Efficient Combustion: The Chemical Engineer’s Quest?

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Introduction

Reversible Process

Less energy

Less or even no \( \text{CO}_2 \) emissions

Products/Electricity

Irreversible Process

More energy

More \( \text{CO}_2 \) 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:

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

Real efficiency

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
From the second law of thermodynamics, for a process to be feasible, the Gibbs free energy change must be negative:

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

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.
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

Reactants \((P_0,T_0)\)  

Process

Products \((P_0,T_0)\)

Energy Balance + Entropy Balance

We can show that Unique temperature at which maximum work can be recovered

\[
\Delta G_{\text{Process}}(T_O, P_O) = \Delta H_{\text{Process}}(T_O, P_O) \left(1 - \frac{T}{T_{\text{Carnot}}}\right)
\]
Irreversible Chemical Process

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

\[ Q(T \neq T_{\text{Carnot}}) \]

\[ \Delta G_{\text{Process}}(T_0, P_0) + T_0 S_{\text{generated}} = \Delta H_{\text{Process}}(T_0, P_0) \left( 1 - \frac{T_0}{T} \right) \]

Lost work due to irreversibility

\[ T_0 S_{\text{generated}} = W_{\text{lost}} = T_0 \Delta H_{\text{process}} \left( \frac{1}{T_{\text{Carnot}}} - \frac{1}{T} \right) \]
Reversible Simple Chemical Process

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

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

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

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

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

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

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

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.
Steam System

\[ \text{Steam Turbine} \]

\[ \text{Work} \]

\[ \text{HRSG} \]

\[ \text{Combustion} \ 1300 \text{ C} \]

\[ \text{Gas Turbine} \]

\[ \Delta H [\text{kJ/mol}] \]

\[ \Delta G [\text{kJ/mol}] \]

\[ \text{Coal/O}_2 \]

\[ 1100 \text{ C} \]

\[ \text{Heat at about 350}^\circ\text{C} \]

\[ \text{As Steam} \]

\[ \text{Syngas Clean up} \]

\[ \text{Region heat supplied} \]

\[ \text{Via steam} \]

\[ \text{Syngas Combustion} \]

\[ T_{\text{Carnot}} = 5442^\circ\text{C} \]

\[ \text{Lost work} = 14\% \]

\[ \eta_{\text{work}} = \frac{W_{\text{output}}}{W_{\text{target}}} = \frac{-297.29}{-394.36} = 0.75 \]

\[ \text{Gasification in the reversible Region heat supplied} \]

\[ \text{HRSG} \]

\[ \text{Gas Turbine inlet Temperature} \]

\[ 620^\circ\text{C} \]

\[ 1300^\circ\text{C} \]

\[ \Delta H [\text{kJ/mol}] \]

\[ \Delta G [\text{kJ/mol}] \]

\[ \text{Steam Turbine inlet Temperature} \]

\[ C + \text{H}_2\text{O} = \text{CO} + \text{H}_2 \]

\[ C + \text{O}_2 = \text{CO}_2 \]
\[ C + H_2O = CO + H_2 \]

\[ \Delta H [kJ/mol] \]

\[ C + O_2 = CO_2 \]

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

\[ \Delta H [kJ/mol] \]

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

\[ \eta_{\text{work}} = \frac{W_{\text{output}}}{W_{\text{target}}} = \frac{-297.29}{-394.36} = 0.75 \]
\[ C + O_2 = CO_2 \]

\[ \Delta H \text{ [kJ/mol]} \]

\[ \Delta G \text{ [kJ/mol]} \]

1. **Steam System**
   - C + H₂O = CO + H₂
   - \( T_{\text{Carnot}} \) [K]

2. **Combustion**
   - NH₃ + O₂ = NO₂ + H₂O
   - \( T_{\text{Carnot}} = 1419^\circ \text{C} \)
   - \( \eta_{\text{work}} = \frac{W_{\text{output}}}{W_{\text{target}}} = \frac{-301.29}{-394.36} = 0.76 \)
   - Lost work = 14%

3. **Gasification in the reversible region heat supplied Via steam**

4. **Syngas Combustion**
   - NH₃ + O₂ = N₂ + H₂O
   - \( T_{\text{Carnot}} = 2352^\circ \text{C} \)
   - Lost work = 9%
   - \( \eta_{\text{work}} = \frac{W_{\text{output}}}{W_{\text{target}}} = \frac{-314.58}{-394.36} = 0.80 \)

5. **Coal/Air**
   - NH₃ + O₂ = NO₂ + H₂O
   - \( T_{\text{Carnot}} = 1419^\circ \text{C} \)
   - Almost no work lost
   - \( \eta_{\text{work}} = \frac{W_{\text{output}}}{W_{\text{target}}} = \frac{-301.29}{-394.36} = 0.76 \)

6. **Heat at about 350°C As Steam**
### Summary

\[ C(s) + O_2(g) = CO_2(g) \]

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

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

<table>
<thead>
<tr>
<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>
</tr>
<tr>
<td>Direct Coal Combustion</td>
<td>-262.15</td>
<td>CO₂</td>
</tr>
<tr>
<td>Gasification Improved IGCC</td>
<td>-297.29</td>
<td>CO₂, H₂O</td>
</tr>
<tr>
<td>Ammonia Route 1</td>
<td>-314.58</td>
<td>CO₂, H₂O, N₂</td>
</tr>
<tr>
<td>Ammonia Route 2</td>
<td>-301.26</td>
<td>CO₂, H₂O, HNO₃ (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?

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