Can Methane Hydrate Be Converted to Carbon-Neutral Energy?

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Methane (gas) hydrate – an enormous reservoir of energy

~730 gigatonnes of CH$_4$ ≈ 38,000 quadrillion BTU (quads)

- More than twice the global natural gas reserve
- Widespread in continental margins & slope sediments

Images from USGS, Geology.com, Ingworldnews.com, AIP.org
Methane hydrate extraction

No commercial extraction yet

- Japan tested offshore methane hydrate extraction from >1.3 km below the ocean surface
- Speed of extraction
- Sea floor stability concern
- Methane transport cost
Methane hydrate extraction: CO\textsubscript{2} substitution

\[ \text{CO}_2 + \text{CH}_4\text{-hydrate} \rightleftharpoons \text{CO}_2\text{-hydrate} + \text{CH}_4 \]

Good idea with challenges

- CO\textsubscript{2} substitution of methane hydrate demonstrated in several laboratory studies
- DOE-ConocoPhillips-Japan Oil demonstration at Prudhoe Bay
- CO\textsubscript{2} sequestration benefits
  - CH\textsubscript{4} transport cost
  - CO\textsubscript{2} transport cost
  - Speed & extent of reaction
The idea: Carbon neutral production of NH$_3$

3CH$_4$-hydrate + 6H$_2$O + 4N$_2$ $\rightleftharpoons$ 3CO$_2$-hydrate + 8NH$_3$

- Methane steam reforming & water-gas shift:
  - CH$_4$ + 2H$_2$O $\rightleftharpoons$ CO$_2$ + 4H$_2$
  - N$_2$ + 3H$_2$ $\rightarrow$ 2NH$_3$

- Preliminary patent application filed by DOE
- Government employee disclosure submitted – awaiting determination of invention rights/ownership
Carbon-neutral NH₃ production from methane hydrate

\[
\text{Air separation}
\]

\[
\begin{align*}
\text{Air} & \rightarrow \text{O}_2 \\
\text{N}_2 + 3 \text{H}_2 & \rightarrow 2 \text{NH}_3 \\
\text{Haber-Bosch} \\
\text{CH}_4 + 2 \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + 4 \text{H}_2 \\
\text{Methane steam reforming & water-gas shift} \\
\text{CO}_2 + \text{CH}_4\text{-hydrate} & \rightleftharpoons \text{CO}_2\text{-hydrate} + \text{CH}_4 \\
\end{align*}
\]

\[
3 \text{CH}_4\text{-hydrate} + 6 \text{H}_2\text{O} + 4 \text{N}_2 \rightleftharpoons 3 \text{CO}_2\text{-hydrate} + 8 \text{NH}_3
\]
What needs to be done?

1. Efficient modular NH$_3$ synthesis – shrink a NH$_3$ production plant to fit an ocean platform

   • Lots of research in recent years on more efficient NH$_3$ synthesis.
   • ARPA-E REFUEL program is supporting modular NH$_3$ synthesis.
   • NH$_3$ production: heat from CH$_4$ combustion; electricity from CH$_4$ gas turbines or wind turbines.
What needs to be done?

2. Cost-effective conversion of CO$_2$-hydrate into permanent CO$_2$ storage

- Deep-ocean liquid CO$_2$ lake
- Reaction with basalt rock
  (carbonate neutralization)

\[
\text{CO}_2\text{-hydrate} \rightleftharpoons \text{CO}_2 + n \text{H}_2\text{O}
\]

\[
\text{CH}_4\text{-hydrate} \rightleftharpoons \text{CH}_4 + n \text{H}_2\text{O}
\]
What needs to be done?

3. Careful study of the effect of ocean floor CO$_2$ on ocean chemistry
Summary: Carbon neutral production of NH₃

\[ 3\text{CH}_4\text{-hydrate} + 6\text{H}_2\text{O} + 4\text{N}_2 \rightleftharpoons 3\text{CO}_2\text{-hydrate} + 8\text{NH}_3 \]

Advantages/Benefits:
- Carbon-neutral fuel production
- Carbon-free NH₃ as a clean fuel
- NH₃ as an ideal carbon-free transportation fuel of the future
- Much reduce fuel transport cost
- In-situ/on-site CO₂ sequestration (not permanent storage yet)