Efficient Combustion: The Chemical Engineer's Quest?

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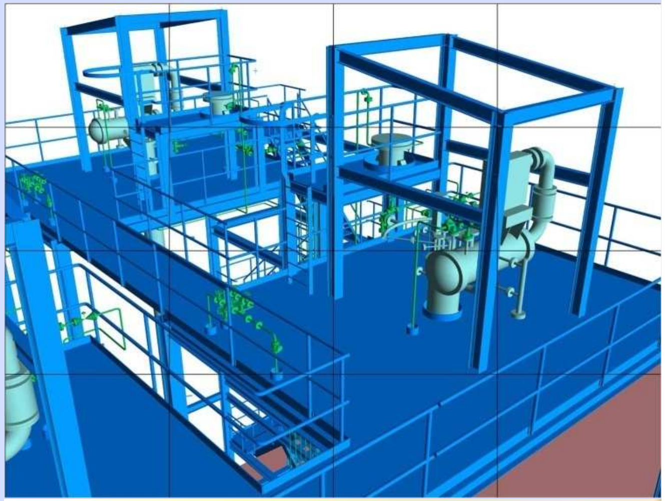

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COMPS
CENTRE OF MATERIAL AND PROCESS SYNTHESIS

Introduction

Reversible Process

Less energy

Less or even no CO_2 emissions

Products/ Electricity

Irreversible Process

More energy

More CO_2 emissions

Products/ Electricity

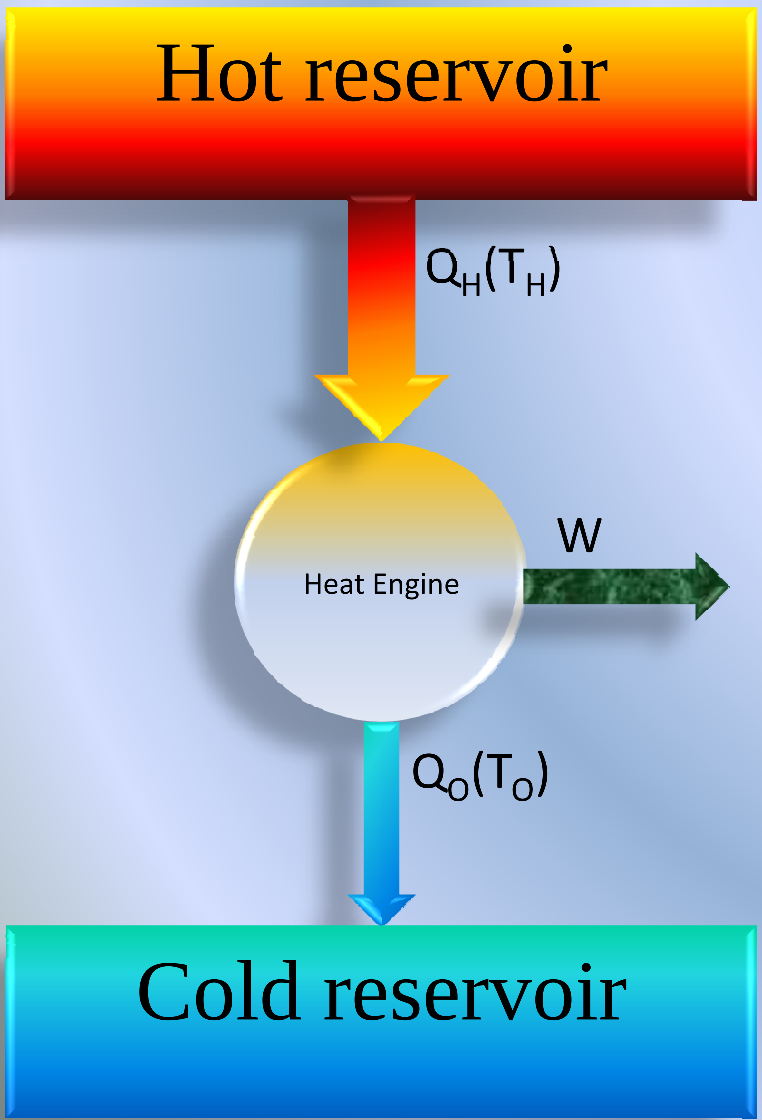
Introduction

Coal Fired Power Stations

- Biggest man-made CO_2 emitters (33%)
- Low efficiency : 40%

This raises concern in terms of both the environment and conservation of resources

Power plant efficiency: The traditional Approach



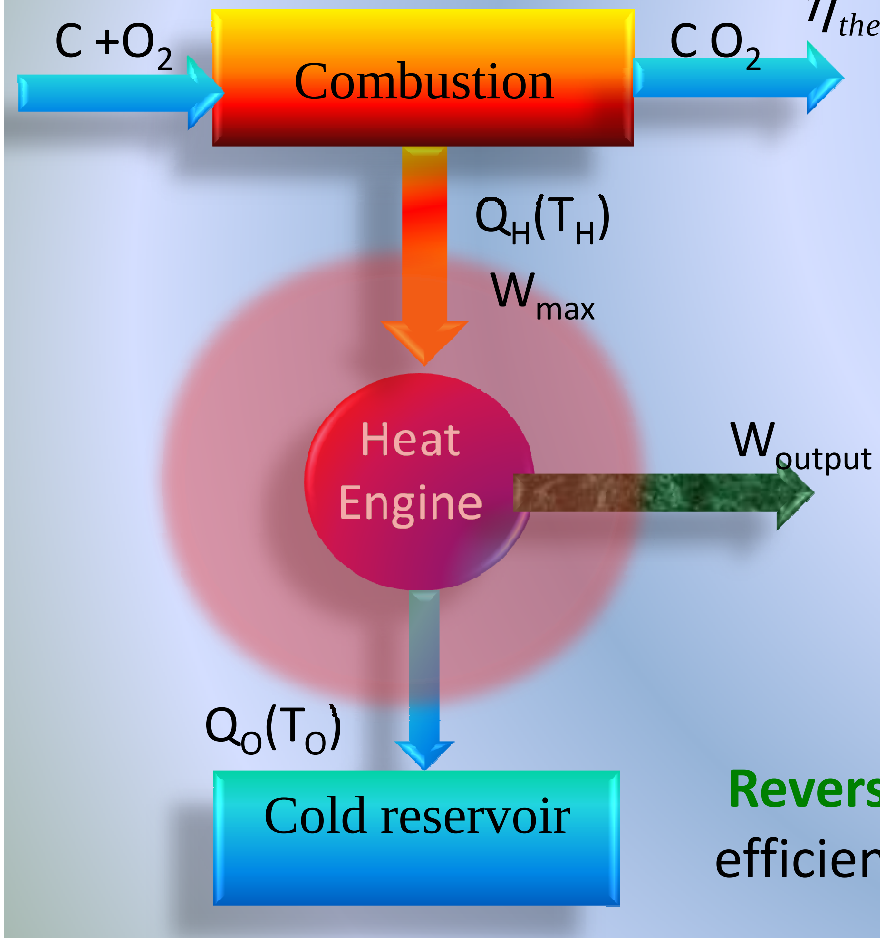
Reversible heat engine system

$$\eta_{thermal} = \frac{W}{Q_H} = \left(1 - \frac{T_O}{T_H}\right)$$

- Power plant design aim at increasing $\boldsymbol{\eta_{thermal}}$ mostly by increasing T_H
- T_H is dictated by material resistance
- Currently for power plant Improvement = High temperature resistant material

Little Room for Improvement

Power plant efficiency:



$$\eta_{thermal} = \frac{W_{\text{output}}}{Q_H} = \left(1 - \frac{T_O}{T_H}\right)$$ Power plant performance

Heat quality / work content of heat /work potential of heat

$$W_{\max} = Q_H \left(1 - \frac{T_O}{T_H}\right)$$

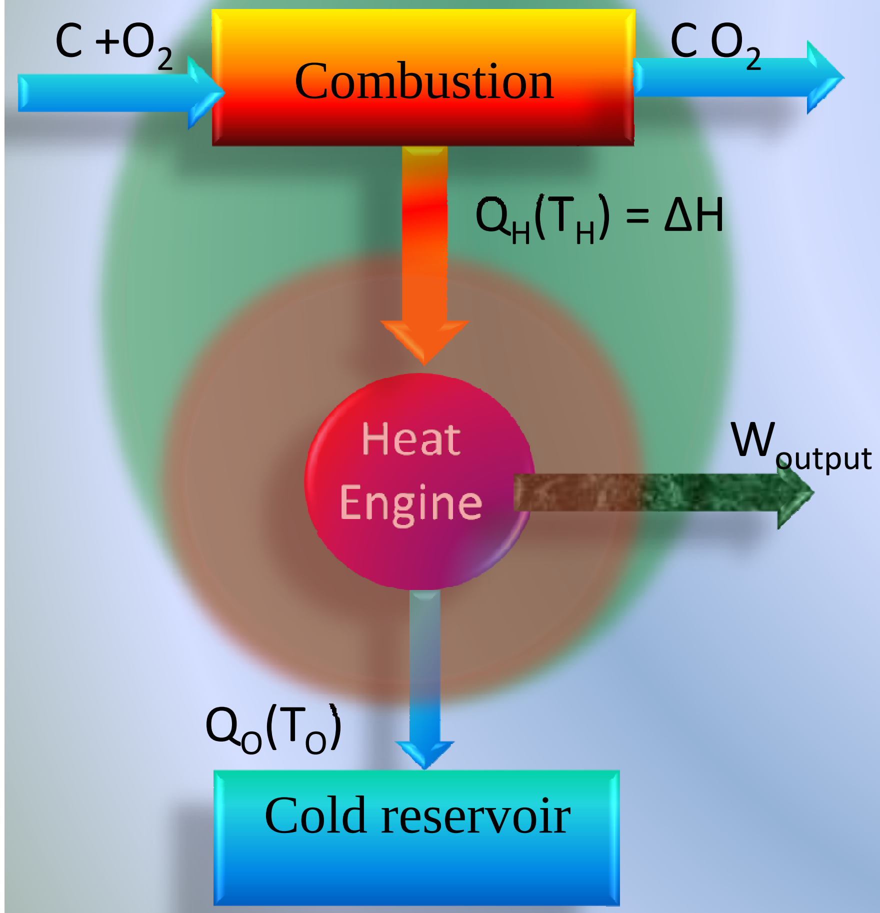
Real efficiency

$$\eta_{Work} = \frac{W_{output}}{W_{\max}}$$

Reversible Heat Engine is essentially **100%** efficient since:

