Theoretical, Practical, and Zero-emission Exergy Recovery in Energy Conversion Processes

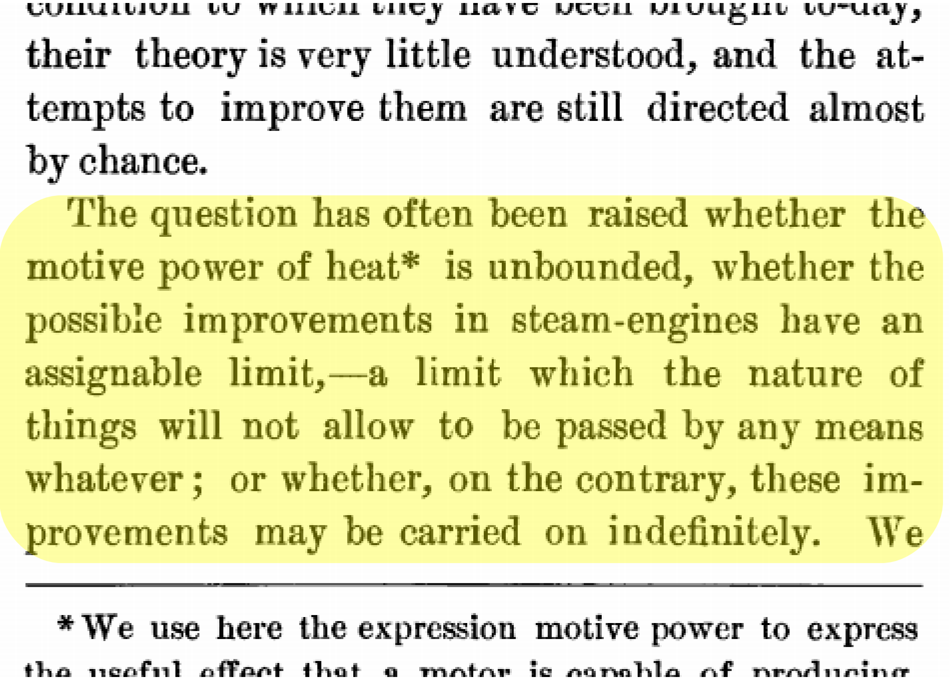
Part I: Definition and importance of the exergy concept

Outline

- Energy versus exergy: Carnot engine
- Exergy definition
- Physical and chemical source of exergy: driving force
- EROI
- A simple example
- Parts of My research
  - Case study 1: Natural gas treatment and transport
  - Case study 2: UCG process with spontaneous CO_2 capture and sequestration
  - Case study 3: Geothermal energy

Energy and its quality

- Nicolas Leonard Sadi Carnot (1796-1832)
- Cycle and reversibility



condition to which they have been brought to-day, their theory is very little understood, and the attempts to improve them are still directed almost by chance.

The question has often been raised whether the motive power of heat* is unbounded, whether the possible improvements in steam-engines have an assignable limit,—a limit which the nature of things will not allow to be passed by any means whatever; or whether, on the contrary, these improvements may be carried on indefinitely. We

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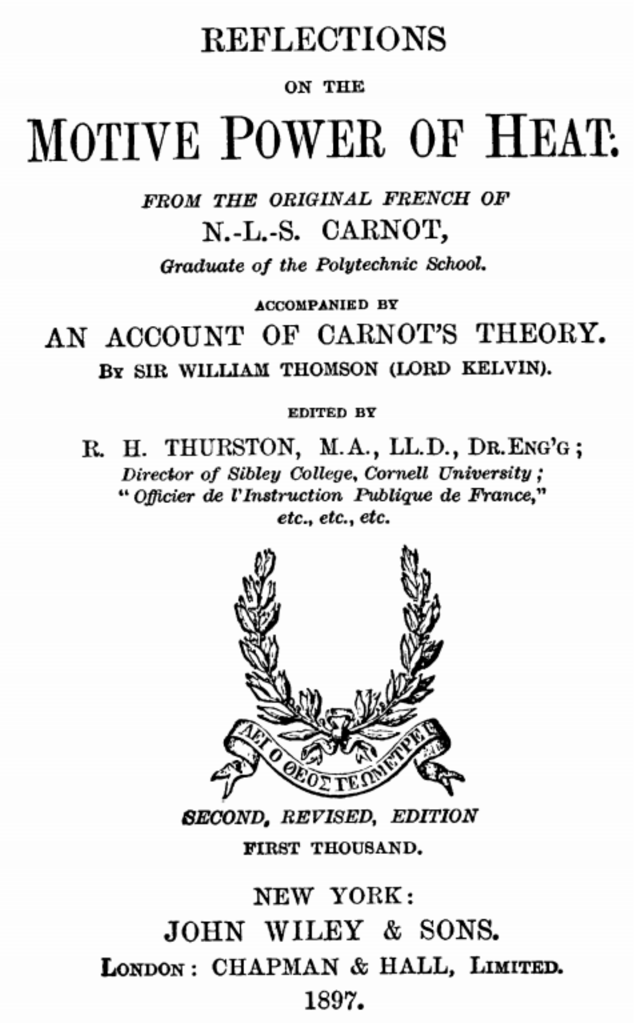
* We use here the expression motive power to express the useful effect that a motor is capable of producing



REFLECTIONS

ON THE

MOTIVE POWER OF HEAT:

FROM THE ORIGINAL FRENCH OF
N.-L.-S. CARNOT,
Graduate of the Polytechnic School.

ACCOMPANIED BY
AN ACCOUNT OF CARNOT'S THEORY.
BY SIR WILLIAM THOMSON (LORD KELVIN).

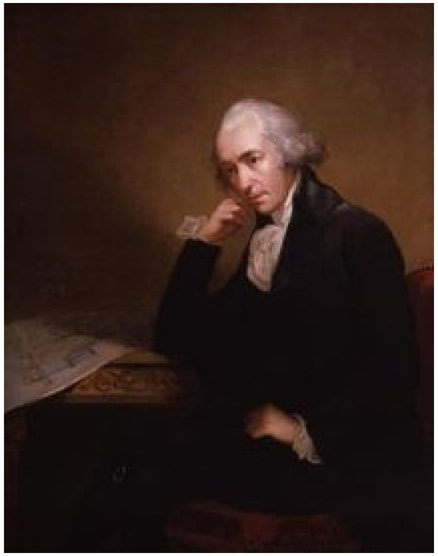
EDITED BY
R. H. THURSTON, M.A., LL.D., DR.ENG'G;
Director of Sibley College, Cornell University;
"Officier de l'Instruction Publique de France,"
etc., etc., etc.

SECOND, REVISED, EDITION
FIRST THOUSAND.

NEW YORK:
JOHN WILEY & SONS.
LONDON: CHAPMAN & HALL, LIMITED.
1897.

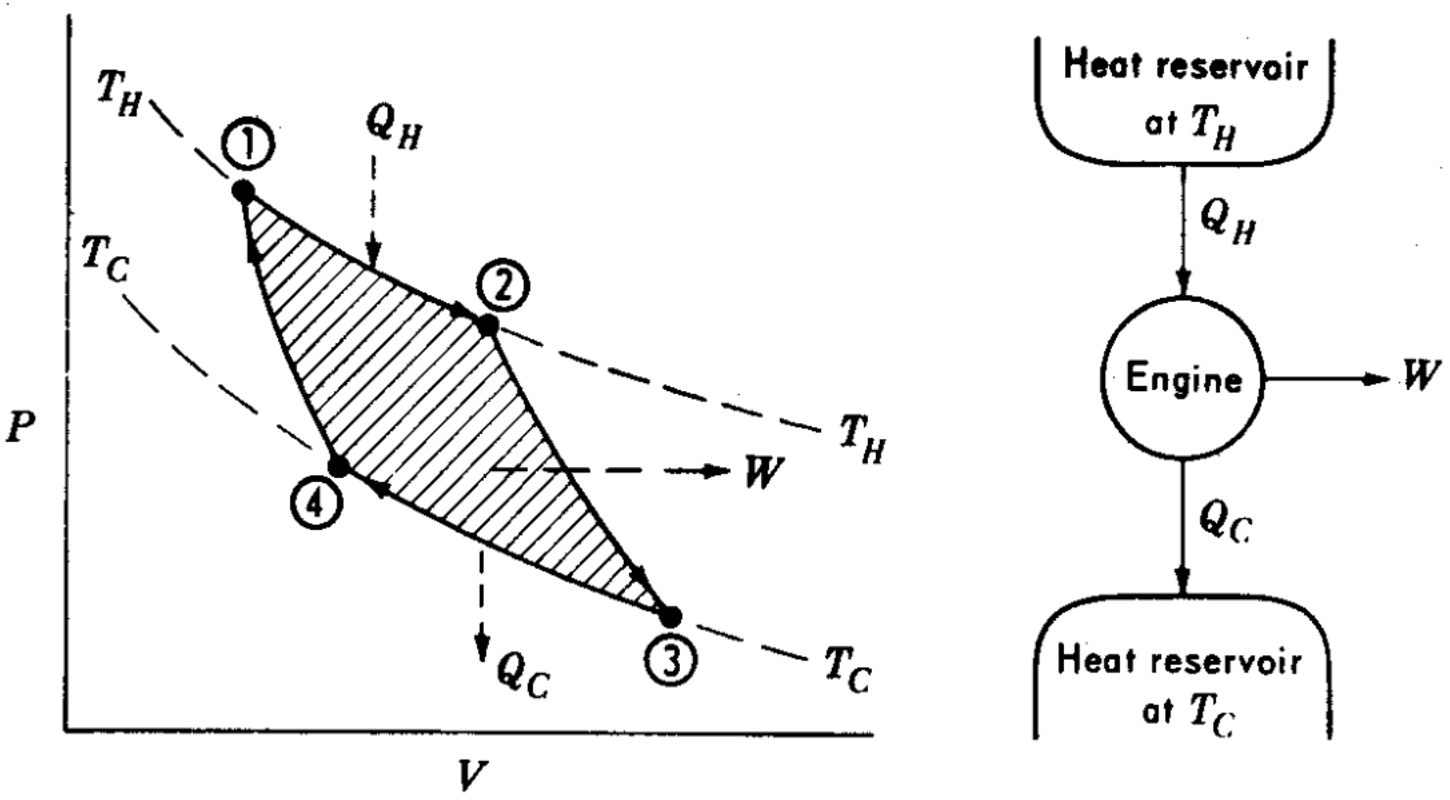
James Joule (1818-1889)

Sadi Carnot (1796-1832)



