Efficient Combustion: The Chemical Engineer’s Quest?

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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

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

- Power plant design aim at increasing \( \eta_{\text{thermal}} \) 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:

\[ \eta_{\text{thermal}} = \frac{W_{\text{output}}}{Q_H} = \left( 1 - \frac{T_O}{T_H} \right) \]

Power plant performance

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

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

Real efficiency

\[ \eta_{\text{work}} = \frac{W_{\text{output}}}{W_{\text{max}}} \]

Reversible Heat Engine is essentially 100% efficient since:

\[ W_{\text{output}} = W_{\text{max}} \]
Power plant efficiency: Fundamental Approach

Combustion

C + O₂ \rightarrow CO₂

Heat

Q_H(T_H) = ΔH

Heat Engine

W_{output}

Cold reservoir

Q_O(T_O)

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

Power plant performance

A more fundamental efficiency

\[ \eta_{\text{Work}} = \frac{W_{\text{output}}}{W_{\text{target}}} \]

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

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

Opportunities for significant Improvement
From the second law of thermodynamic
For a process to be feasible

\[ \Delta G_{\text{process}} < 0 \]

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

\[ \Delta G_{\text{Process}}(T_o, P_o) = \Delta H_{\text{Process}}(T_o, P_o) \left( 1 - \frac{T}{T_{\text{Carnot}}} \right) \]

We can show that there is a unique temperature at which maximum work can be recovered.
Irreversible Chemical Process

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

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

Lost work due to irreversibility
Reversible Simple Chemical Process

Reactants \((P_0, T_0)\) → Process → Products \((P_0, T_0)\)

\[ W = Q(T) \]

\[ \Delta G_{\text{Process}} (T_O, P_O) = \Delta H_{\text{Process}} (T_O, P_O) \]

\[ T_{\text{Carnot}} = \frac{T_O}{1 - \frac{\Delta G_{\text{Process}}}{\Delta H_{\text{Process}}}} \]

Our ability to reach \(T_{\text{Carnot}}\) depends on the ratio of \(\Delta G\) and \(\Delta H\)
- Adding Heat at an appropriate temperature is sufficient to satisfy the Work requirement
- Can be feasible and reversible

- Can recover Work by removing heat at an appropriate temperature
- Can be feasible and reversible
- 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

\[ \Delta G = -394.38 \text{ kJ/mol} \]

\[ Q_H (T_H) = \Delta H = -393.51 \text{ kJ/mol} \]

To take out maximum Work potential with heat

\[ T_H = T_{\text{Carnot}} = -134815 \text{ K} \]

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

\[ T_O S_{\text{generated}} = W_{\text{lost}} = T_O \Delta H \left( \frac{1}{T_{\text{Carnot}}} - \frac{1}{T_{\text{Feasible}}} \right) \]
Coal combustion as a chemical process

\[ \text{C} + \text{O}_2 \xrightarrow{\text{Combustion}} \text{CO}_2 \]

Chemical potential
\[ \Delta G = -394.38 \text{ kJ/mol} \]

\[ Q_H(T_H) = \Delta H = -393.51 \text{ kJ/mol} \]

\[ T_H = T_{\text{Steam}} = 620^\circ \text{C} \]

Reversible Heat Engine

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

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

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 $T_{\text{carnot}}$ is negative or in region 3A with high $T_{\text{carnot}}$

Hence making it impossible to efficiently combust conventional fuels in a single step.
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 find 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 starts with the highest temperature of about 1300°C.