$$W_{output} = W_{\max}$$

Power plant efficiency: Fundamental Approach



$$\eta_{thermal} = \frac{W_{output}}{\Delta H} = \left(1 - \frac{T_O}{T_H}\right)$$

Power plant performance ✗

A more fundamental efficiency

$$\eta_{Work} = \frac{W_{output}}{W_{target}}$$

✓

Target work = Chemical potential of process = Gibbs Free Energy across the process

$$\eta_{Work} = \frac{\Delta H\left(1 - \frac{T_O}{T_H}\right)}{\Delta G}$$

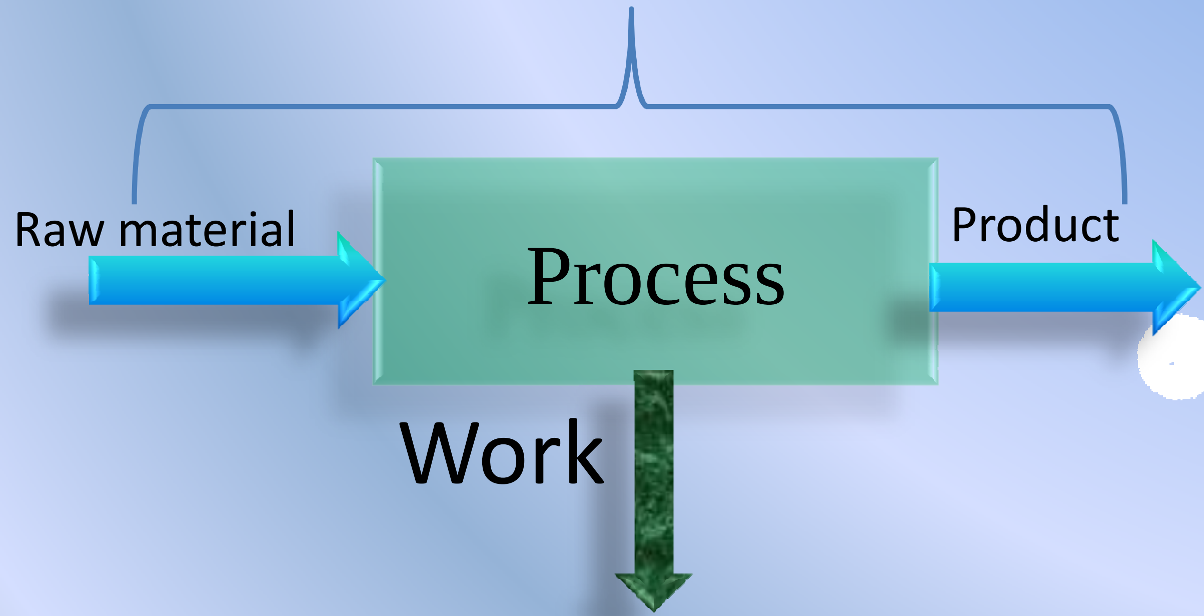
Opportunities for significant Improvement

Chemical processes

From the second law of thermodynamic

For a process to be feasible

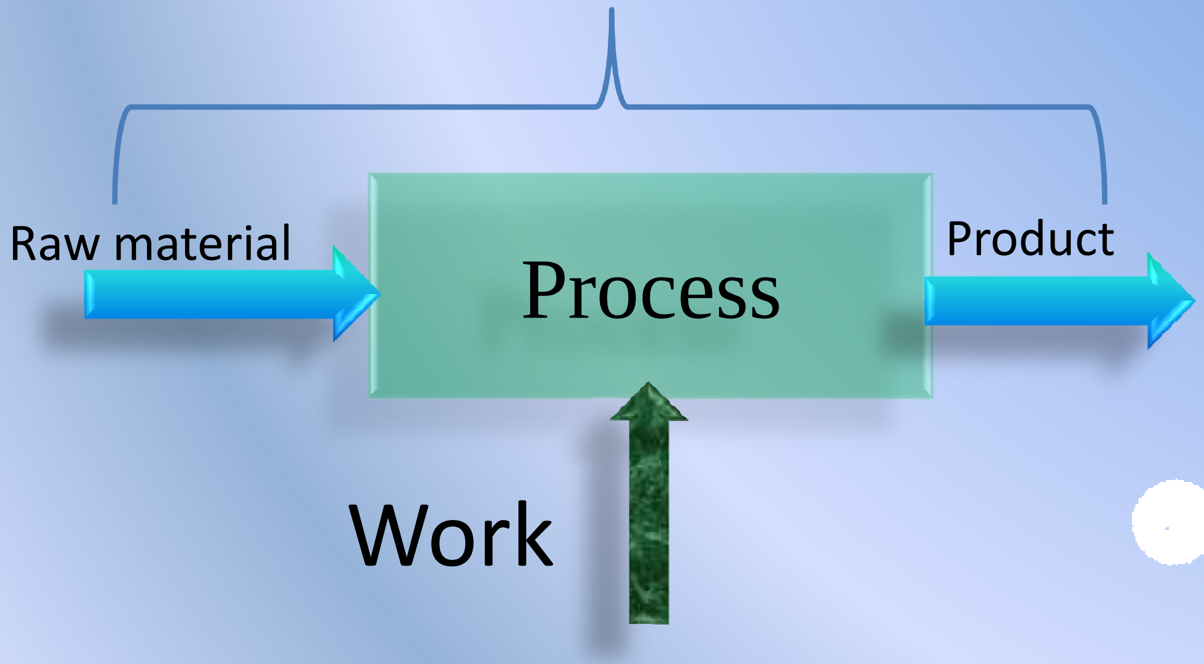
$$\Delta G_{process} < 0$$



The process has the potential to do **work** when the Gibbs free energy is negative