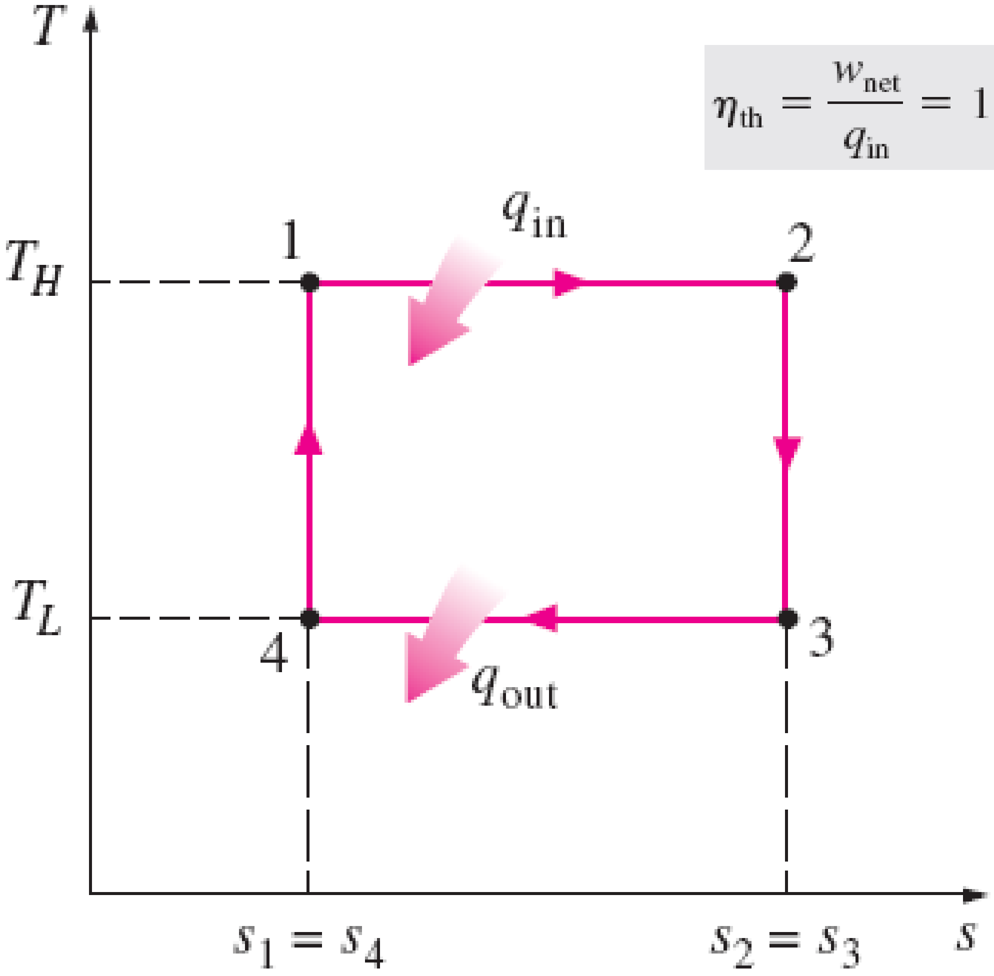
James Watt (1736-1819)

Carnot Cycle



The Carnot engine cycle
Ref: Van Ness, H. C., Understanding Thermodynamics

T-S Diagram of Carnot Cycle

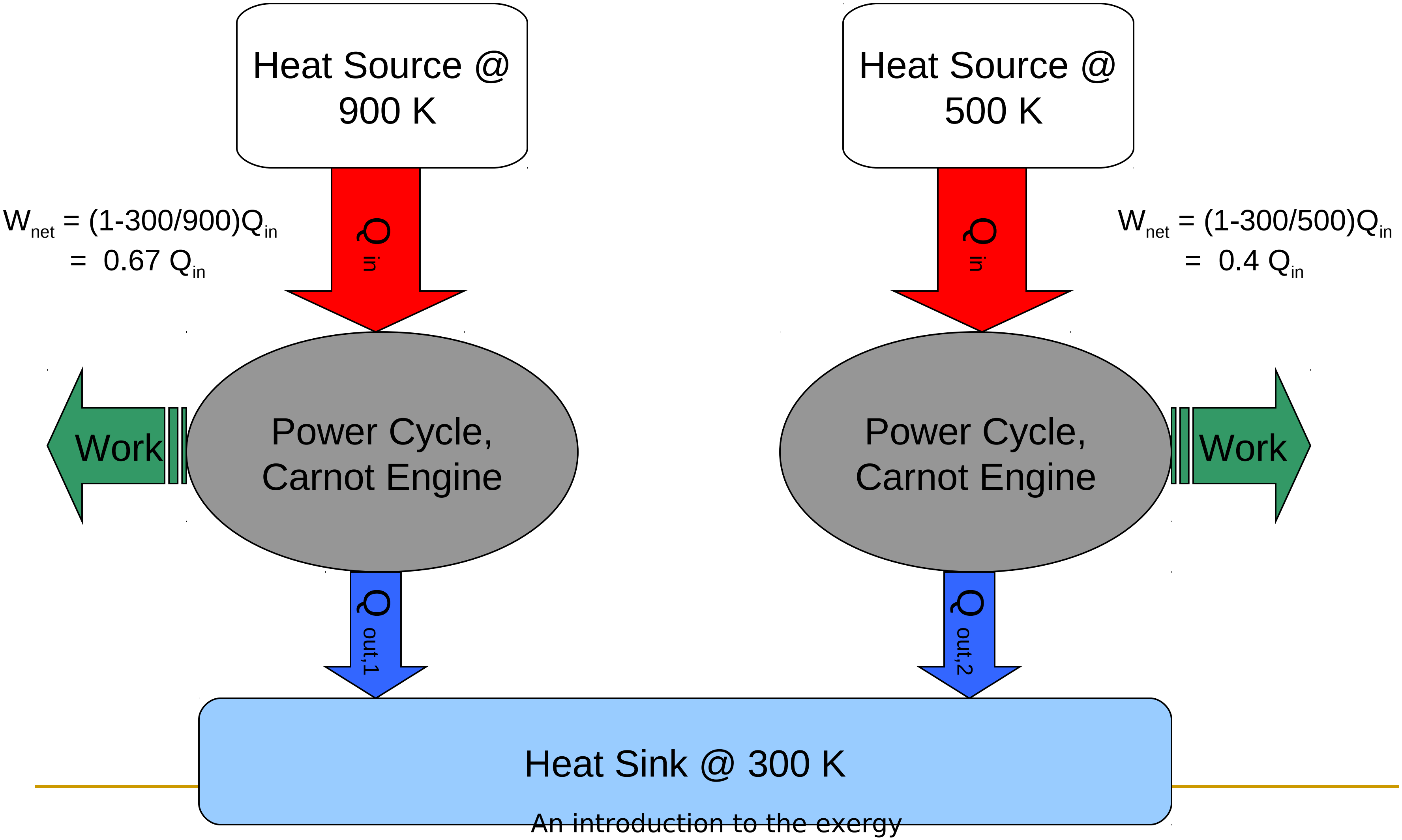


$$\eta_{\text{th}} = \frac{w_{\text{net}}}{q_{\text{in}}} = 1 - \frac{q_{\text{out}}}{q_{\text{in}}} = 1 - \frac{T_L(s_2 - s_1)}{T_H(s_2 - s_1)} = 1 - \frac{T_L}{T_H}$$

$$\eta_{\text{th,Carnot}} = 1 - \frac{T_L}{T_H}$$

Cendel Y. A., Boles M. A., “Thermodynamics; an engineering approach”, 5th edition

Energy or Exergy



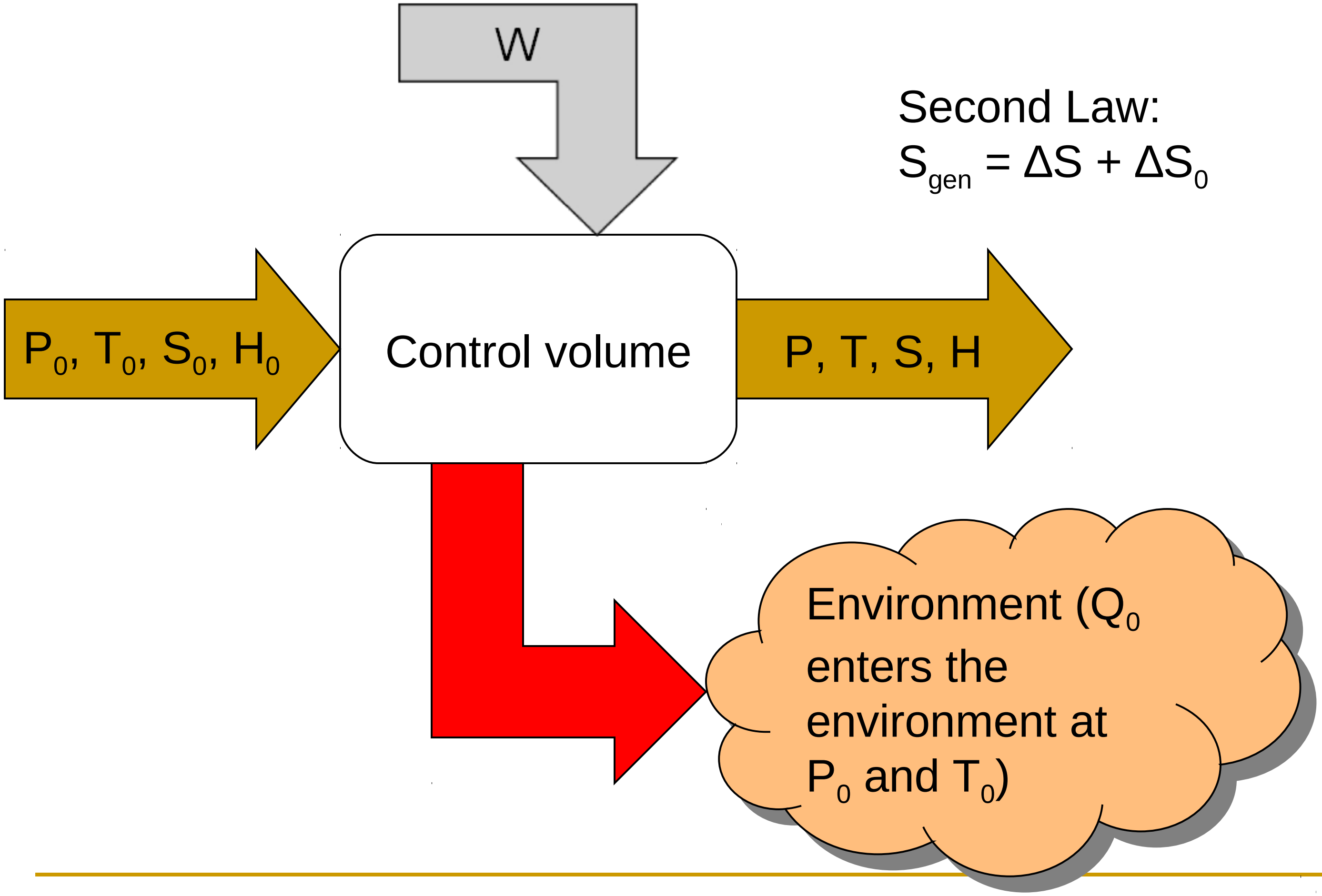
$W_{net} = (1-300/900)Q_{in}$
$= 0.67\ Q_{in}$

$W_{net} = (1-300/500)Q_{in}$
$= 0.4\ Q_{in}$

Quantitative Definition

First Law:
$W = Q_0 + \Delta H$

Second Law:
$S_{gen} = \Delta S + \Delta S_0$ $\Delta S_0 = Q_0/T_0$



Quantitative Definition

$W = \Delta H - T_0\,\Delta S + T_0\,S_{gen}$ and $\Delta H = H - H_0$

$\Delta S = S - S_0$

Gives:

$W^{min} = H - H_0 - T_0\,(S - S_0) + T_0\,S_{gen}$ and Isentropic path ($S_{gen} = 0$)

Gives:

$W^{min} = (H - T_0\,S) - (H_0 - T_0\,S_0)$

Definitions:

Availability:

$B_{T,\,P} = H_{T,\,P} - T_0\,S_{T,\,P}$

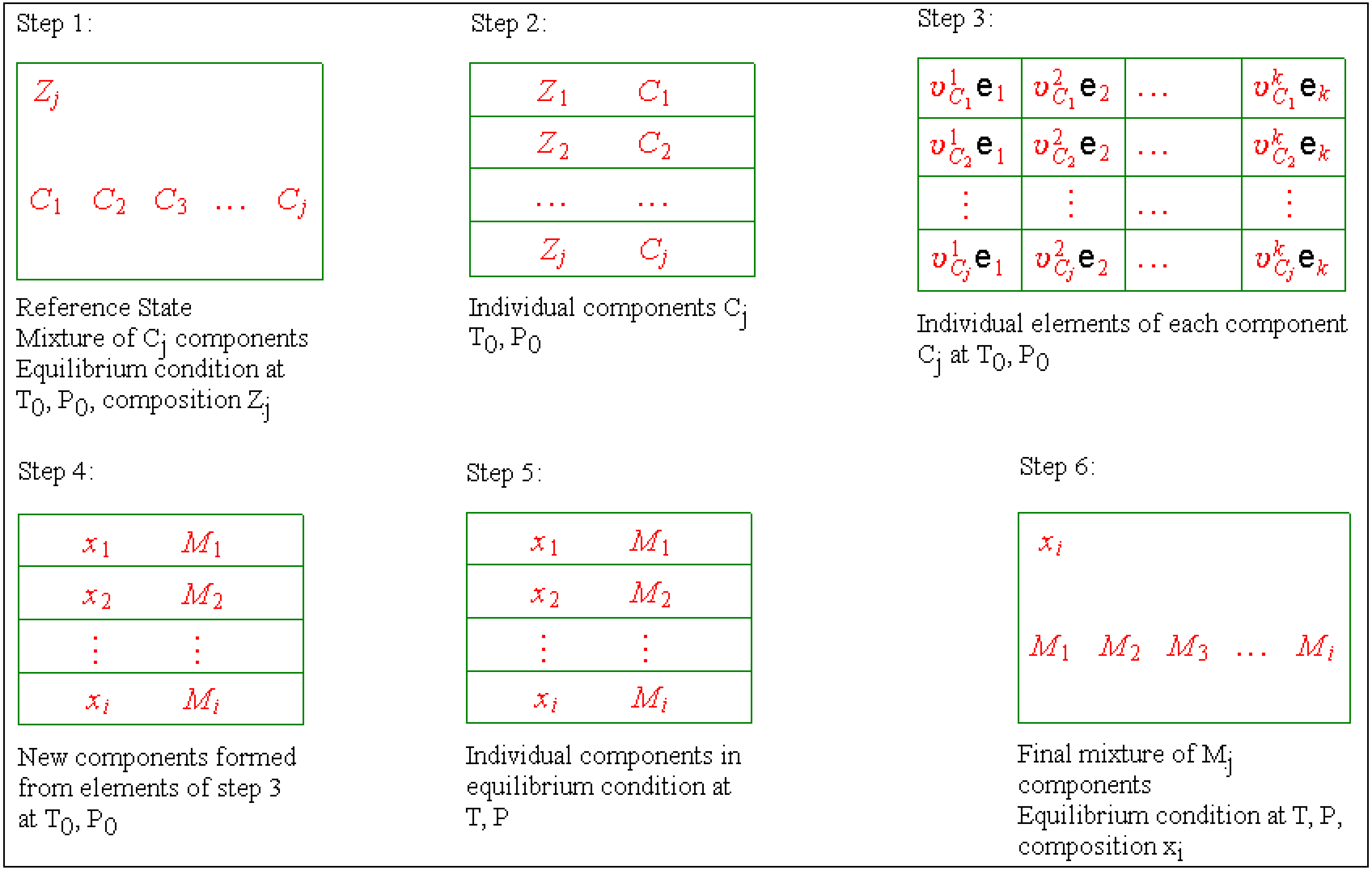
Exergy:

$Ex_{T,\,P} = B_{T,\,P} - B_{T0,\,P0}$

Driving Force (Δ)

- Potential energy (ΔZ)
- Kinetic energy (ΔV)
- Chemical energy (Δx)
- Heat (ΔT)
- Mechanical energy (ΔP)

Chemical Exergy



Step 1:

Z_j

$C_1 \quad C_2 \quad C_3 \quad \ldots \quad C_j$

Reference State
Mixture of C_j components
Equilibrium condition at
T_0, P_0, composition Z_j

Step 2:

Z_1	C_1
Z_2	C_2
$\ldots$	$\ldots$
Z_j	C_j

Individual components C_j
T_0, P_0

Step 3:

$\upsilon^1_{C_1} e_1$	$\upsilon^2_{C_1} e_2$	$\ldots$	$\upsilon^k_{C_1} e_k$
$\upsilon^1_{C_2} e_1$	$\upsilon^2_{C_2} e_2$	$\ldots$	$\upsilon^k_{C_2} e_k$
$\vdots$	$\vdots$	$\ldots$	$\vdots$
$\upsilon^1_{C_j} e_1$	$\upsilon^2_{C_j} e_2$	$\ldots$	$\upsilon^k_{C_j} e_k$

Individual elements of each component
C_j at T_0, P_0

Step 4:

x_1	M_1
x_2	M_2
$\vdots$	$\vdots$
x_i	M_i

New components formed
from elements of step 3
at T_0, P_0

Step 5:

x_1	M_1
x_2	M_2
$\vdots$	$\vdots$
x_i	M_i

Individual components in
equilibrium condition at
T, P

Step 6:

x_i

$M_1 \quad M_2 \quad M_3 \quad \ldots \quad M_i$

Final mixture of M_j
components
Equilibrium condition at T, P,
composition x_i

Chemical Exergy

- Standard chemical exergy of elements has been reported in the literature based on the average composition of earth's crust, oceans, and the atmosphere
- $Ex^0_{ch,j} = \Delta_f G^0_{j,T0} + \sum v_i Ex^0_{ch,i}$
- $\sum v_i e_i \rightarrow C_j$
- $Ex^0_{ch,i}$ is the standard chemical exergy of element i
- $\Delta_f G^0_{j,T0}$ is the standard Gibbs free energy of formation of component j

Theoretical, Practical, and Zero-emission Exergy Recovery in Energy Conversion Processes

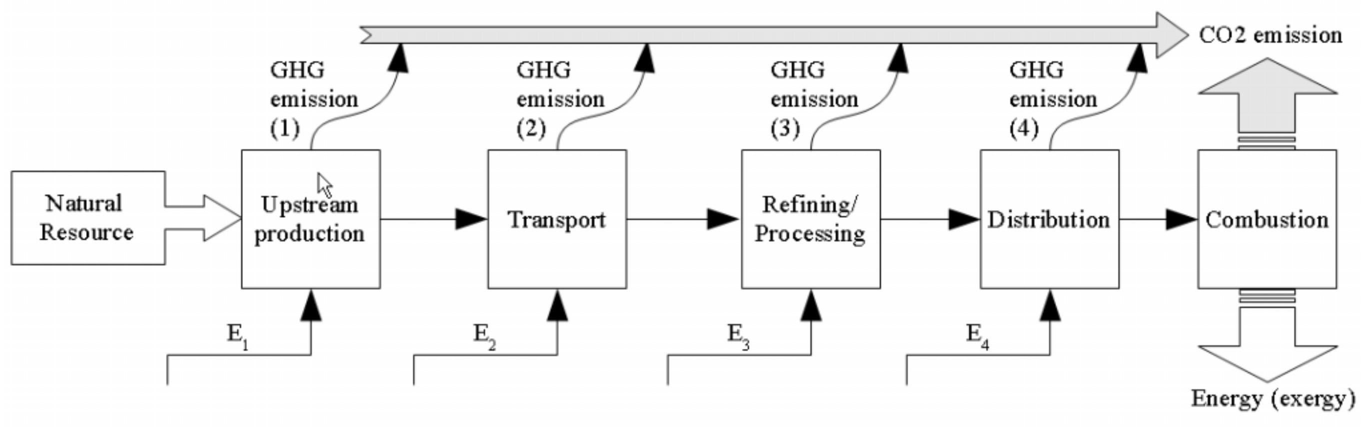
Part II: Formulation and Case studies

EROEI

- Energy Return On Energy Investment
- Definition:
  - How much of the energy available in a “natural resource” can be extracted per unit energy consumed in the recovery process, e.g., upstream operation, transportation, etc.
- Shortcomings:
  - Does not consider the energy quality, i.e. exergy
  - Highly depends on the current state of technology and its development

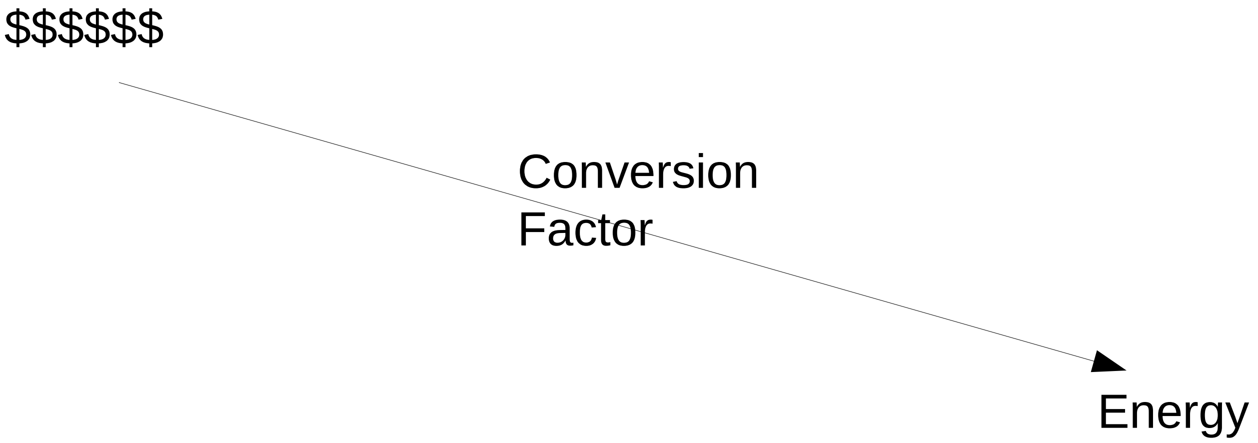
EROEI

- How much of the energy available in a natural resource can be extracted per unit energy consumed in the recovery process, e.g., upstream operation, transportation, etc.



Data?

- Translate the recorded economical data to energy data using commercial databases



$$$$$$

Conversion Factor

Energy

What happens?