Therefore we would, ideally, want to reach the target work at this temperature, by combusting appropriate fuels.
The diagram illustrates the energy flow and efficiency calculations in a coal/oxygen steam system. The primary reactions shown are:

1. **C + H₂O = CO + H₂**
2. **C + O₂ = CO₂**

The energy supplied to the system is approximately steam at 1300°C. The steam Turbine inlet Temperature is 620°C, and the Steam Turbine outlet Temperature is 149°C. The Gas Turbine inlet Temperature is 189°C, and the Gas Turbine outlet Temperature is 63°C. The Carnot temperature, T_Carnot = 5442°C, results in a lost work of 14%. The efficiency, η, is calculated as:

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

The heat at about 350°C is used as steam. Gasification in the reversible region results in heat supplied via steam.
C + H₂O = CO + H₂

T_{Carnot} \text{[K]}

Gasification in the reversible

NH₃ + O₂ = N₂ + H₂O
T_{Carnot} = 2352°C Lost work = 9%

C + O₂ = CO₂
T_{Carnot} = 5442°C Lost work = 14%

NH₃ + O₂ = N₂ + H₂O

Heat at about 350°C As Steam

Syngas Clean up

1100 C

Coal/Air

1A

NH₃

190 C

Heat at about 350°C

Syngas Combustion

T_{Carnot} = 5442°C

Ammonia Synthesis

Region heat supplied Via steam

Work target WW

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

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C + H₂O = CO + H₂

T_Carnot [K]

Combustion

NH₃
190 °C

Coal/Air

NO₂, H₂O

Steam System

Work

Steam Turbine

HRSG

C + O₂ = CO₂

Syngas Clean up

Gasification in the reversible
Region heat supplied Via steam

Ammonia Synthesis

NH₃ + O₂ = NO₂ + H₂O
T_Carnot = 1419°C almost no work lost

NH₃ + O₂ = N₂ + H₂O
T_Carnot = 2352°C Lost work = 9%

C + O₂ = CO₂

∆H [kJ/mol]

∆G [kJ/mol]

Gas Turbine

Combustion

3B

Syngas Combustion
T_Carnot = 5442°C Lost work = 14%

Work

amic target

η_work = \frac{W_output}{W_target} = \frac{-314.58}{-394.36} = 0.80

η_work = \frac{W_output}{W_target} = \frac{-297.29}{-394.36} = 0.75

3A

NH₃ + O₂ = NO₂ + H₂O
T_Carnot = 1419°C almost no work lost

η_work = \frac{W_output}{W_target} = \frac{-301.29}{-394.36} = 0.76

1100 °C

Heat at about 350°C
As Steam

Syngas

Clean up

1A

Combustion

NO₂, H₂O

Work

Steam Turbine

HRSG

C + H₂O = CO + H₂

T_Carnot [K]

Gasification in the reversible
Region heat supplied Via steam

Ammonia Synthesis

NH₃ + O₂ = NO₂ + H₂O
T_Carnot = 1419°C almost no work lost

NH₃ + O₂ = N₂ + H₂O
T_Carnot = 2352°C Lost work = 9%

C + O₂ = CO₂

∆H [kJ/mol]

∆G [kJ/mol]
### Summary

\[ C_{(s)} + O_{2(g)} = CO_{2(g)} \]

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

\[ \eta_{Work} = \frac{W_{output}}{W_{target}} \]

<table>
<thead>
<tr>
<th></th>
<th>Work recovered [kJ/mol]</th>
<th>Efficiency</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Work Potential in Coal</td>
<td>-394.36</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>Direct Coal Combustion</td>
<td>-262.15</td>
<td>0.66</td>
<td>CO$_2$</td>
</tr>
<tr>
<td>Gasification Improved IGCC</td>
<td>-297.29</td>
<td>0.75</td>
<td>CO$_2$, H$_2$O</td>
</tr>
<tr>
<td>Ammonia Route 1</td>
<td>-314.58</td>
<td>0.80</td>
<td>CO$_2$, H$_2$O, N$_2$,</td>
</tr>
<tr>
<td>Ammonia Route 2</td>
<td>-301.26</td>
<td>0.76</td>
<td>CO$_2$, H$_2$O, HNO$_3$ (Fertilisers)</td>
</tr>
</tbody>
</table>
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?

Acknowledgement:

Mellon Mentoring Programme