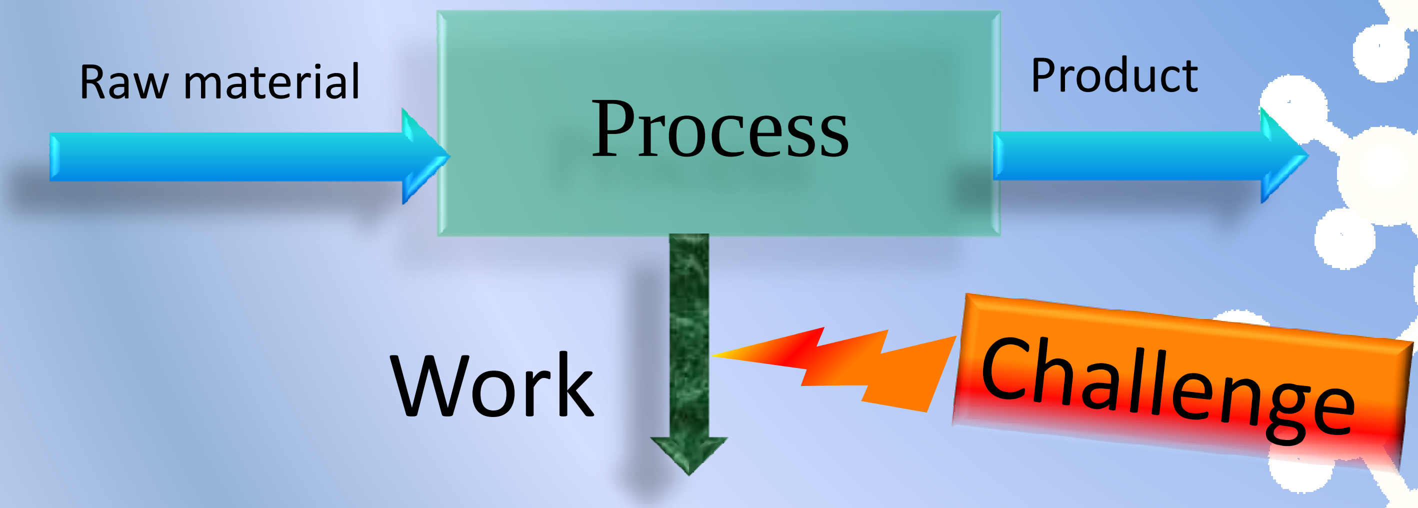
Chemical processes

$$\Delta G_{process} > 0$$



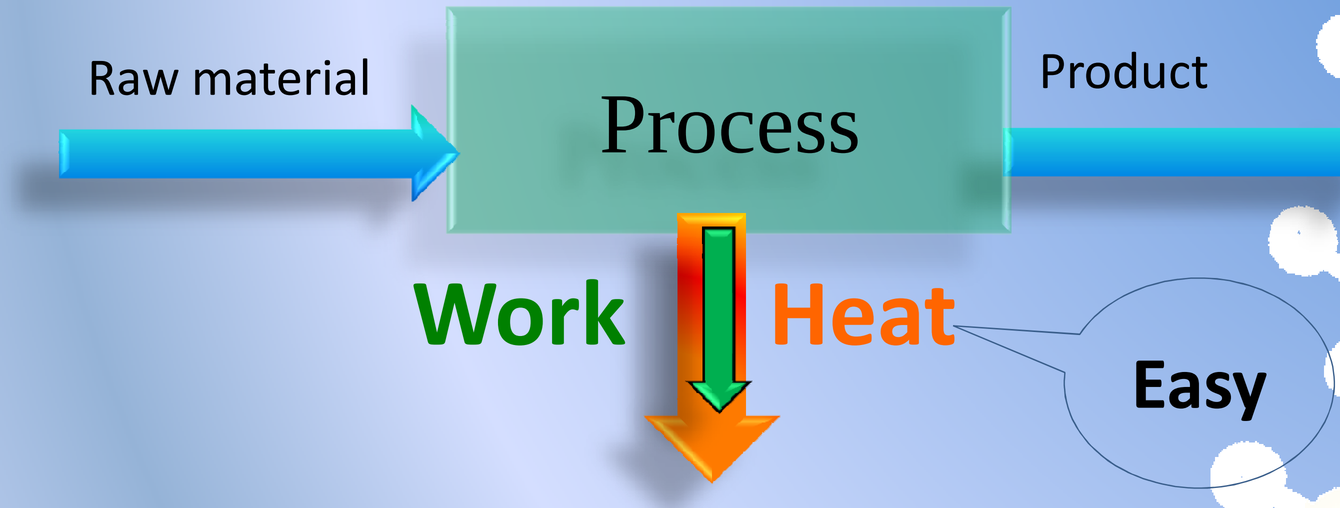
For the process to be feasible, we need to supply **work** when the Gibbs free energy is positive

Chemical processes



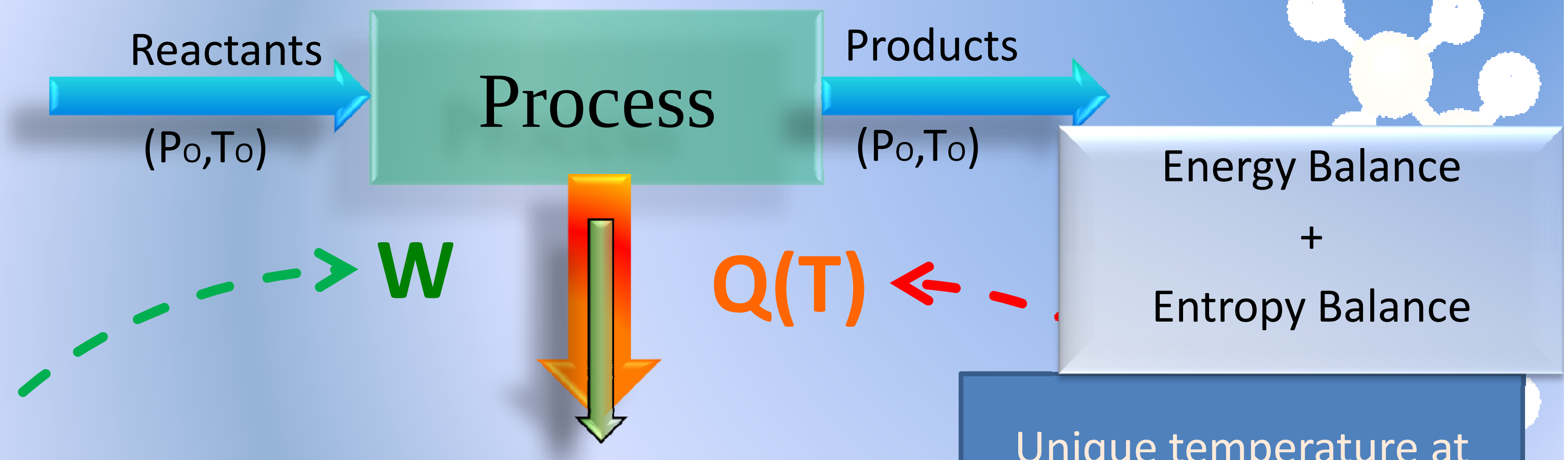
The challenge usually lies on how work is recovered from the process.

Chemical processes



- We would want to take out work with the heat.
- However when this is not done properly it introduces major **irreversibility** in the process

Reversible Simple Chemical Process

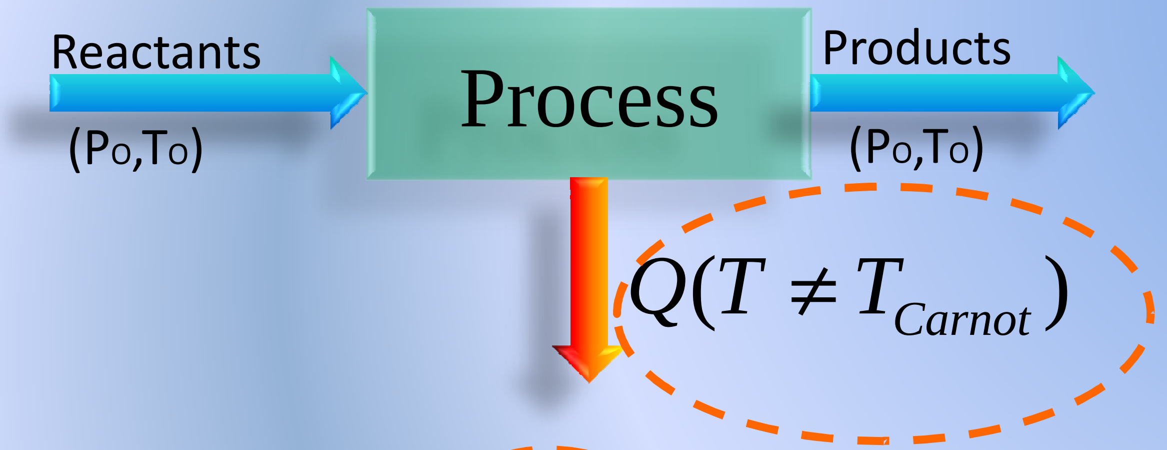


We can show that

Unique temperature at which maximum work can be recovered

$$\Delta G_{Process}(T_O, P_O) = \Delta H_{Process}(T_O, P_O)\left(1 - \frac{T}{T_{Carnot}}\right)$$

Irreversible Chemical Process

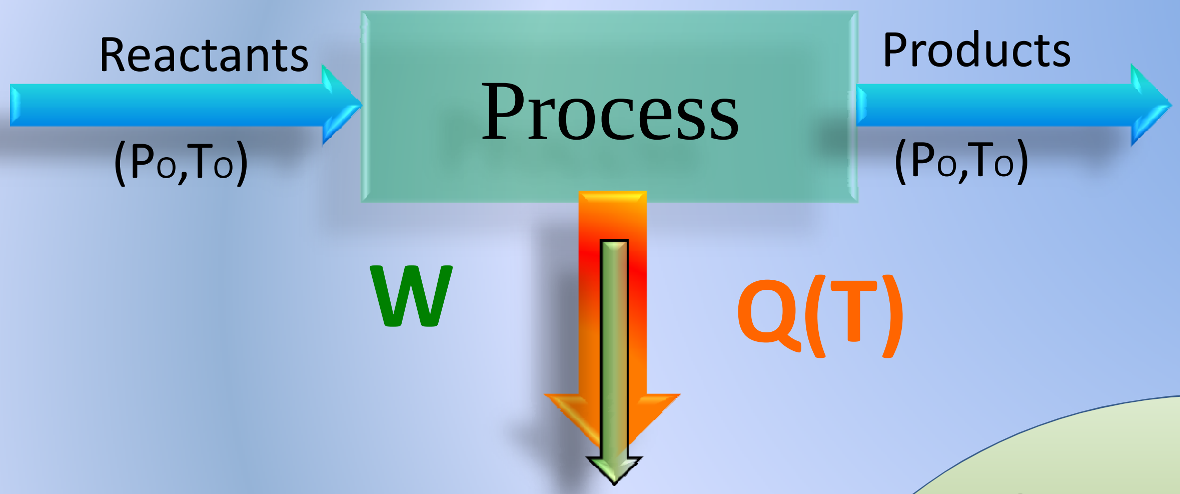


$$\Delta G_{Process}(T_O, P_O) + T_O S_{generated} = \Delta H_{Process}(T_O, P_O)\left(1 - \frac{T_O}{T}\right)$$