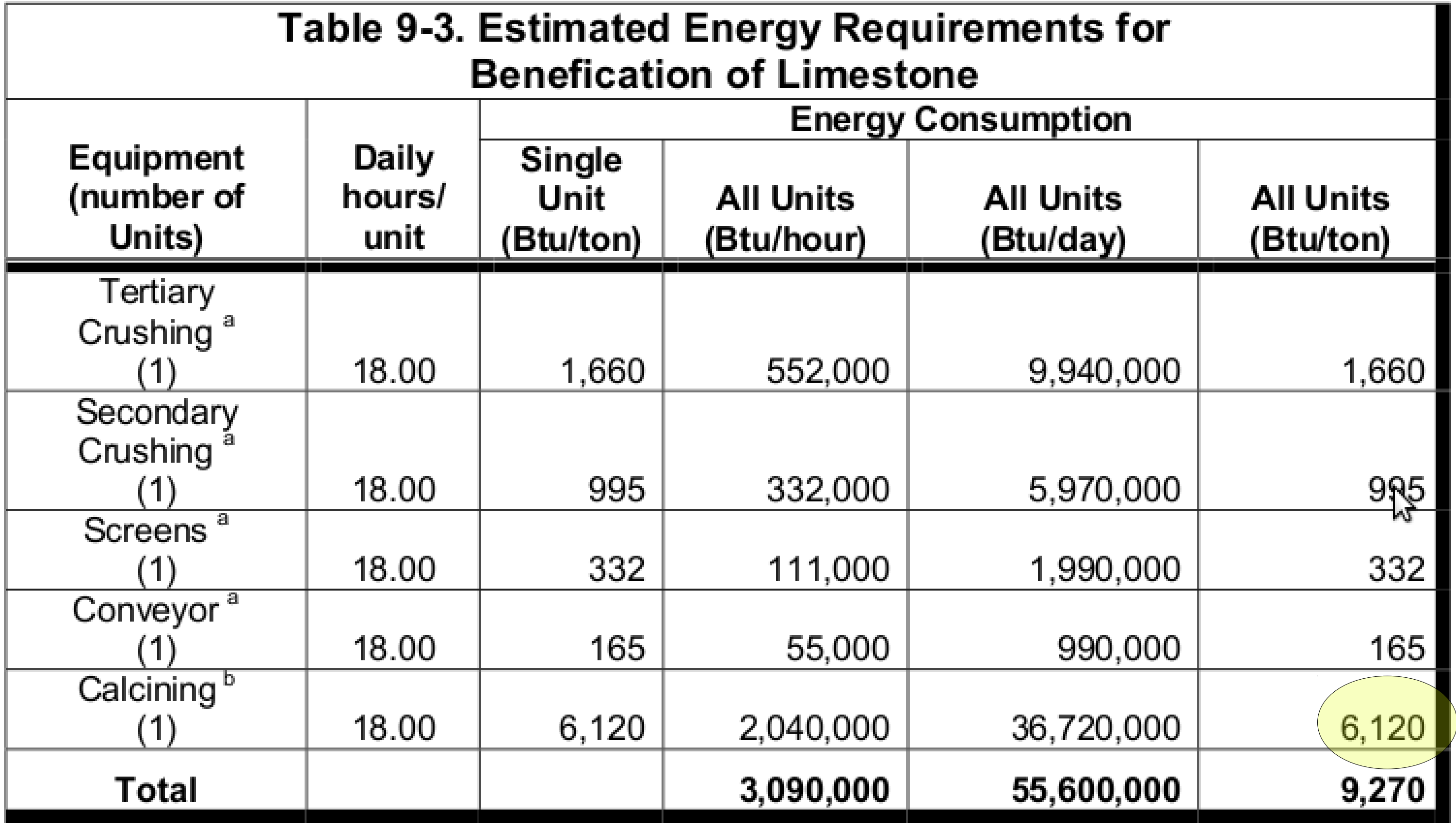


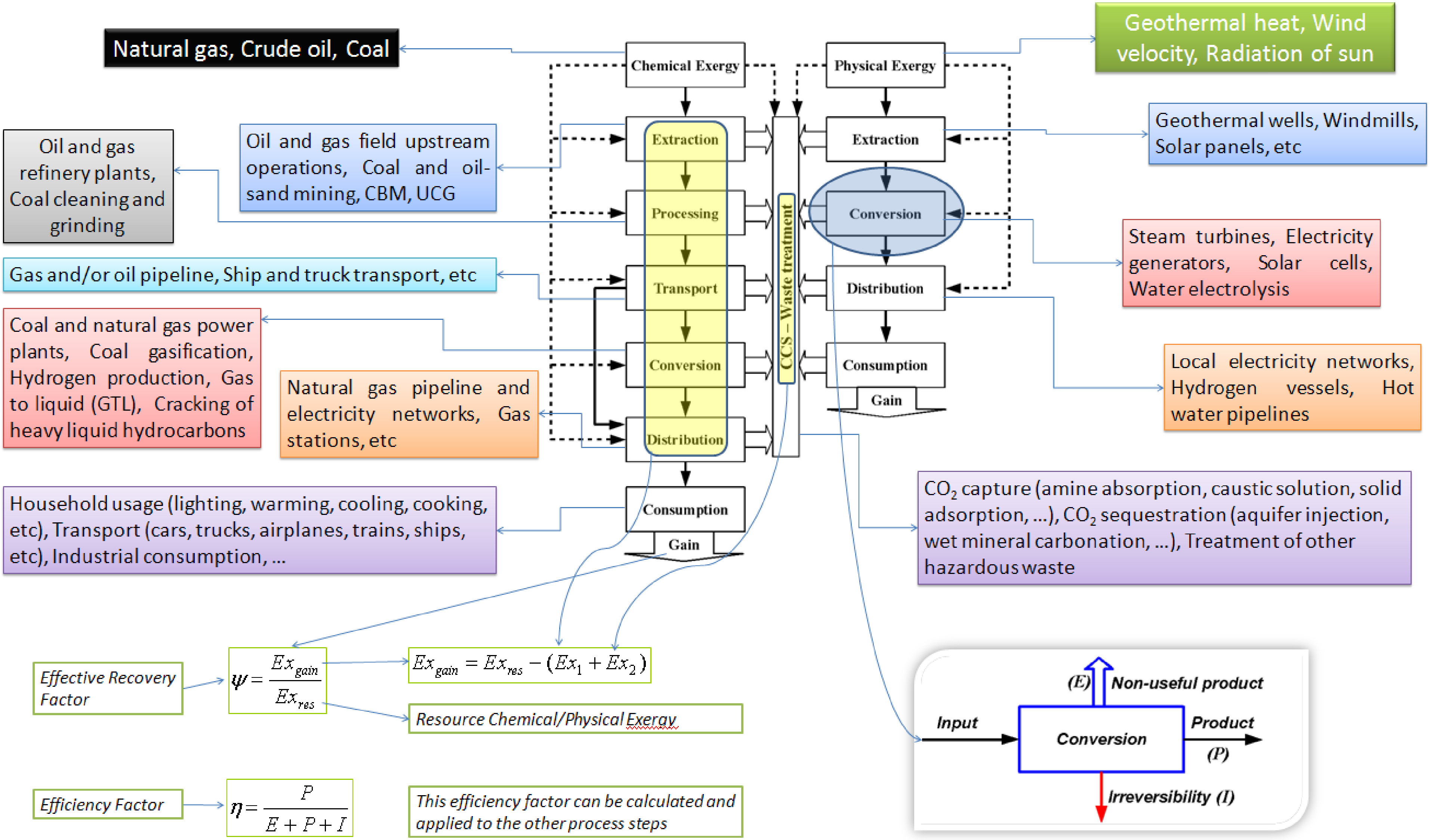
Table 9-3. Estimated Energy Requirements for Benefication of Limestone

Equipment (number of Units)	Daily hours/ unit	Energy Consumption			
		Single Unit (Btu/ton)	All Units (Btu/hour)	All Units (Btu/day)	All Units (Btu/ton)
Tertiary Crushing [a] (1)	18.00	1,660	552,000	9,940,000	1,660
Secondary Crushing [a] (1)	18.00	995	332,000	5,970,000	995
Screens [a] (1)	18.00	332	111,000	1,990,000	332
Conveyor [a] (1)	18.00	165	55,000	990,000	165
Calcining [b] (1)	18.00	6,120	2,040,000	36,720,000	6,120
Total			**3,090,000**	**55,600,000**	**9,270**

?!!

$CaCO_3 + Q \leftrightarrow CaO + CO_2$ Q(calculated) = 3074 kJ/kg CaO

Process Flow Diagram



Natural gas, Crude oil, Coal

Geothermal heat, Wind velocity, Radiation of sun

Oil and gas refinery plants, Coal cleaning and grinding

Oil and gas field upstream operations, Coal and oil-sand mining, CBM, UCG

Geothermal wells, Windmills, Solar panels, etc

Steam turbines, Electricity generators, Solar cells, Water electrolysis

Gas and/or oil pipeline, Ship and truck transport, etc

Coal and natural gas power plants, Coal gasification, Hydrogen production, Gas to liquid (GTL), Cracking of heavy liquid hydrocarbons

Natural gas pipeline and electricity networks, Gas stations, etc

Local electricity networks, Hydrogen vessels, Hot water pipelines

Household usage (lighting, warming, cooling, cooking, etc), Transport (cars, trucks, airplanes, trains, ships, etc), Industrial consumption, ...

CO$_2$ capture (amine absorption, caustic solution, solid adsorption, ...), CO$_2$ sequestration (aquifer injection, wet mineral carbonation, ...), Treatment of other hazardous waste

