CO-PRODUCTION OF SYNGAS AND LIME BY COMBINED THERMO-NEUTRAL CALCINATION OF LIMESTONE WITH CO$_2$-REFORMING/PARTIAL OXIDATION OF METHANE OR CARBON

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Introduction

The calcination of limestone to produce lime and cement, as well as the steam/CO$_2$ reforming of natural gas, are highly energy-intensive processes, which together contribute more than 6% to the global anthropogenic CO$_2$ emissions.\(^1\)

\[
\text{CaCO}_3 = \text{CaO} + \text{CO}_2 \quad \Delta H_{298K}^0 = 178\text{kJ/mol} \quad (1)
\]

\[
\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2 \quad \Delta H_{298K}^0 = 206\text{kJ/mol} \quad (2)
\]

\[
\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2 \quad \Delta H_{298K}^0 = 247\text{kJ/mol} \quad (3)
\]

By combining these endothermic processes with the exothermic partial oxidation of methane,

\[
\text{CH}_4 + \frac{1}{2}\text{O}_2 = \text{CO} + 2\text{H}_2 \quad \Delta H_{298K}^0 = -38\text{kJ/mol} \quad (4)
\]

it is possible to design overall thermo-neutral processes for the co-production of lime and the valuable syngas. In such a combination of the CO$_2$-emitting calcination with the CO$_2$-consuming reforming, most of the CO$_2$ release would be avoided. Also, the endothermicity of these processes would be compensated by the exothermicity of the CH$_4$ partial oxidation, resulting in fuel saving. The thermodynamic constraints for such combined processes were determined at 1200 and 1400 K. An analogous thermo-neutral co-production of metals and syngas has recently been developed.\(^2\)

Such combined processes, which both release CO$_2$ and utilize it, could be an attractive option for greenhouse gas mitigation.\(^3\)

Results

The calculated equilibrium composition as a function of temperature from 800 to 1450 K for an initial reaction mixture of CaCO$_3$ – CH$_4$ – O$_2$ – H$_2$O is presented in Figure 1. As shown in the Figure, above 1100 K, CaO, H$_2$, and CO are stable reaction products. Equilibrium compositions for thermo-neutral reactions of CaCO$_3$ with O$_2$ and either CH$_4$ or carbon, in the absence and presence of added H$_2$O, are shown in Table 1. Carbon was taken for these calculations as a proxy of coal, which would be used in actual practice. The purpose of including H$_2$O in the reactant mixtures is to promote the in situ water-gas-shift reaction,

\[
\text{H}_2\text{O} + \text{CO} = \text{H}_2 + \text{CO}_2 \quad \Delta H_{298K}^0 = -41\text{kJ/mol} \quad (5)
\]

thus raising the H$_2$ to CO molar ratio to H$_2$/CO = 2, as required for the synthesis of methanol, which could be one of the useful products from syngas.

This preliminary assessment of the combined calcination of limestone with the partial oxidation of CH$_4$ or carbon predicts considerably decreased CO$_2$ emission, as well as competitive economics, justifying further study.

References

Figure 1. Equilibrium composition vs. temperature for CaCO₃ – CH₄ – O₂ – H₂O, initially with molar ratio 1 : 3 : 2.55 : 3.2 at 300 K and 1 bar.

Table 1. Computed equilibrium compositions for thermo-neutral reactions of CaCO₃ with O₂ and either CH₄ or carbon in the absence or presence of H₂O at 1200 K and 1 bar. Yields of H₂ are relative to the CH₄ input, while the CO yields are vs. the total carbon input (CaCO₃ + CH₄ or Carbon).

<table>
<thead>
<tr>
<th>Initial mol</th>
<th>Initial mol</th>
<th>Initial O₂ mol</th>
<th>Initial H₂O mol</th>
<th>ΔH kJ/mol</th>
<th>H₂ Yield %</th>
<th>CO Yield %</th>
<th>H₂/CO molar ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃ 1.00</td>
<td>CH₄ 2.00</td>
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<td>-12.0</td>
<td>59.8</td>
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<tr>
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<td>57.7</td>
<td>1.99</td>
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<tr>
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<td>Carbon 2.00</td>
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<td>-</td>
<td>-1.2</td>
<td>-</td>
<td>53.3</td>
<td>-</td>
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<tr>
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<td>8.00</td>
<td>-5.2</td>
<td>5.0⁵</td>
<td>6.7</td>
<td>1.99</td>
</tr>
</tbody>
</table>

* H₂ yield calculated relative to H₂O input.