Lost work due to irreversibility

$$T_O S_{generated} = W_{lost} = T_O \Delta H_{process}\left(\frac{1}{T_{Carnot}} - \frac{1}{T}\right)$$

Reversible Simple Chemical Process

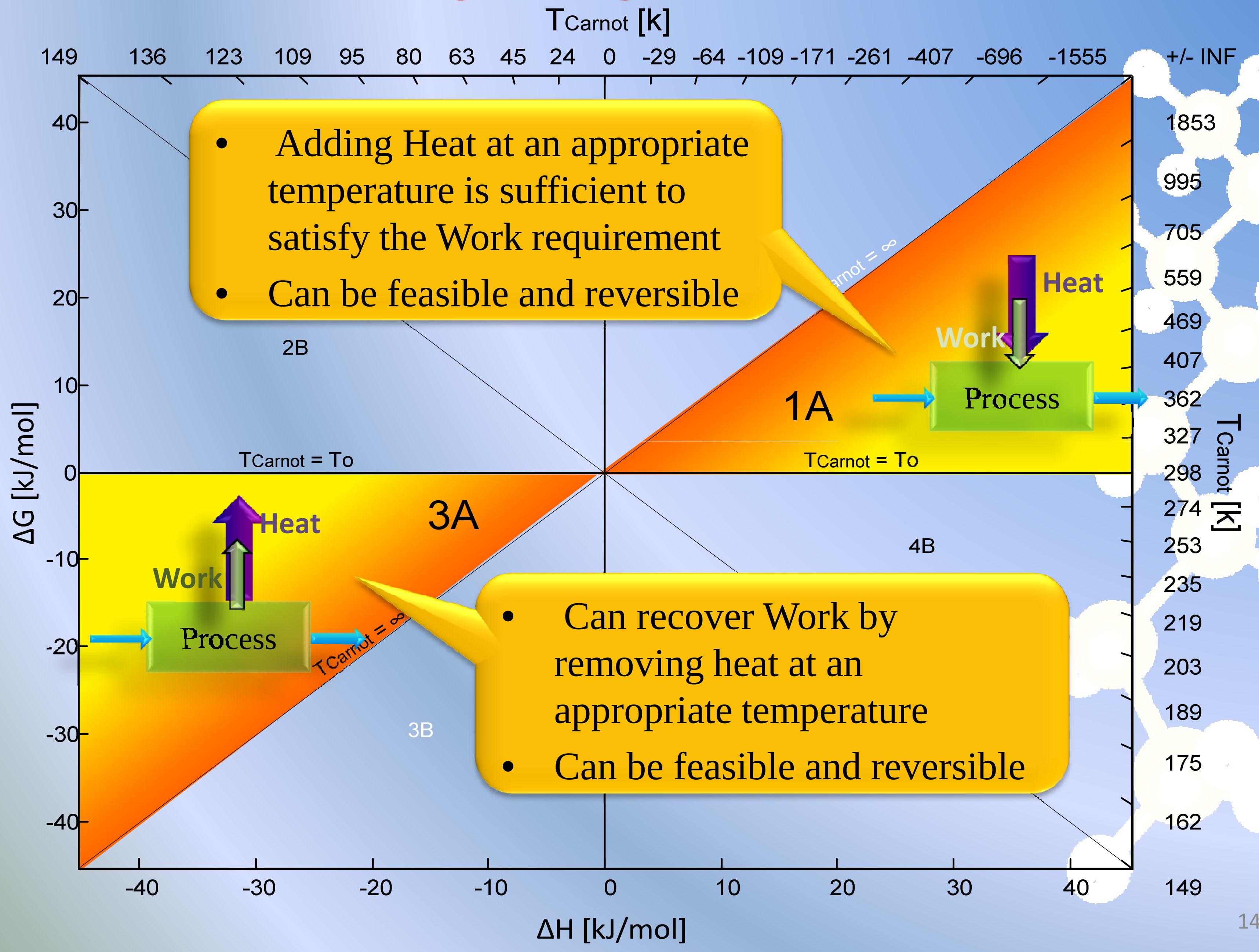


$$\Delta G_{Process}(T_O, P_O) = \Delta H_{Process}(T_O$$

$$T_{Carnot} = \frac{T_O}{1 - \frac{\Delta G_{Process}}{\Delta H_{Process}}}$$

Our ability to reach T_{carnot} depends the ratio of ΔG and ΔH

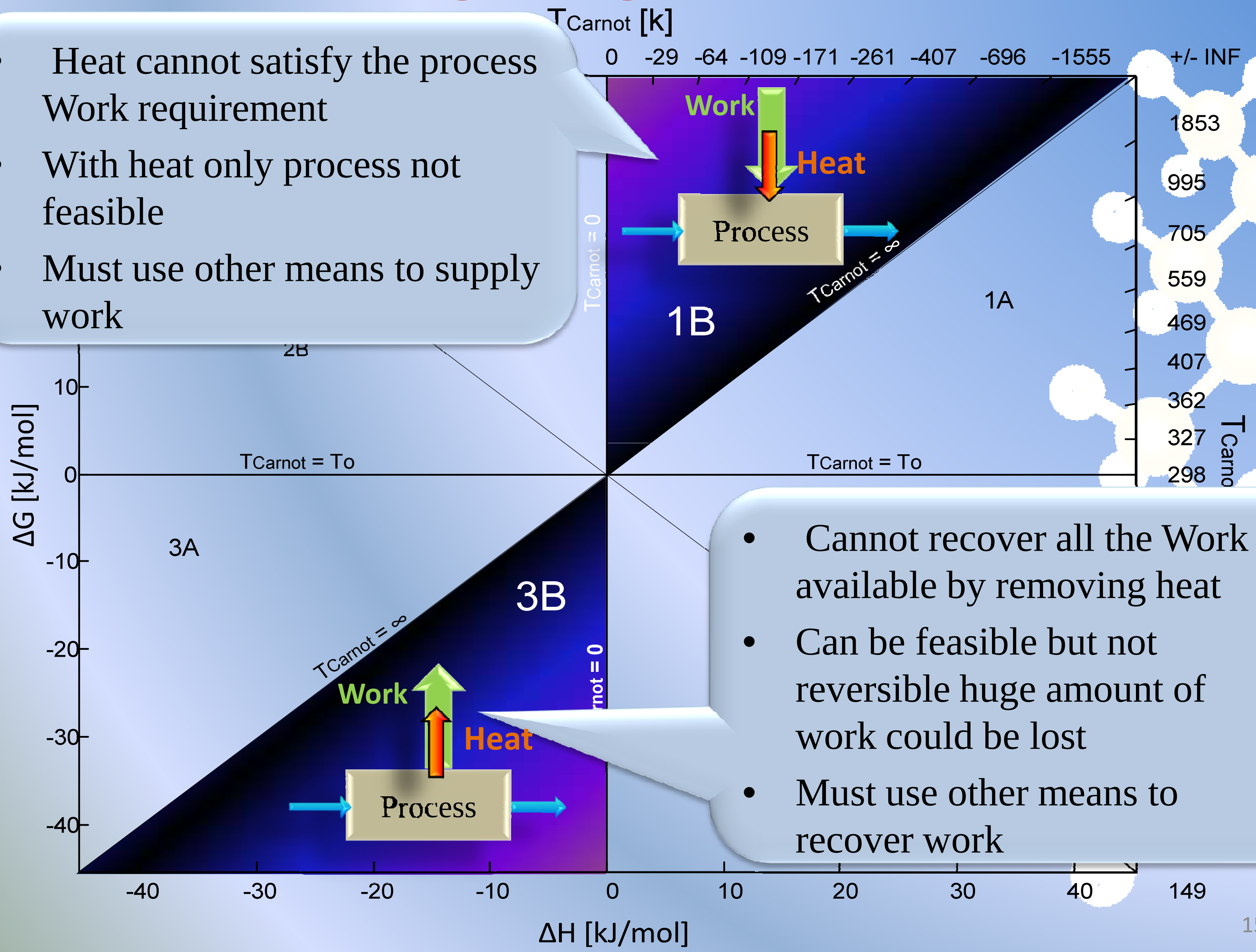
gh-Diagram



TCarnot [k]
149 136 123 109 95 80 63 45 24 0 -29 -64 -109 -171 -261 -407 -696 -1555 +/- INF
1853 995 705 559 469 407 362 327 298 274 253 235 219 203 189 175 162 149
TCarnot [k]
ΔG [kJ/mol]
40 30 20 10 0 -10 -20 -30 -40
-40 -30 -20 -10 0 10 20 30 40
ΔH [kJ/mol]
Adding Heat at an appropriate temperature is sufficient to satisfy the Work requirement
Can be feasible and reversible
Heat
Work
Process
1A
2B
TCarnot = To
TCarnot = To
3A
Heat
Work
Process
TCarnot = ∞
4B
3B
Can recover Work by removing heat at an appropriate temperature
Can be feasible and reversible