Effective Recovery Factor

$$\psi = \frac{Ex_{gain}}{Ex_{res}}$$

$$Ex_{gain} = Ex_{res} - (Ex_1 + Ex_2)$$

Resource Chemical/Physical Exergy

Efficiency Factor

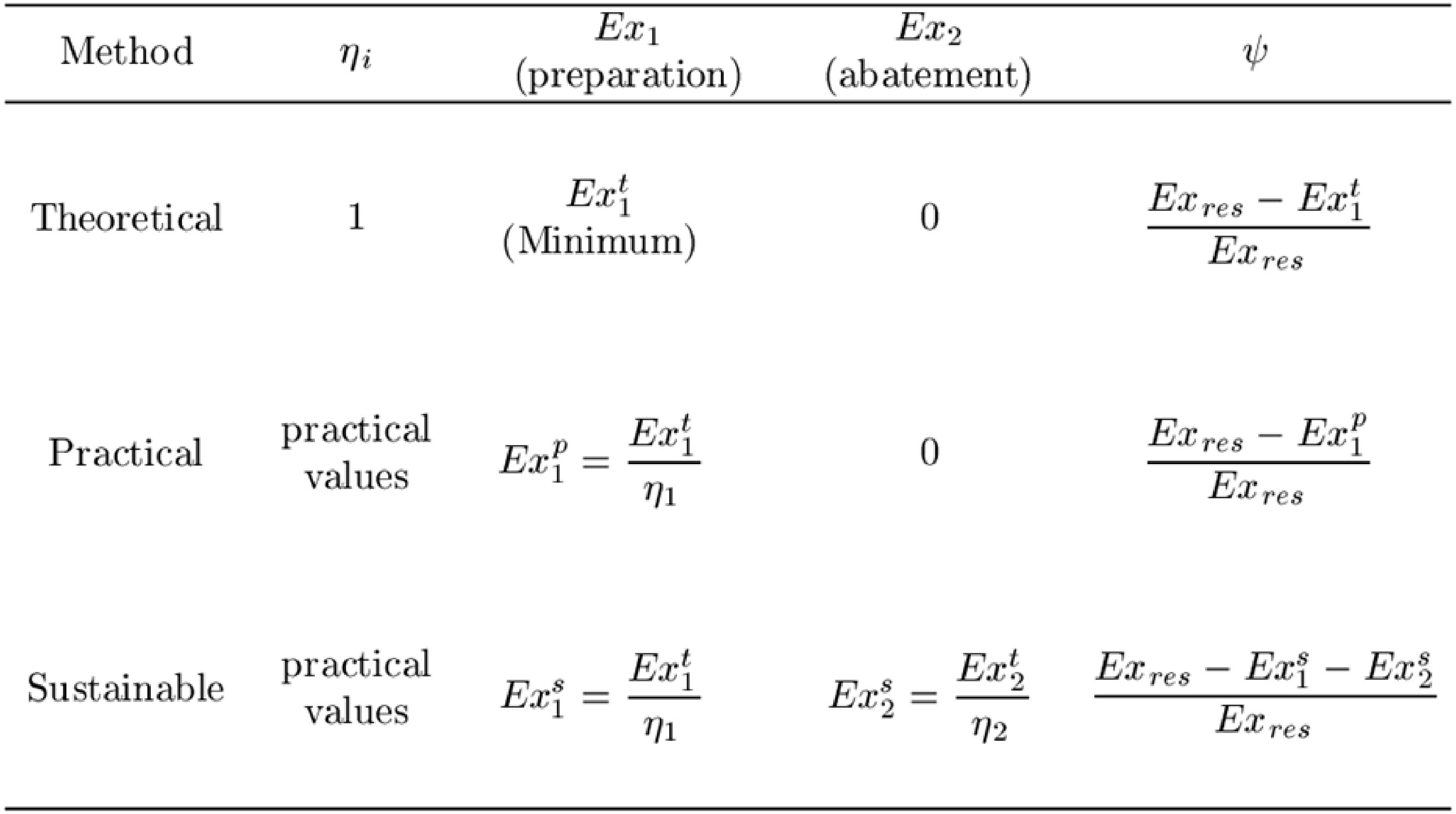
$$\eta = \frac{P}{E + P + I}$$

This efficiency factor can be calculated and applied to the other process steps

Theoretical, Practical, and zero-emission exergy recovery

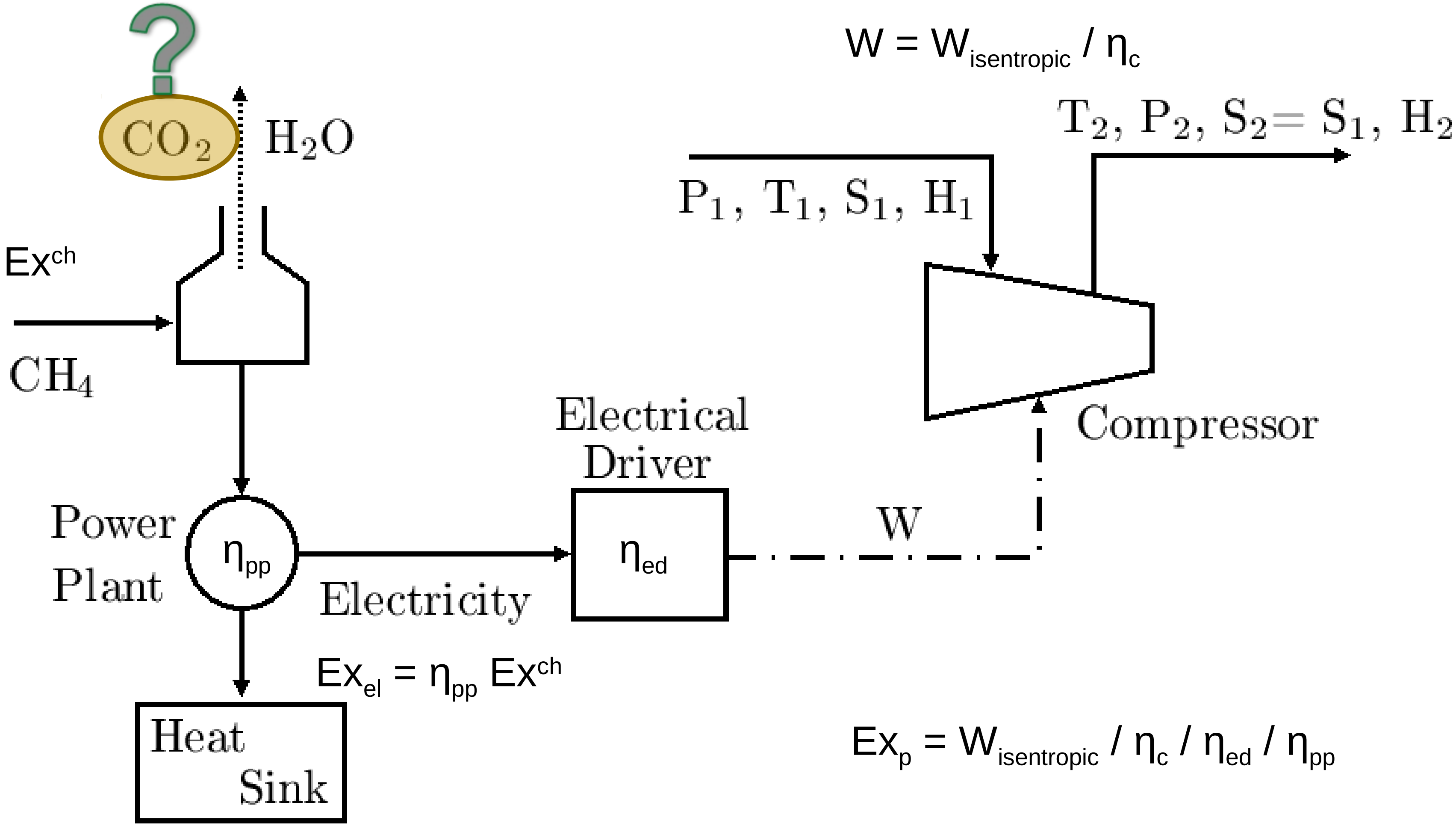
- Theoretical exergy recovery
  - Based on the reversible processes shows the maximum possible exergy recovery with the following assumptions:
    - No mechanical exergy loss in the process equipments
    - No cumulative exergy consumptions (CExC) in the material and energy streams
- Practical exergy recovery
  - Based on the irreversible processes and considering the current technology, uses the following assumptions:
    - Mechanical efficiency of process equipments
    - Cumulative exergy consumption (CExC) in the material and energy streams
- Zero-emission exergy recovery
  - Considering the exergy consumption in cleaning the environmental footprints of fossil fuel life cycle in addition to the practical recovery

Calculation of theoretical, practical and sustainable exergy consumption



Method	η_i	Ex_1 (preparation)	Ex_2 (abatement)	ψ
Theoretical	1	Ex_1^t (Minimum)	0	$\frac{Ex_{res} - Ex_1^t}{Ex_{res}}$
Practical	practical values	$Ex_1^p = \frac{Ex_1^t}{\eta_1}$	0	$\frac{Ex_{res} - Ex_1^p}{Ex_{res}}$
Sustainable	practical values	$Ex_1^s = \frac{Ex_1^t}{\eta_1}$	$Ex_2^s = \frac{Ex_2^t}{\eta_2}$	$\frac{Ex_{res} - Ex_1^s - Ex_2^s}{Ex_{res}}$

A simple example

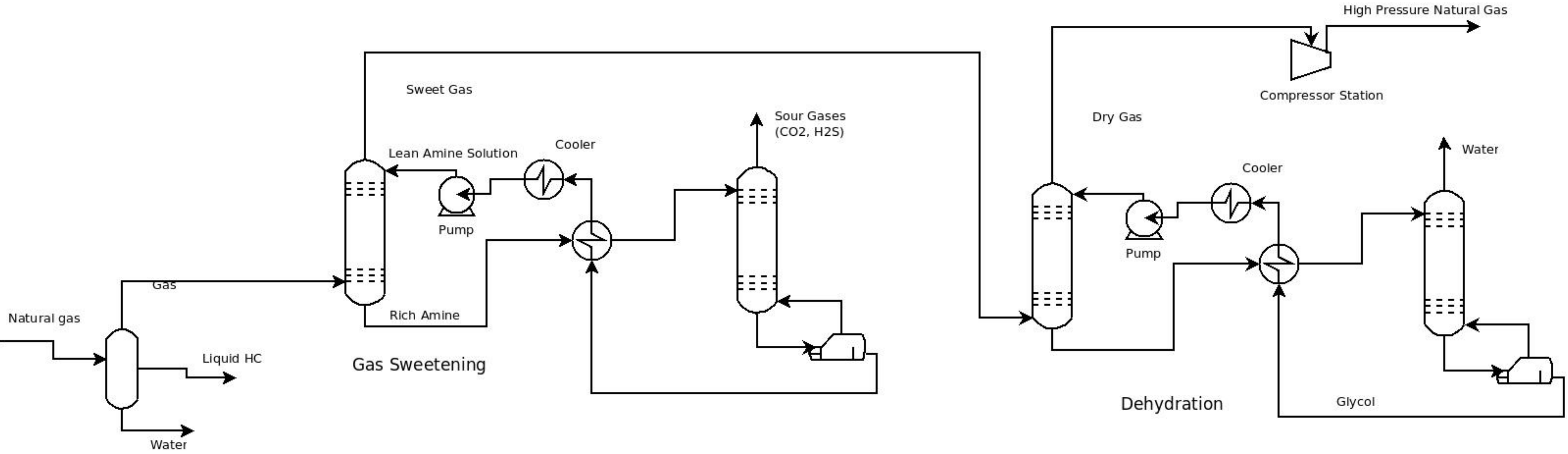


$W = W_{isentropic} / \eta_c$

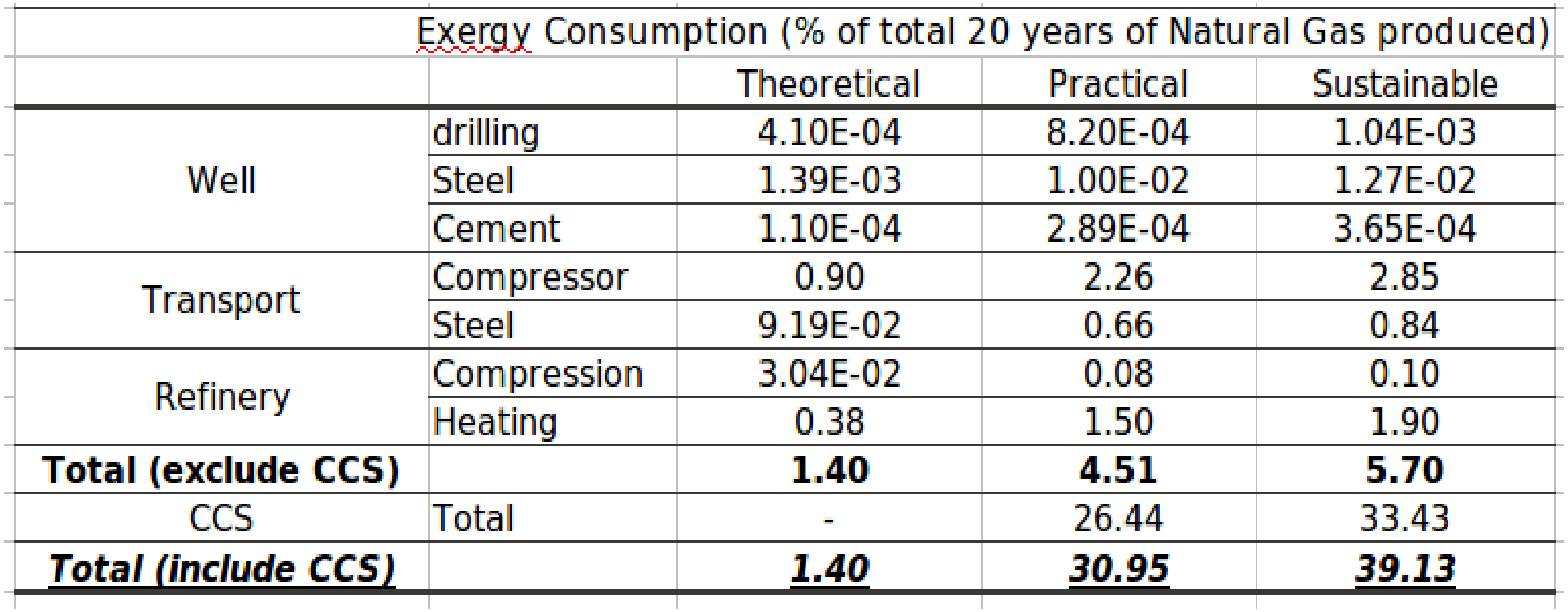
$Ex_{el} = \eta_{pp} Ex^{ch}$

$Ex_p = W_{isentropic} / \eta_c / \eta_{ed} / \eta_{pp}$

Natural Gas


High Pressure Natural Gas
Compressor Station
Sweet Gas
Dry Gas
Sour Gases
(CO2, H2S)
Water
Lean Amine Solution
Cooler
Cooler
Pump
Pump
Gas
Natural gas
Rich Amine
Liquid HC
Gas Sweetening
Dehydration
Glycol
Water

