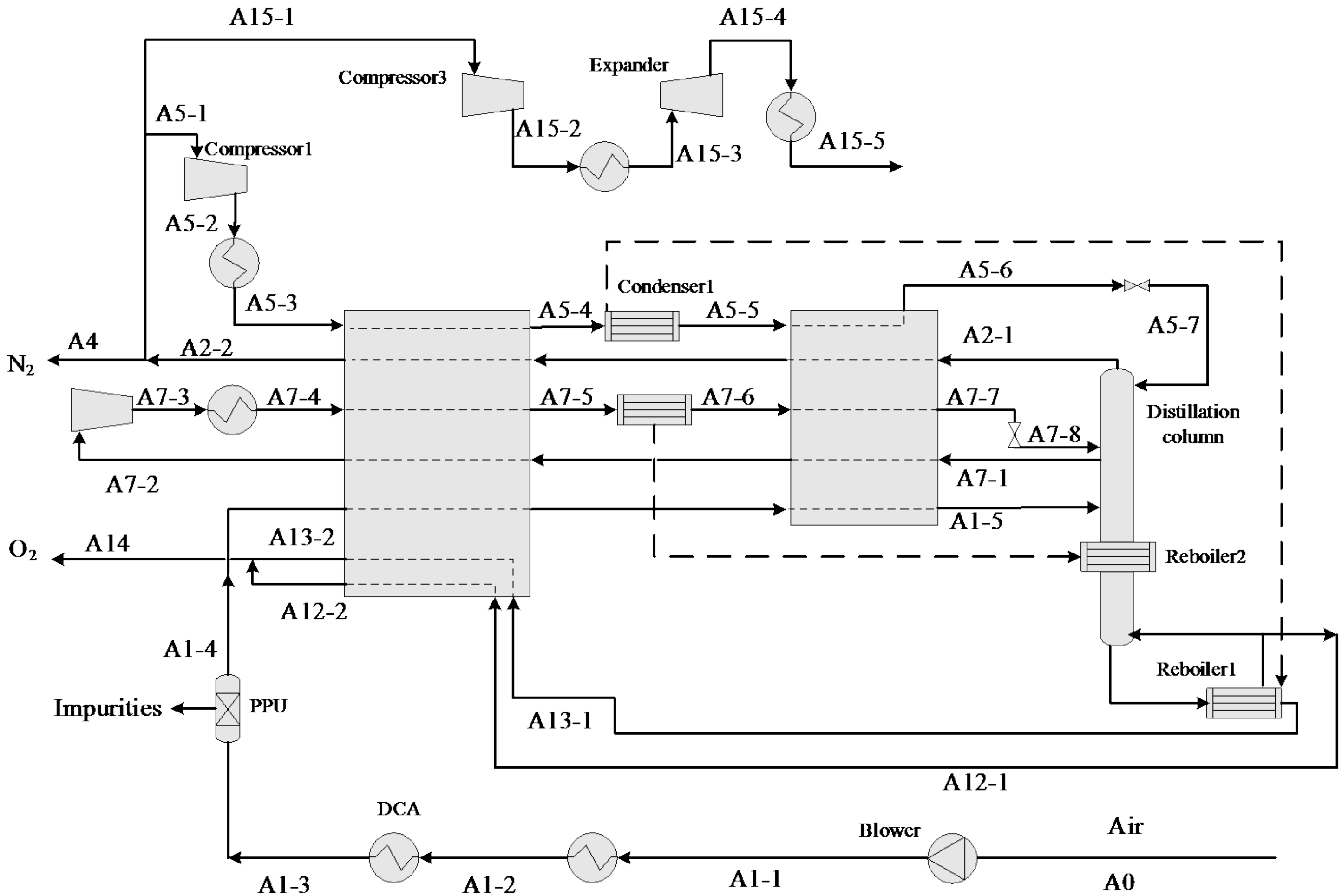
Vapor Recompression with Dual-Reboiler



Specific Shaftwork for Separation: **0.166** kWh/kgO_2

Fu C. and Gundersen T., "Using PSE to develop Innovative Cryogenic Air Separation Processes", accepted for the 11th Intl. Symp. on Process Systems Engineering (PSE 2012), Singapore, 15-19 July, 2012

Intermediate & Recuperative Vapor Compression Cycle



Specific Shaftwork for Separation: **0.159** kWh/kgO_2

Performance Comparison

	O_2 purity, %	Specification Shaftwork for Separation, kWh/kgO_2	Power savings
Cycle 1 (reference) Conventional double column cycle	95.0	0.193	**Ref. Case**
Cycle 2 Vapor recompression cycle	95.4	0.178	-7.8 %
Cycle 3 Vapor recompression cycle with dual reboiler	95.5	0.166	-14.0 %
Cycle 4 Intermediate vapor recompression cycle	95.1	0.159	**-17.6 %**

Patented

OPEX is down; what about CAPEX ??

*Fu C., Gundersen T. and Eimer D., "Air Separation", **GB Patent**, Application number GB1112988.9, July 2011*

Is this the Optimum (Local or Global)?

Summary of the Presentation

- Demonstrated the use of **Thermodynamics** in Design
  - Pinch Analysis and Exergy Analysis
  - McCabe-Thiele and Column Grand Composite Curve
- Demonstrated **Innovations**
  - The Liquefied Energy Chain (LEC)
  - New Air Separation Cycles (ASUs)
- Demonstrated **Energy Efficiency**
  - LEC with 47.1% efficiency vs. 42.5% for Conventional
  - New ASU cycles saving almost 20% on Energy
- Applications relate to **Carbon Capture & Storage**
  - Making environmentally friendly LNG even more friendly
  - Elegant CCS solution for natural gas based Power Stations
  - Making the Oxy-combustion route even more attractive
- Hopefully demonstrated the Power of using PSE (Process Synthesis and Process Integration) in designing Energy and Production Systems