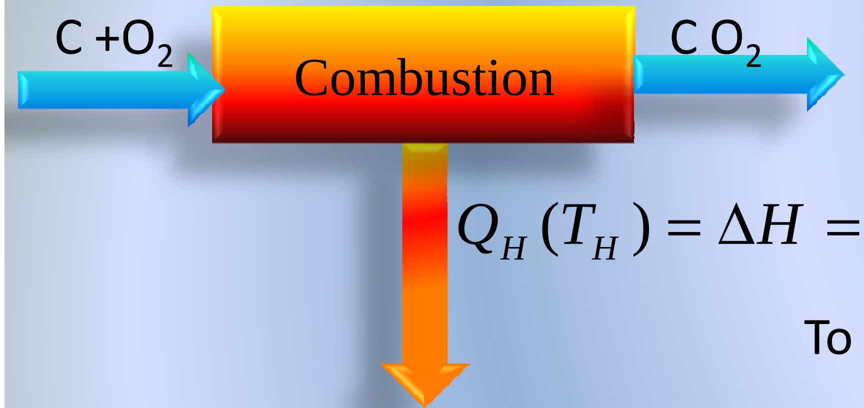
gh-Diagram

- Heat cannot satisfy the process Work requirement
- With heat only process not feasible
- Must use other means to supply work



- Cannot recover all the Work available by removing heat
- Can be feasible but not reversible huge amount of work could be lost
- Must use other means to recover work

Coal combustion as a chemical process



Chemical potential

$$\Delta G = -394.38\, {}^{kJ}\!/_{mol} \rightarrow W_{potential}$$

$$Q_H(T_H) = \Delta H = -393.51\, {}^{kJ}\!/_{mol}$$

To take out maximum Work potential with heat

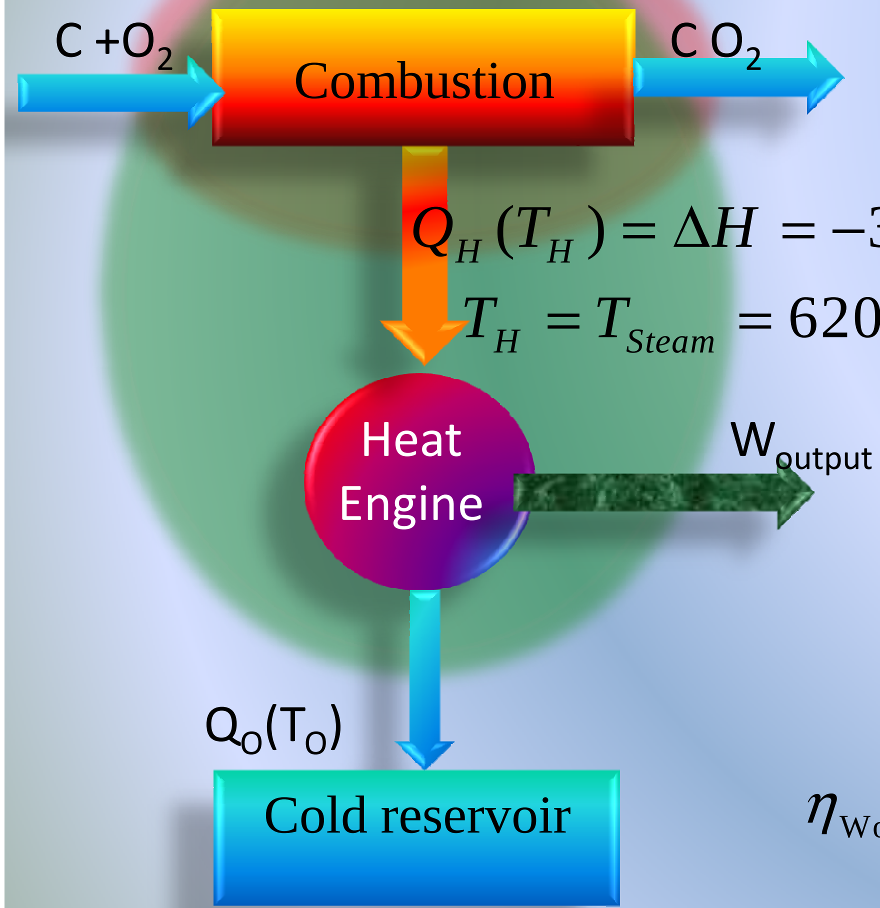
$$T_H = T_{Carnot} = -134815\text{K}$$

Not Feasible

Work will be lost if heat is taken at a feasible temperature

$$T_O S_{generated} = W_{lost} = T_O \Delta H \left(\frac{1}{T_{Carnot}} - \frac{1}{T_{Feasible}} \right)$$