Results for Natural Gas



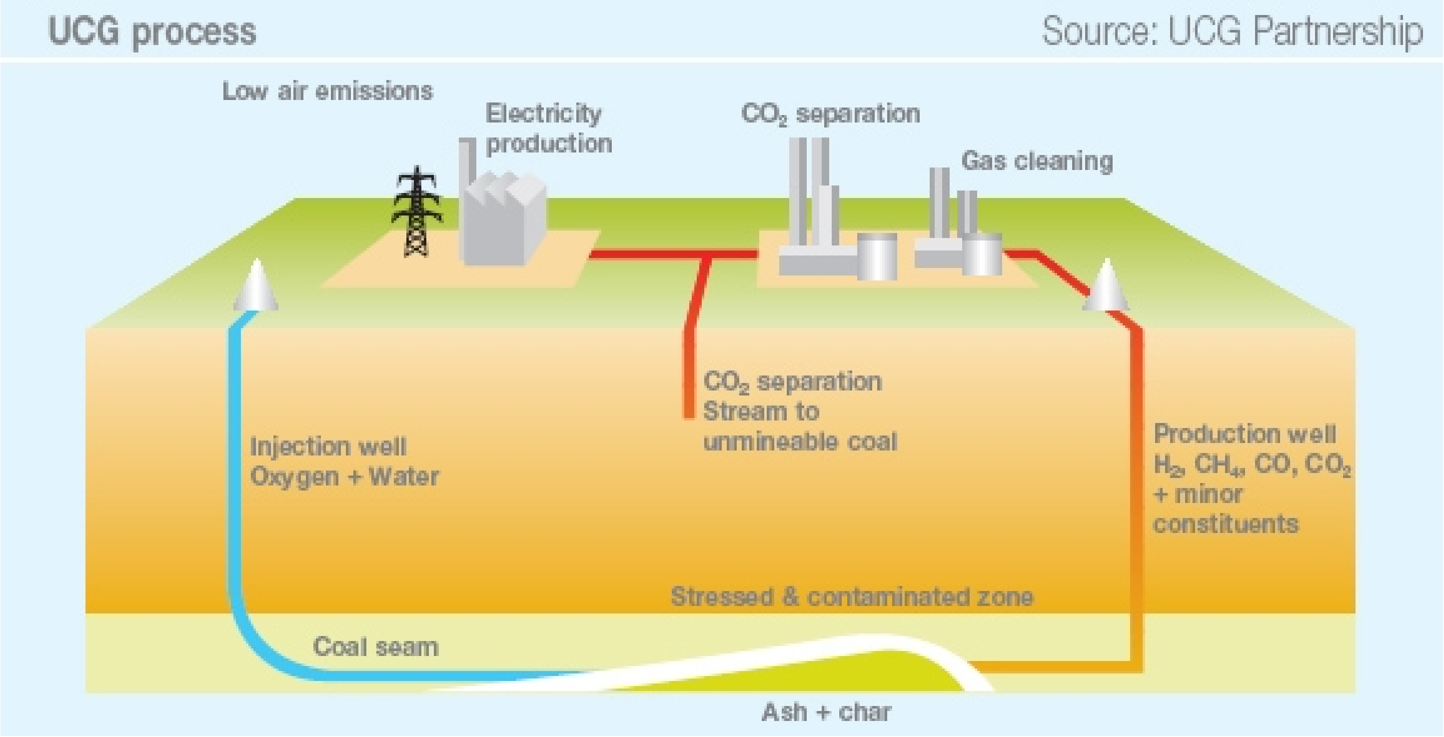
		Exergy Consumption (% of total 20 years of Natural Gas produced)		
		Theoretical	Practical	Sustainable
Well	drilling	4.10E-04	8.20E-04	1.04E-03
	Steel	1.39E-03	1.00E-02	1.27E-02
	Cement	1.10E-04	2.89E-04	3.65E-04
Transport	Compressor	0.90	2.26	2.85
	Steel	9.19E-02	0.66	0.84
Refinery	Compression	3.04E-02	0.08	0.10
	Heating	0.38	1.50	1.90
Total (exclude CCS)		**1.40**	**4.51**	**5.70**
CCS	Total	-	26.44	33.43
Total (include CCS)		***1.40***	***30.95***	***39.13***

Underground Coal Gasification (UCG)

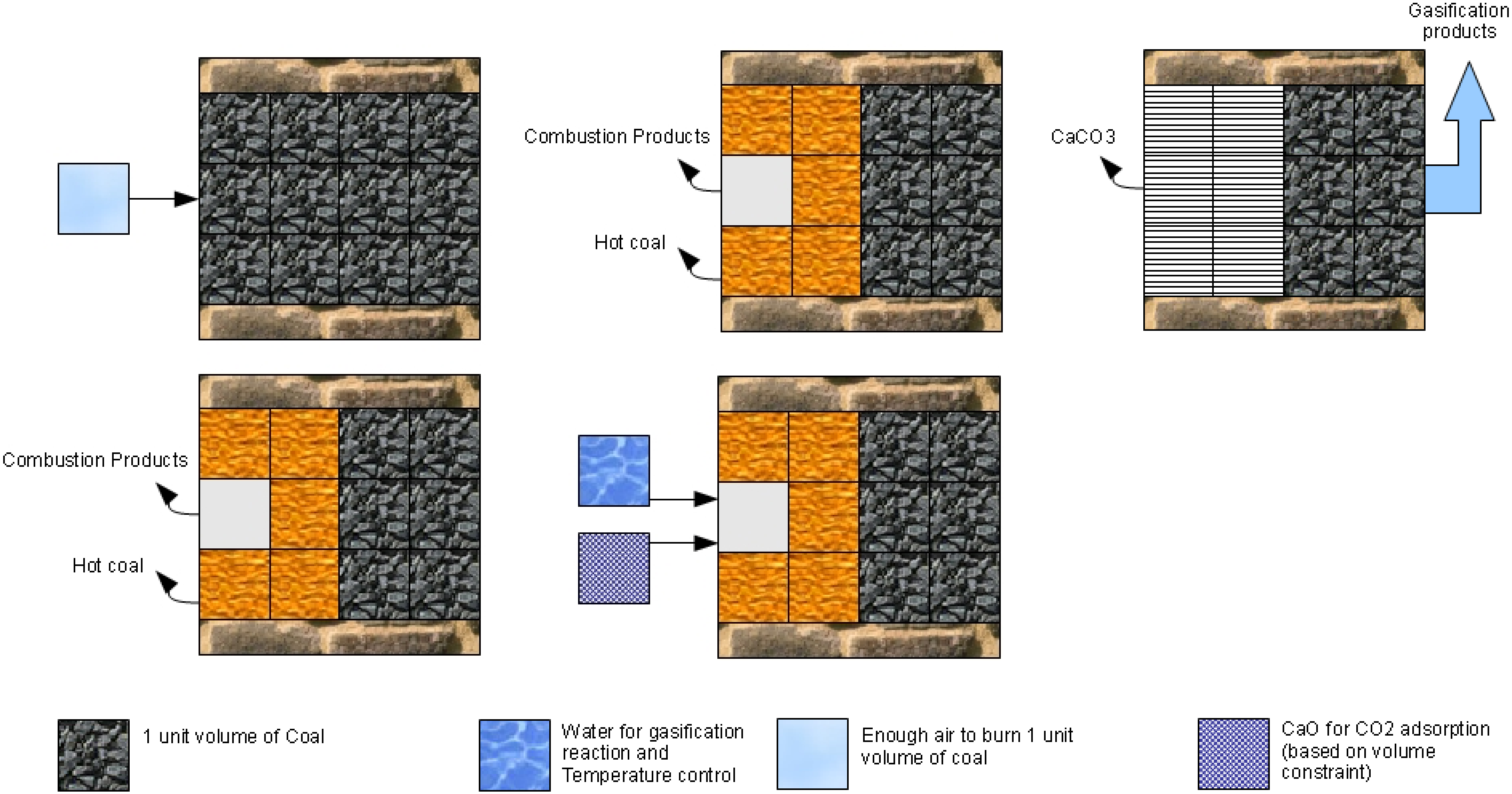
- Un-minable coal resources: less than 15% of the known coal resources can be extracted using conventional mining methods

-Environmental issues of mining

-Low quality coal seams



UCG with mineral injection



Chemical reactions

- Combustion
  - $C + O_2 \rightarrow CO_2$ + 393.77 kJ/mol
- Gasification
  - Global reaction
    - $C + 2\,H_2O + CaO \leftrightarrow CaCO_3 + 2\,H_2$ + 87.9 kJ/mol
  - Boudouard reaction
    - $C + CO_2 \leftrightarrow 2\,CO$ – 172.58 kJ/mol
  - Shift reaction
    - $CO + H_2O \leftrightarrow CO_2 + H_2$ – 41.98 kJ/mol
  - Methanation
    - $C + 2\,H_2 \leftrightarrow CH_4$ + 74.90 kJ/mol

Equilibrium relations

$$\prod_i \left(y_i \hat{\varphi}_i\right)^{v_{i,j}} = \left(\frac{P}{P^o}\right)^{-v_j} K_j$$

y_i: gas phase mole fraction

P^0: standard pressure (1 bar)