Coal combustion as a chemical process



$$Q_H(T_H) = \Delta H = -393.51\, {}^{kJ}\!/\!_{mol}$$

$$T_H = T_{Steam} = 620°C$$

Chemical potential

$$\Delta G = -394.38\, {}^{kJ}\!/\!_{mol} \rightarrow W_{target}$$

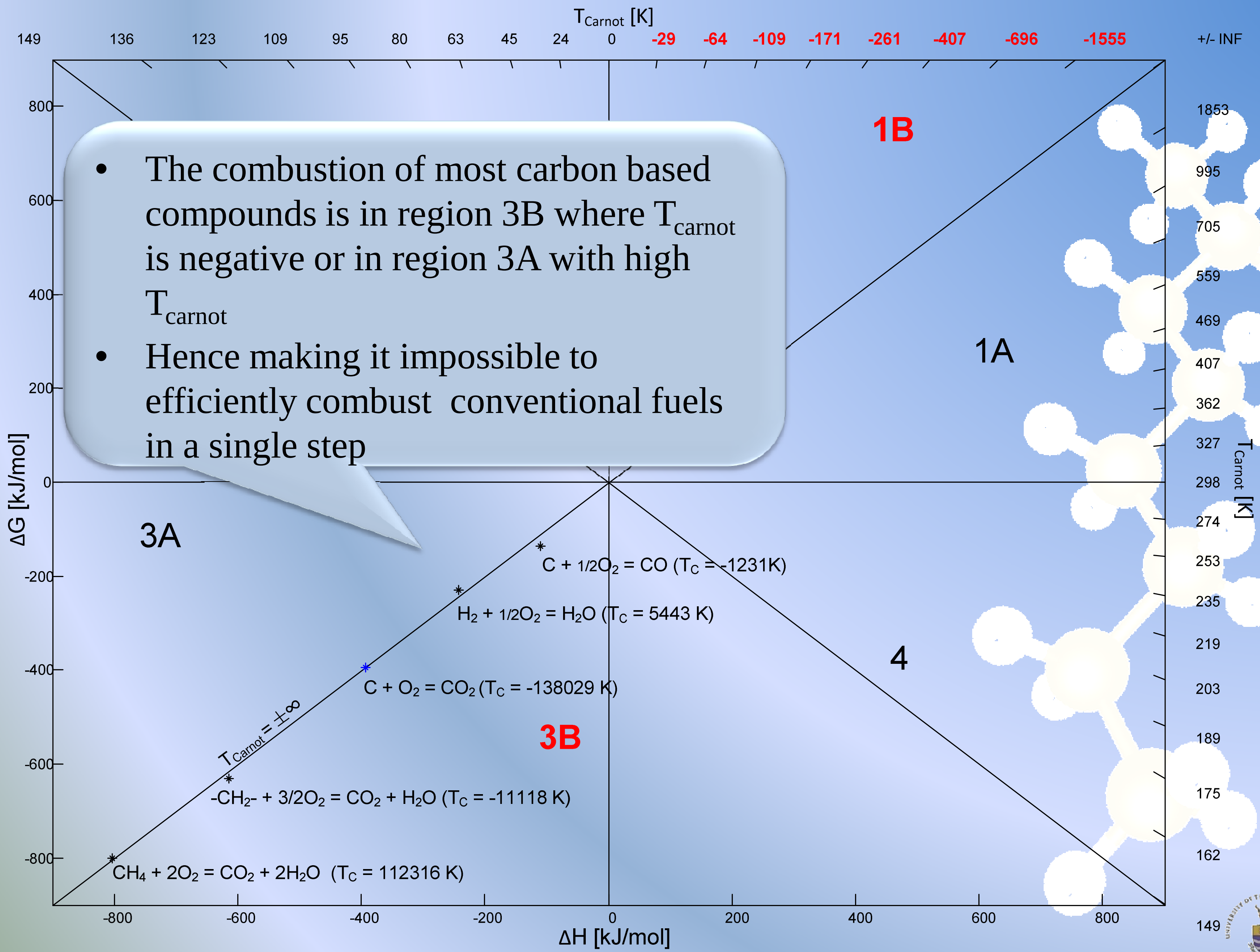
Reversible Heat Engine

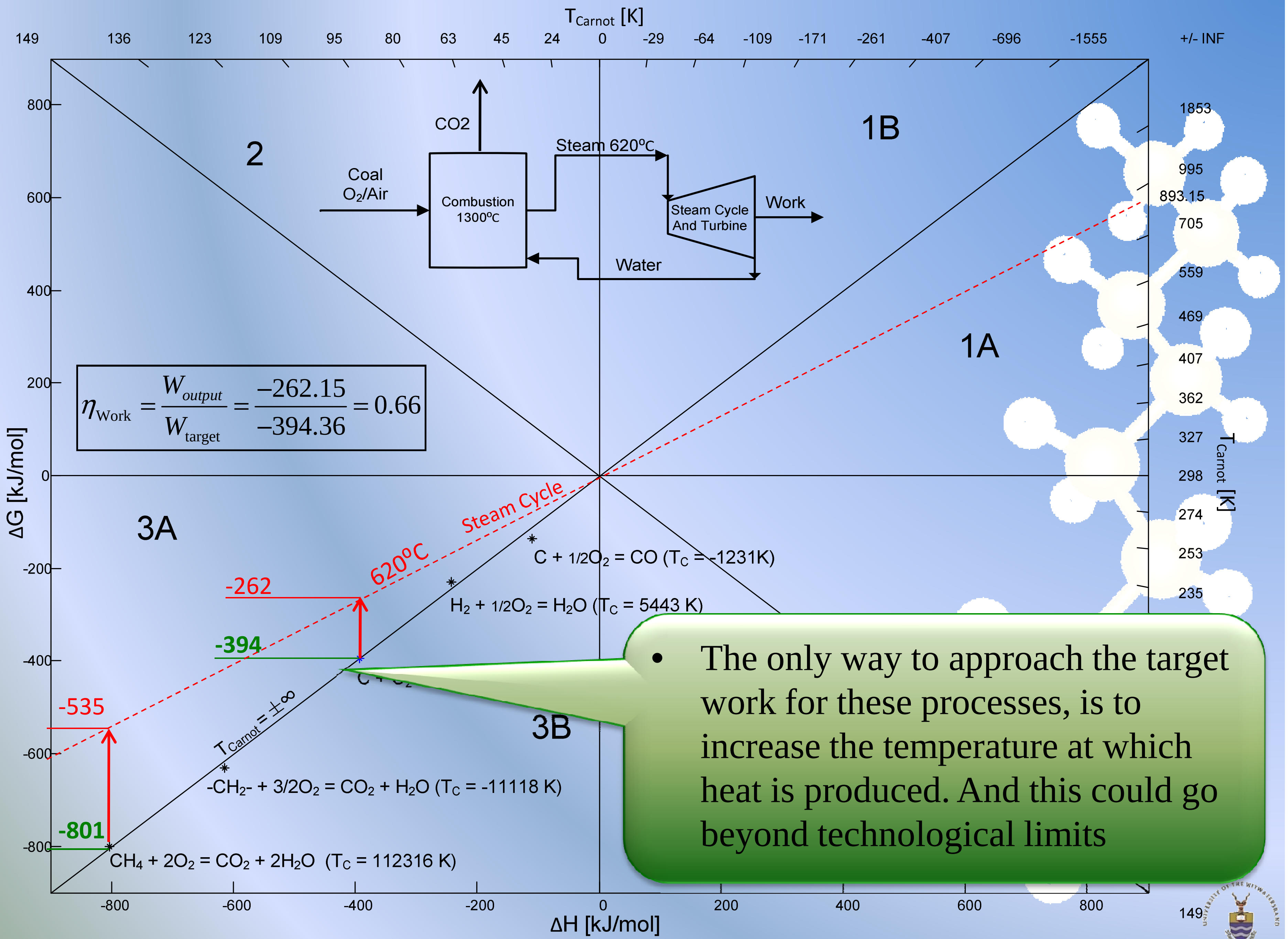
$$W_{output} = W_{\max} = \Delta H\left(1 - \frac{T_O}{T_{Steam}}\right)$$

$$\eta_{Work} = \frac{W_{output}}{W_{target}} = \frac{-393.51\left(1 - \frac{298.15}{893.15}\right)}{-394.38} = 0.66$$

Even with a reversible heat engine system, power plants will still lose work: about 34%

- The combustion of most carbon based compounds is in region 3B where T_{carnot} is negative or in region 3A with high T_{carnot}
- Hence making it impossible to efficiently combust conventional fuels in a single step