P: system pressure

K_j: equilibrium constant of reaction j

$v_{i,j}$: stoichiometric coefficient of component i in reaction j

Φ_i: fugacity coefficient of component i in a gas mixture

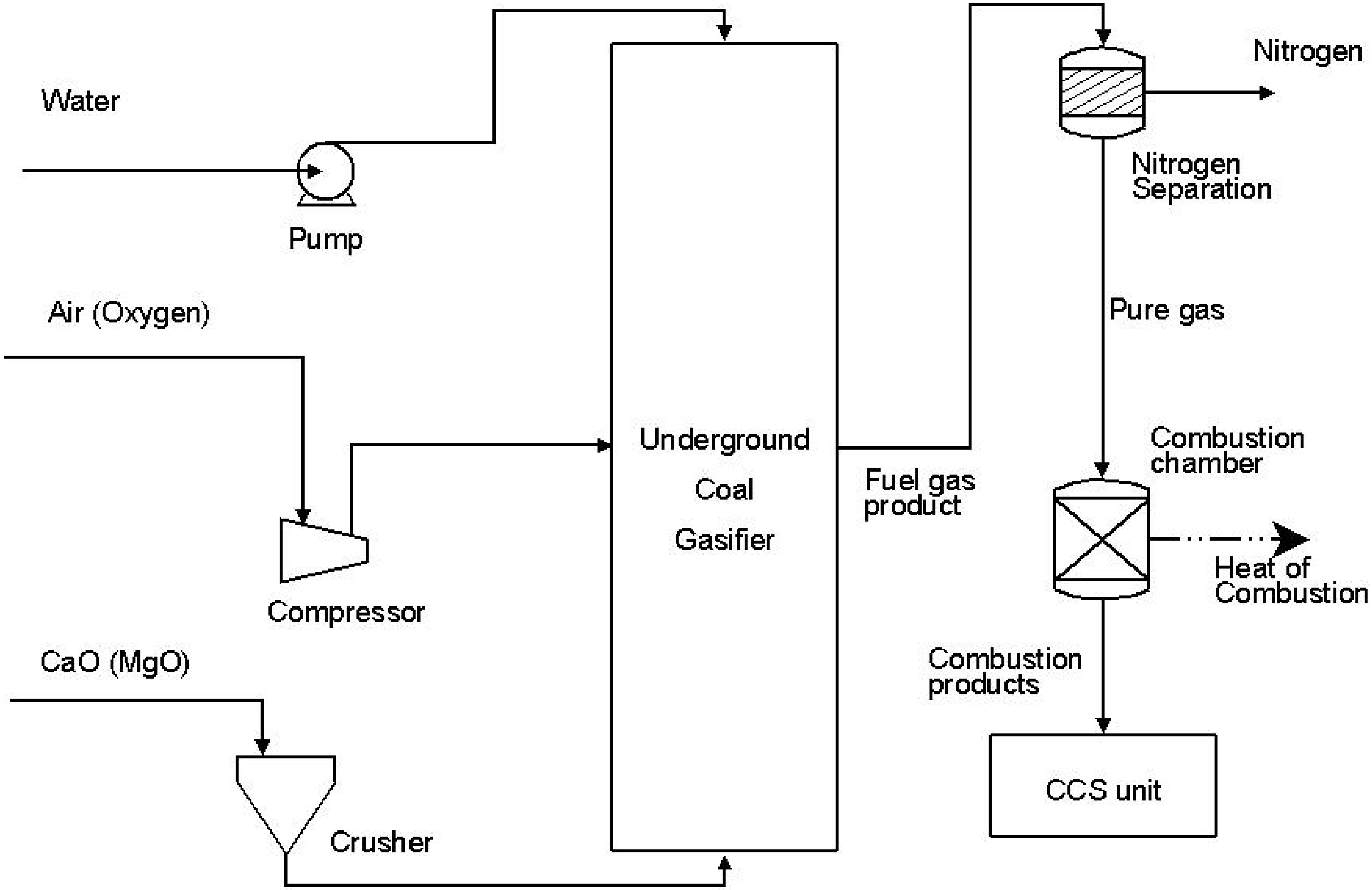
$$\exp \frac{-\sum_i v_{i,j} G_i^o}{RT} \equiv K_j$$

$$\frac{\Delta G^o}{RT} = \frac{\Delta G_0^o - \Delta H_0^o}{RT_0} + \frac{\Delta H_0^o}{RT} + \frac{1}{T}\int_{T_0}^{T} \frac{\Delta C_P^o}{R} dT - \int_{T_0}^{T} \frac{\Delta C_P^o}{RT} dT$$

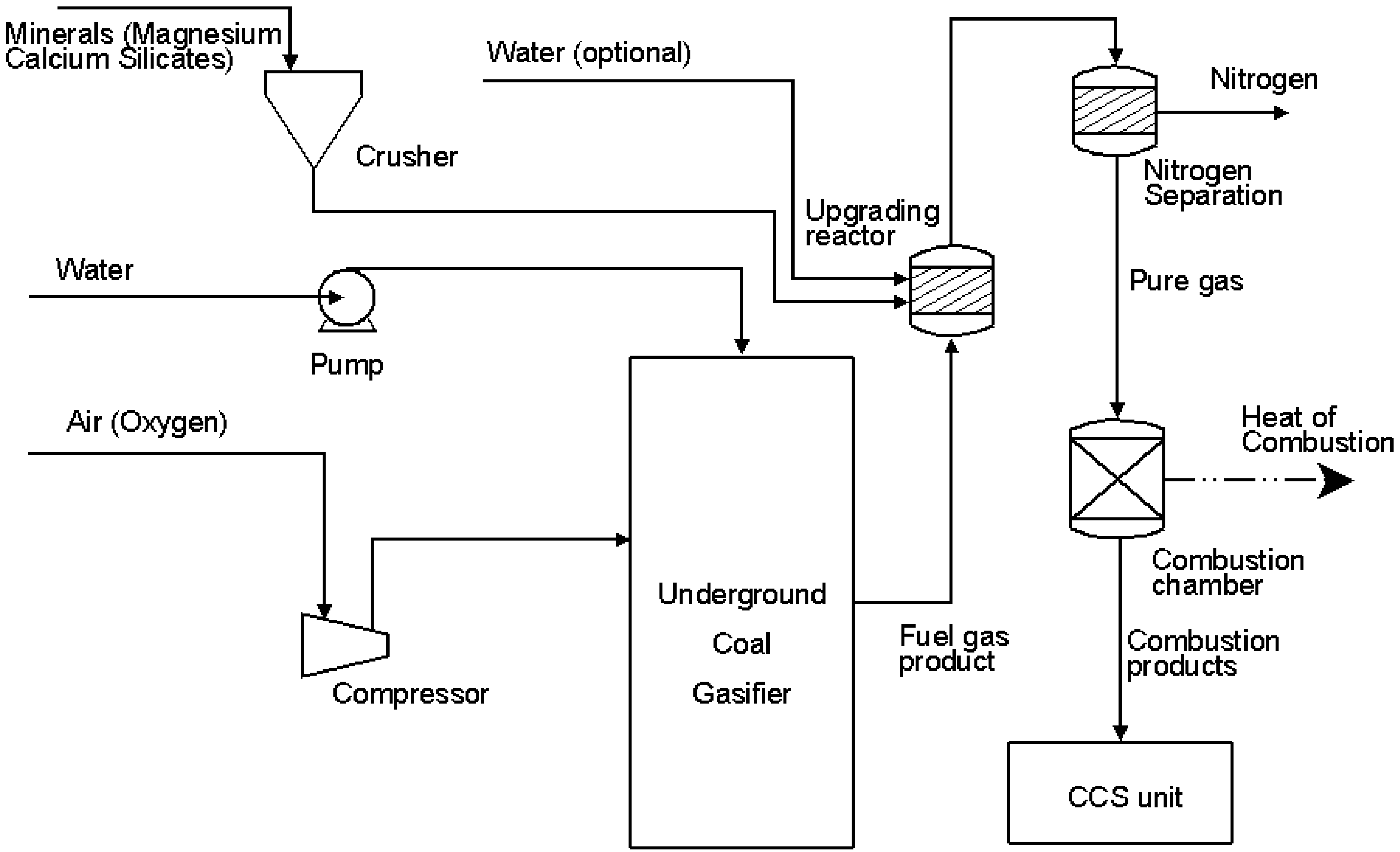
$$\sum_i v_{i,j} H_{0\mathrm{i}}^o \equiv \Delta H_0^o$$

$$\sum_i v_{i,j} C_{P_i}^o \text{¿} \Delta C_{P^o}$$

UCG process flow diagram (1)



UCG process flow diagram (2)



Application in UCG process

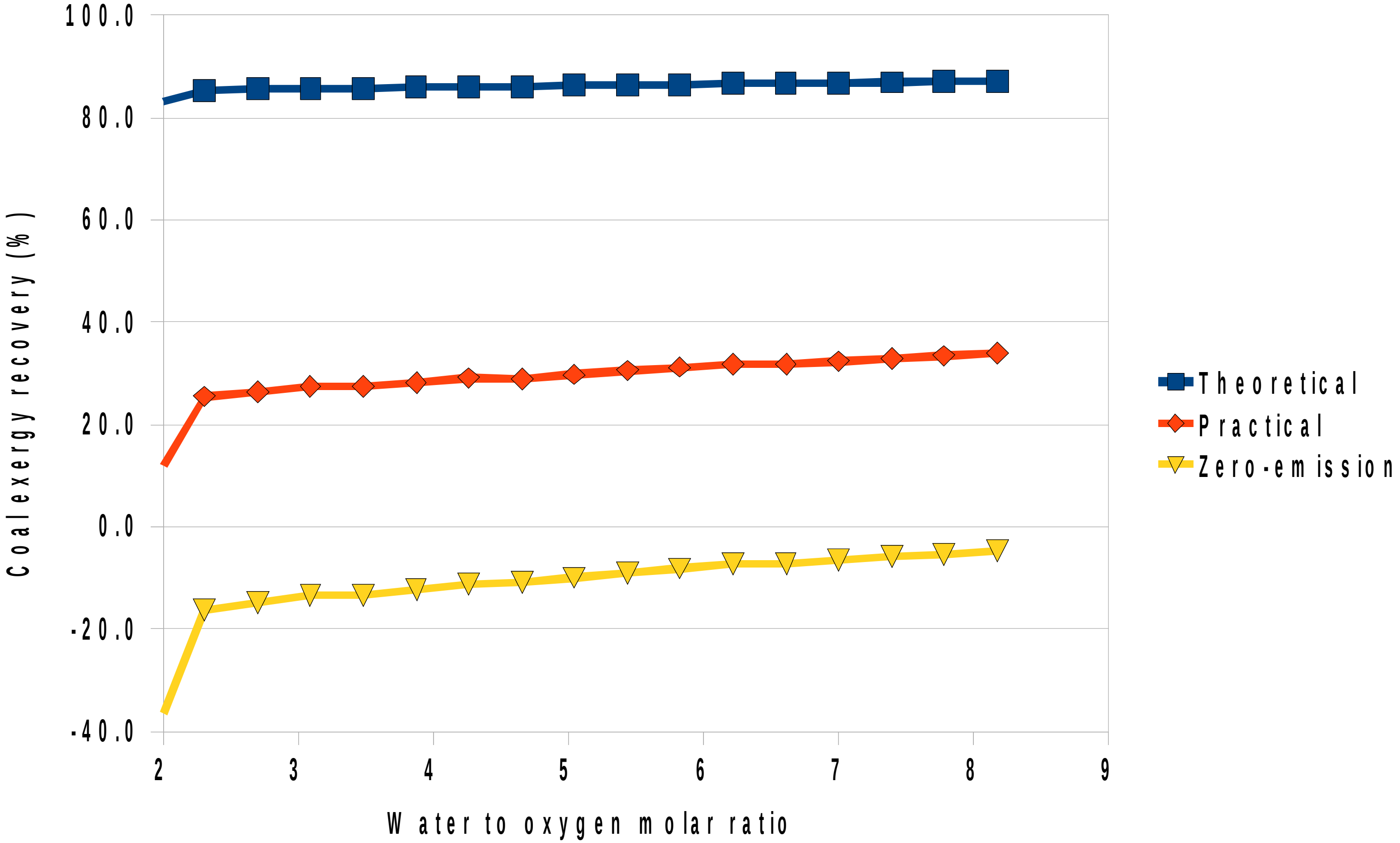
$$R_{coal}^{UCG} = \frac{Ex_{prod} - Ex_{con}}{Ex_{coal}^{Ch}}$$