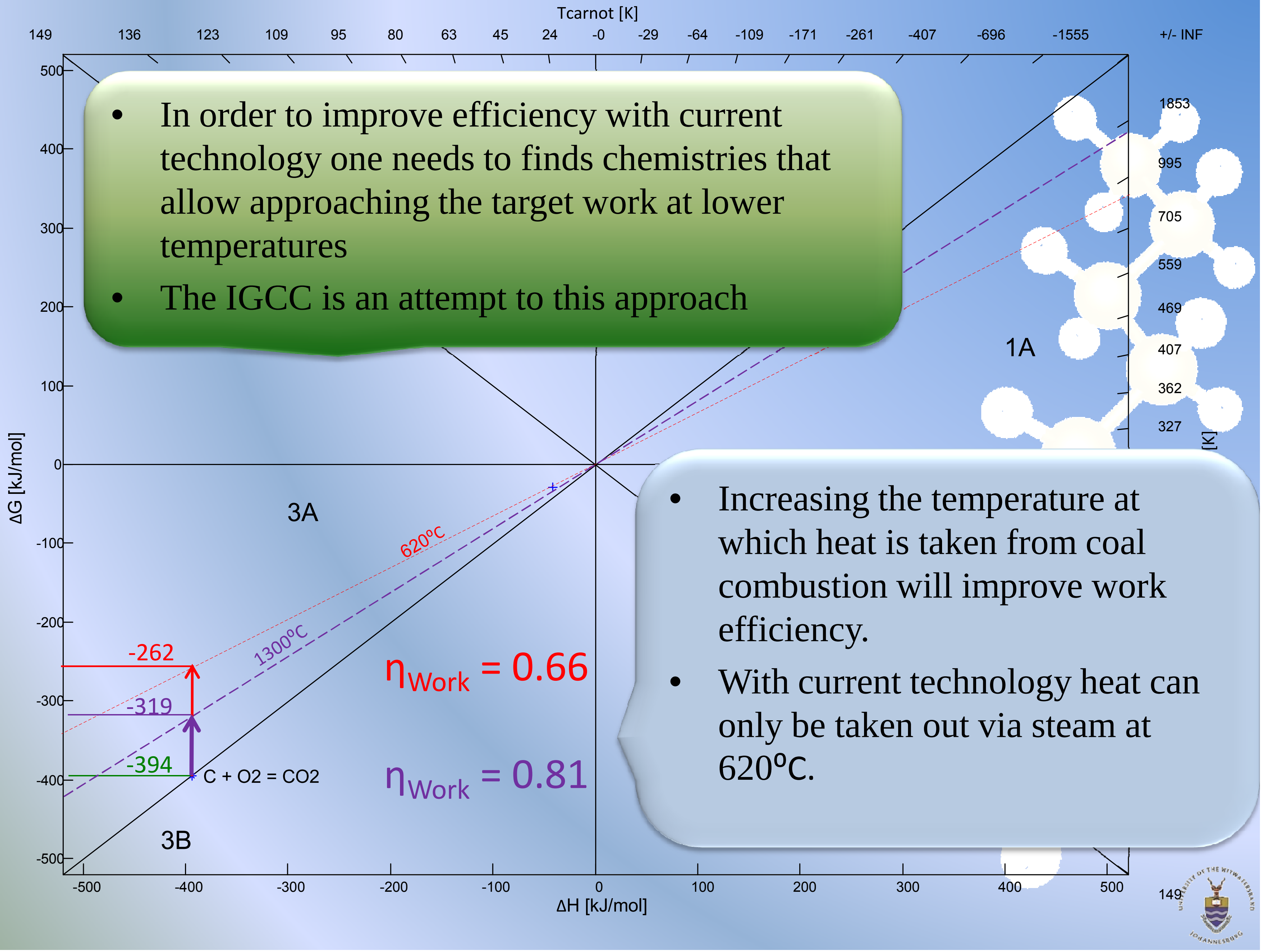




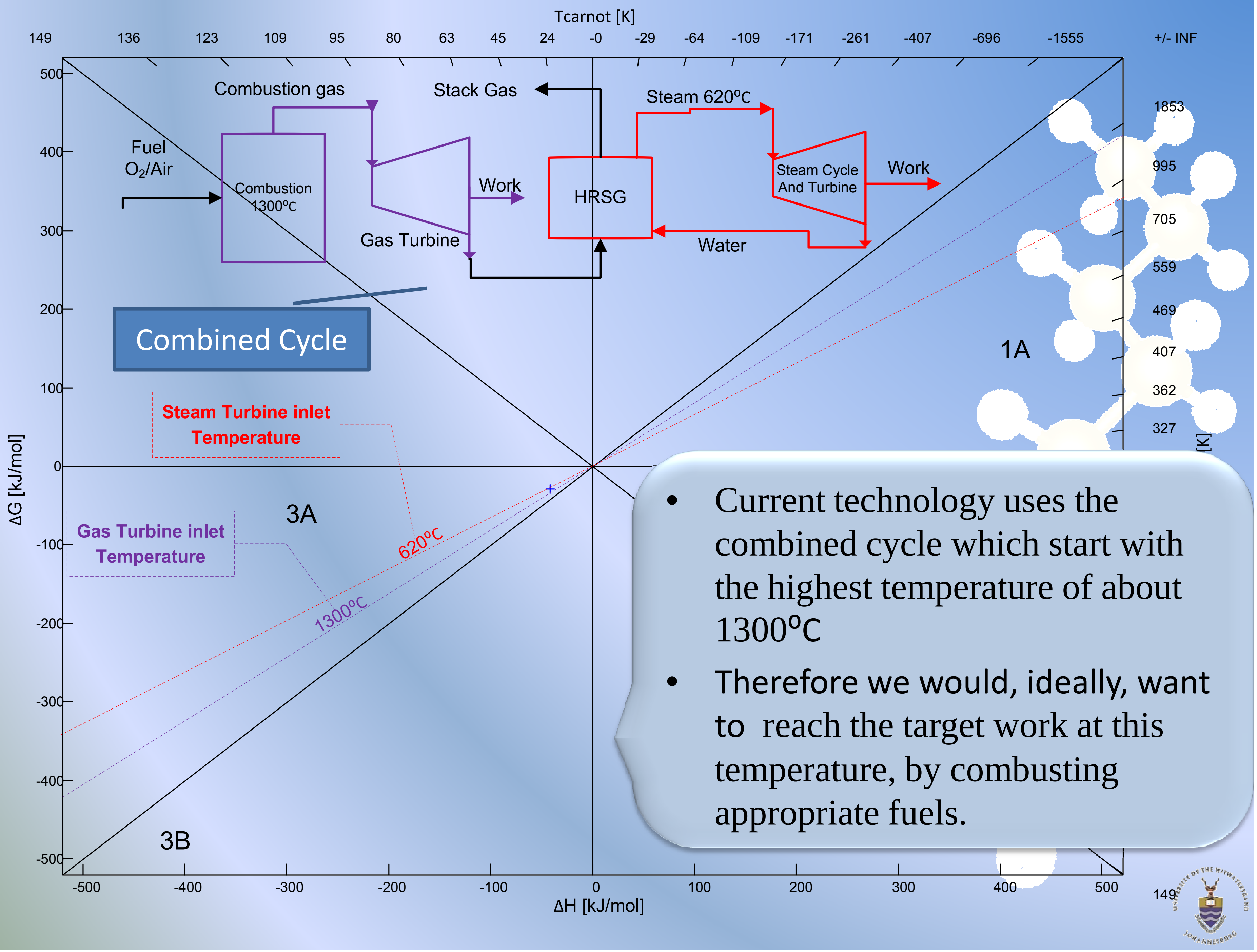
$$\eta_{\text{Work}} = \frac{W_{output}}{W_{target}} = \frac{-262.15}{-394.36} = 0.66$$

- The only way to approach the target work for these processes, is to increase the temperature at which heat is produced. And this could go beyond technological limits

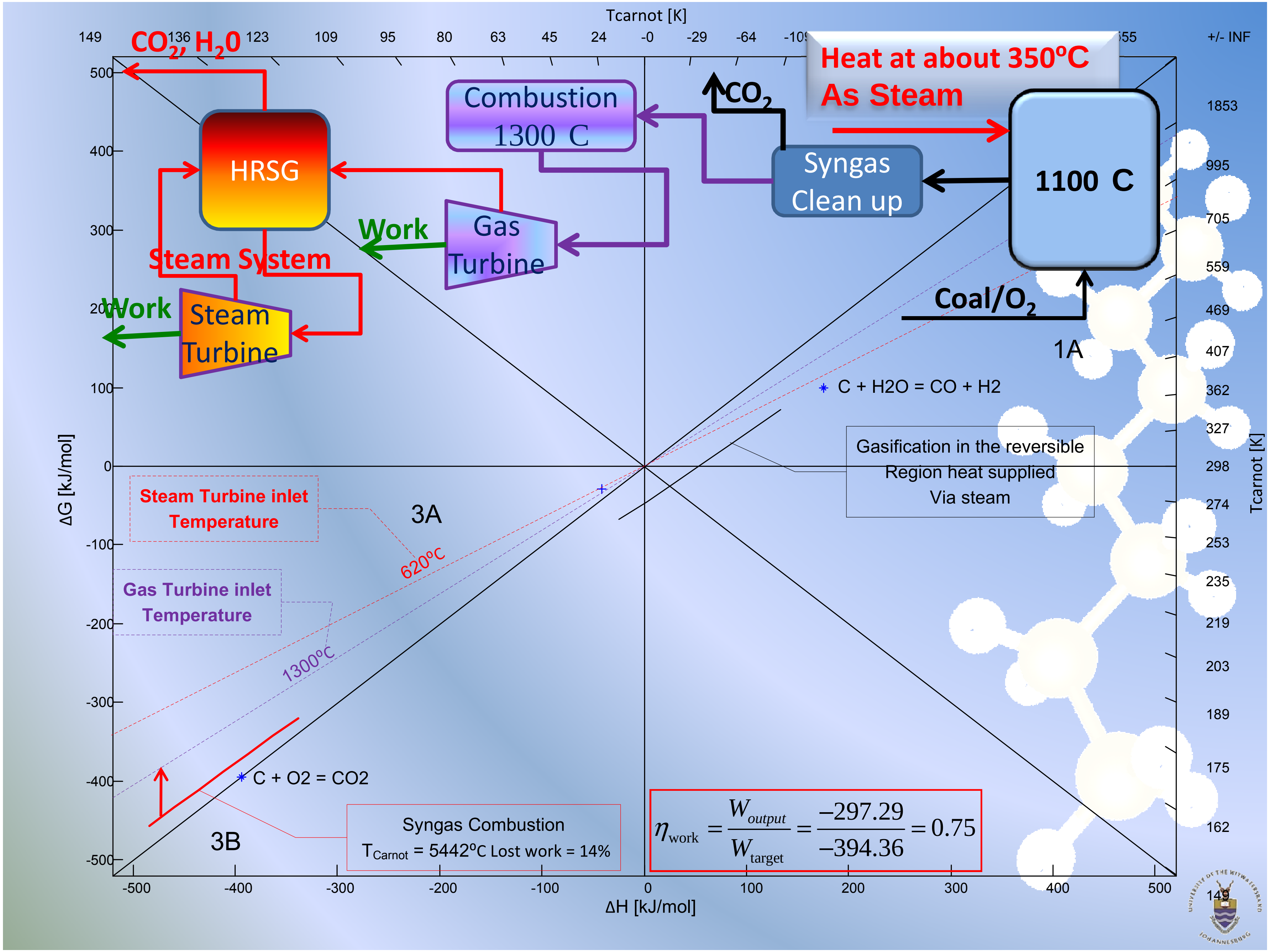
- In order to improve efficiency with current technology one needs to finds chemistries that allow approaching the target work at lower temperatures
- The IGCC is an attempt to this approach

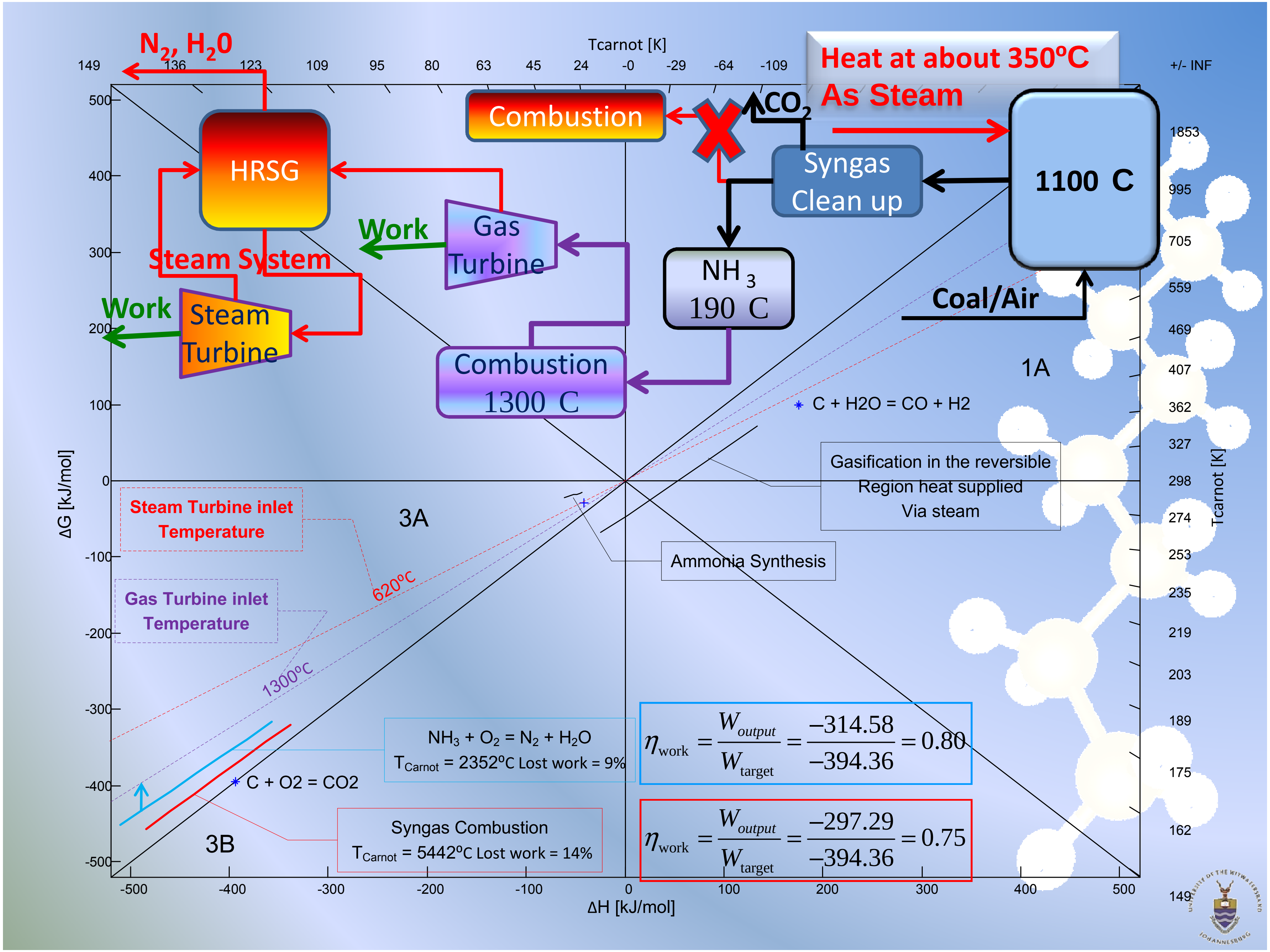


- Increasing the temperature at which heat is taken from coal combustion will improve work efficiency.
- With current technology heat can only be taken out via steam at 620°C.



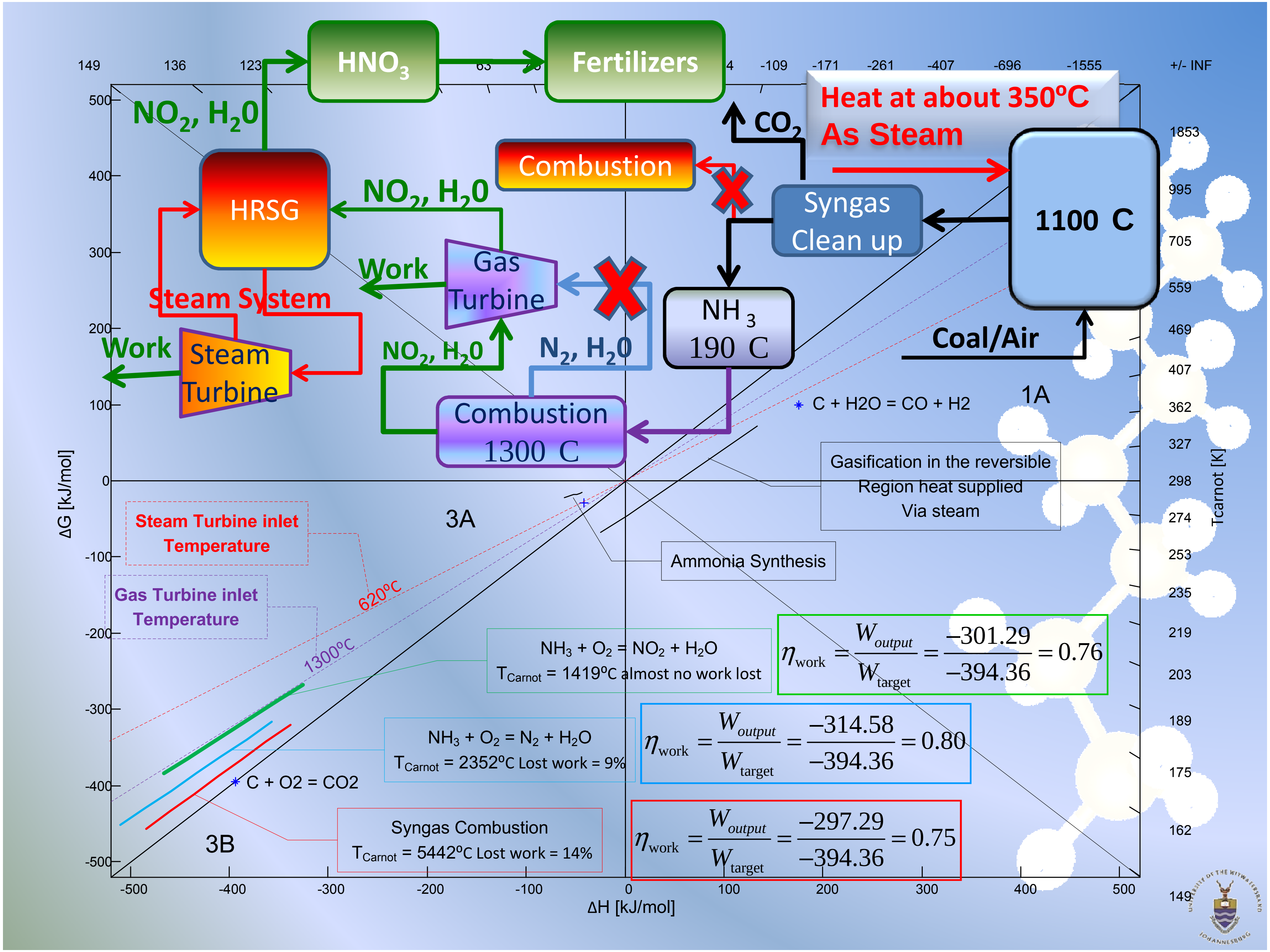
- Current technology uses the combined cycle which start with the highest temperature of about 1300ºC
- Therefore we would, ideally, want to reach the target work at this temperature, by combusting appropriate fuels.


Tcarnot [K]
149
136
123
109
95
80
63
45
24
-0
-29
-64
+/- INF
CO_2, H_20
Heat at about 350°C
As Steam
Combustion
1300 C
CO_2
Syngas
Clean up
1100 C
HRSG
Work
Gas
Turbine
Steam System
Work
Steam
Turbine
Coal/O_2
1A
C + H2O = CO + H2
Gasification in the reversible
Region heat supplied
Via steam
Steam Turbine inlet
Temperature
3A
620°C
Gas Turbine inlet
Temperature
1300°C
C + O2 = CO2
3B
Syngas Combustion
T_{Carnot} = 5442°C Lost work = 14%
$\eta_{work} = \frac{W_{output}}{W_{target}} = \frac{-297.29}{-394.36} = 0.75$
ΔG [kJ/mol]
500
400
300
200
100
0
-100
-200
-300
-400
-500
ΔH [kJ/mol]
-500
-400
-300
-200
-100
0
100
200
300
400
500
Tcarnot [K]
1853
995
705
559
469
407
362
327
298
274
253
235
219
203
189
175
162
149



$$\eta_{work} = \frac{W_{output}}{W_{target}} = \frac{-314.58}{-394.36} = 0.80$$

$$\eta_{work} = \frac{W_{output}}{W_{target}} = \frac{-297.29}{-394.36} = 0.75$$



HNO3
Fertilizers
NO2, H20
HRSG
Combustion
CO2
Heat at about 350°C
As Steam
1100 C
Syngas
Clean up
NO2, H20
Work
Gas
Turbine
Steam System
Work
Steam
Turbine
NO2, H20
N2, H20
NH 3
190 C
Combustion
1300 C
Coal/Air
C + H2O = CO + H2
1A
Gasification in the reversible
Region heat supplied
Via steam
3A
Steam Turbine inlet
Temperature
Gas Turbine inlet
Temperature
620°C
1300°C
Ammonia Synthesis
NH3 + O2 = NO2 + H2O
TCarnot = 1419°C almost no work lost
η work = W output / W target = −301.29 / −394.36 = 0.76
NH3 + O2 = N2 + H2O
TCarnot = 2352°C Lost work = 9%
η work = W output / W target = −314.58 / −394.36 = 0.80
C + O2 = CO2
3B
Syngas Combustion
TCarnot = 5442°C Lost work = 14%
η work = W output / W target = −297.29 / −394.36 = 0.75
ΔG [kJ/mol]
ΔH [kJ/mol]
Tcarnot [K]

Summary

$C_{(s)} + O_{2(g)} = CO_{2(g)}$

Work Potential = $\Delta G(T_o, P_o)$ = -394 kJ/mol = W_{target}

$$\eta_{Work} = \frac{W_{output}}{W_{target}}$$

	Work recovered [kJ/mol]	Efficiency	Products
Total Work Potential in Coal	-394.36	1	
Direct Coal Combustion	-262.15	0.66	CO_2
Gasification Improved IGCC	-297.29	0.75	CO_2, H_2O
Ammonia Route 1	-314.58	0.80	CO_2, H_2O, N_2,
Ammonia Route 2	-301.26	0.76	CO_2,H_20, HNO_3 (Fertilisers)

Conclusion

- The ability of chemical processes to do work lies within their chemical potential, rather than in the heat they produce. Assessing process efficiency in terms of chemical potential could reveal opportunities for more improvement
- Recovering the chemical potential as useful work via heat, is the most challenging task for chemical engineers, mostly due to technological limitations. This explains inefficiencies in coal fired power plants.
- However, certain molecules, such as NH3, are capable of more reversible combustion, making it possible to recover almost maximum chemical potential, using available technology.
- Storing chemical potential from coal in such molecules could significantly improve power plant efficiency and could in addition produce useful chemicals as by-products.

Thank you

QUESTIONS?

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THRIP

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