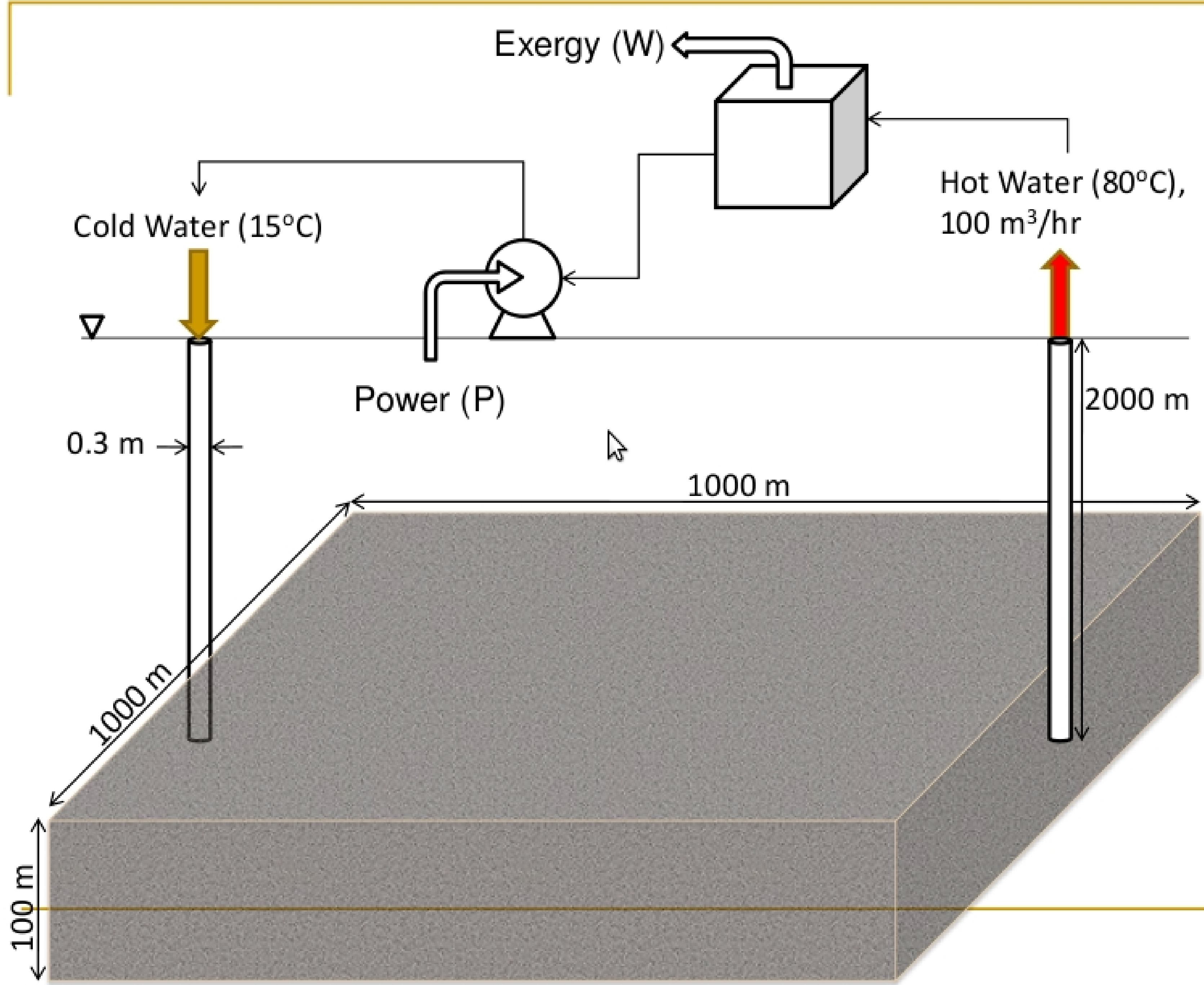
$$Ex_{con}^{th} = W_{pump} + W_{comp} + Ex_{CaO}^{Ch} + Ex_{water}^{Ch}$$

$$Ex_{con}^{pr} = \frac{W_{pump}}{\eta_{pump}\eta_{elec}} + \frac{W_{comp}}{\eta_{comp}\eta_{elec}} + \frac{Ex_{CaO}^{Ch}}{\eta_{CaO}^{prod}} + \frac{Ex_{water}^{Ch}}{\eta_{water}^{prod}}$$

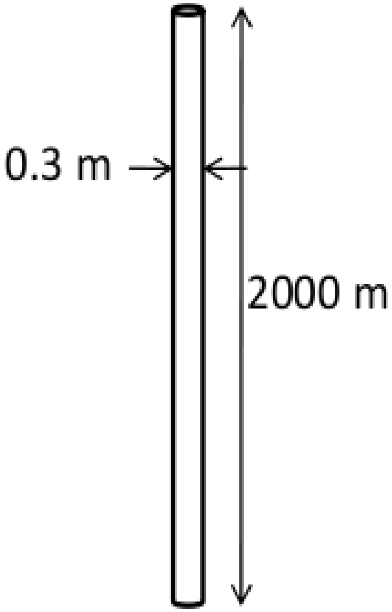
$$\begin{aligned} Ex_{con} \quad = \quad & \frac{W_{pump}}{\eta_{pump}\eta_{elec}} + \frac{W_{comp}}{\eta_{comp}\eta_{elec}} + \frac{Ex_{CaO}^{Ch}}{\eta_{CaO}^{prod}} + \frac{Ex_{water}^{Ch}}{\eta_{water}^{prod}} \\ & + Ex_{ccs}^{in} + Ex_{ccs}^{out} + Ex_{ccs}^{comb} \end{aligned}$$

Exergetic recovery of UCG (1)




Exergy (W)
Hot Water (80°C), 100 m³/hr
Cold Water (15°C)
Power (P)
0.3 m
2000 m
1000 m
1000 m
100 m

Pressure drop in the pipes



$$\frac{\Delta P}{\rho} = 4 f \frac{L}{D} \frac{V^2}{2}$$

f = friction factor:

$$f = \frac{16}{\mathrm{Re}}$$ For laminar flow

For f in other flow regimes, see Moody diagram

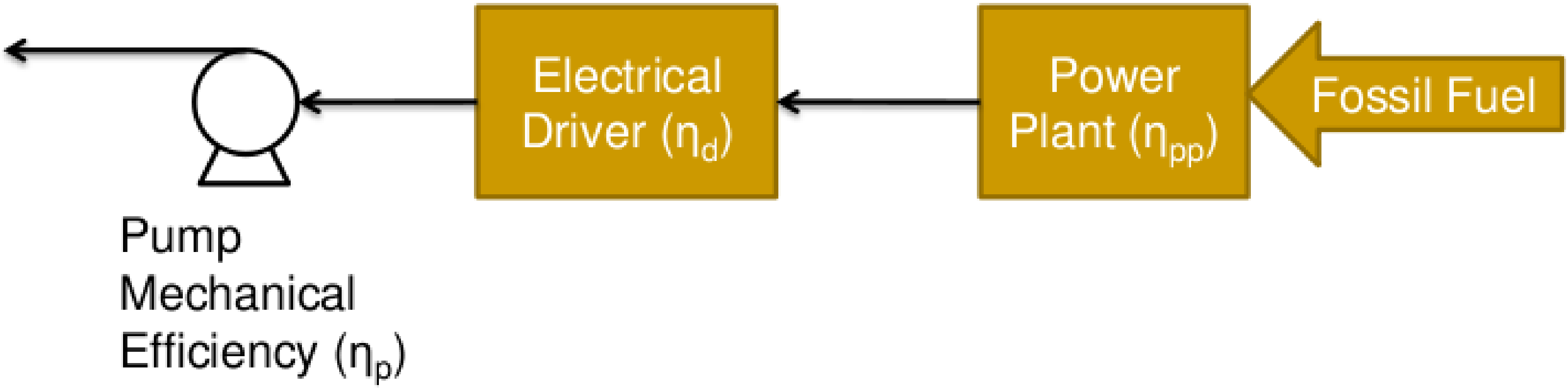
L = Length of pipe [m]
D = Diameter of pipe [m]
V = Liquid flow velocity [m/s]
ρ = Liquid density [kg/m^3]
ΔP = Pressure drop [Pa]

Pressure drop in porous media

ΔP = Pressure drop [Pa]
μ = Fluid viscosity [Pa.s]
k = Permeability [m^2]
u = Darcy velocity [m/s]
L = Length of porous media [m]

$$\Delta P = \frac{\mu}{k} u L$$

Pumping exergy



Electrical Driver (η_d)

Power Plant (η_{pp})

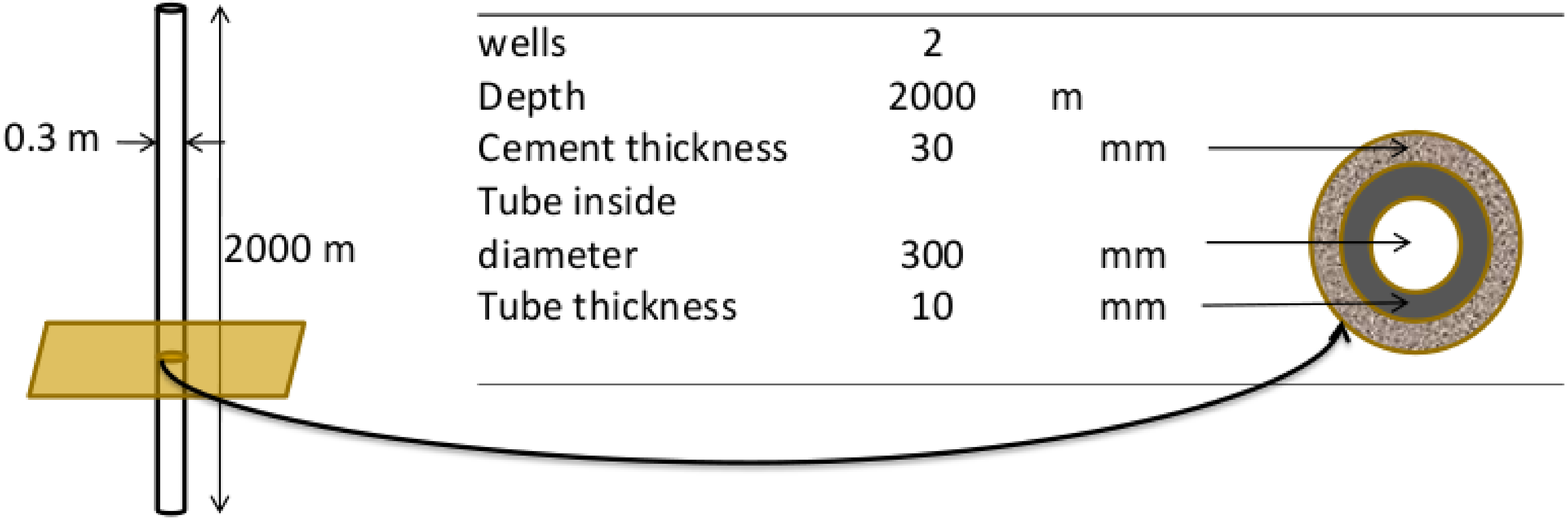
Fossil Fuel

Pump Mechanical Efficiency (η_p)

$$Ex_p = \frac{Q\left(\Delta P_{pipe} + \Delta P_{PM}\right)}{\eta_p \eta_{pp} \eta_d}$$

Ex_p = Pump exergy consumption [J/s]
Q = Volumetric flow of water [m^3/s]
ΔP_{pipe} = pressure drop in pipes [Pa]
ΔP_{PM} = pressure drop in porous media [Pa]

Steel and Cement embodied exergy



wells	2	
Depth	2000	m
Cement thickness	30	mm
Tube inside diameter	300	mm
Tube thickness	10	mm

Steel	58094.71	kJ/kg
Cement	2323.79	kJ/kg
Steel density	7850	kg/m^3
Cement density	2000	kg/m^3

Exergy Consumption & Production

	kJ/s	%
Pump	8.29	21.91
Drilling	0.44	1.15
Piping	28.15	74.44
Cement	0.94	2.50
Sum	37.82	100.00

$$\eta_{Ex} = \frac{Ex_p - Ex_c}{Ex_p} \times 100$$

$$= \frac{623.38 - 37.82}{623.38} \times 100$$

$$= 93.9\%$$

Exergy Production = 623.38 kJ/s

Sustainable exergetic recovery of fossil fuels