The Promise of Methanol

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Increasing world population
Increase in standard of living

Increase in fossil fuel use
- Oil, gas, coal (hydrocarbons)
Finite sources – non-renewable
On the human timescale

Increase in carbon dioxide content of the atmosphere
Greenhouse effect (Global warming). 400 ppm
World population (in millions)

<table>
<thead>
<tr>
<th>Year</th>
<th>1650</th>
<th>1750</th>
<th>1800</th>
<th>1850</th>
<th>1900</th>
<th>1920</th>
<th>1952</th>
<th>2000</th>
<th>Projection 2050 *</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>545</td>
<td>728</td>
<td>906</td>
<td>1171</td>
<td>1608</td>
<td>1813</td>
<td>2409</td>
<td>6200</td>
<td>8000 to 11000</td>
</tr>
</tbody>
</table>

* Medium estimate. Source: United Nations, Population Division

- **150 petawatt-hours ~ 15 terawatts** (15,000 power plants of 1 gigawatt)
- **21 TW by 2025**
- **30 TW by 2050**

World Primary Energy Consumption, 1970 to 2025

Based on data from Energy information Administration (EIA)
More than 80% of our energy comes from fossil fuels.

Distribution of the World Total Primary Energy Supply in 2006.
Based on data from the International Energy Agency (IEA)
Key World Energy Statistics 2008
<table>
<thead>
<tr>
<th>Century</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>17th-19th Century</td>
<td>industrial revolution coal</td>
</tr>
<tr>
<td>19th Century</td>
<td>coal, oil</td>
</tr>
<tr>
<td>20th Century</td>
<td>coal, oil, natural gas (fossil fuels)</td>
</tr>
<tr>
<td>21st Century</td>
<td>fossil fuels, carbon dioxide</td>
</tr>
<tr>
<td>Already exploited</td>
<td>To be developed</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------------</td>
</tr>
<tr>
<td><strong>Tar sands</strong></td>
<td>• Oil shale</td>
</tr>
<tr>
<td>Exploited on a large scale in Canada (2 million barrels /day)</td>
<td>• Methane hydrates</td>
</tr>
<tr>
<td><strong>Tight gas sands and shale</strong></td>
<td>Both have large potential but ways to exploit them economically have to be found</td>
</tr>
<tr>
<td>Already accounts for &gt; 20% of the natural gas production in US</td>
<td></td>
</tr>
<tr>
<td><strong>Coalbed methane</strong></td>
<td></td>
</tr>
<tr>
<td>Currently represents about 10% of the natural gas production in US</td>
<td></td>
</tr>
</tbody>
</table>
# World's Top Ten Countries with Large Natural Gas Reserves (2012 data)

<table>
<thead>
<tr>
<th></th>
<th>Conventional</th>
<th>Tight</th>
<th>Shale</th>
<th>Coal-bed Methane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Russia</td>
<td>105 tcm</td>
<td>112 tcm</td>
<td>114 tcm</td>
<td>141 tcm</td>
</tr>
<tr>
<td>USA</td>
<td>36 tcm</td>
<td>45 tcm</td>
<td>71 tcm</td>
<td>73 tcm</td>
</tr>
<tr>
<td>China</td>
<td>3 tcm</td>
<td>5 tcm</td>
<td>42 tcm</td>
<td>51 tcm</td>
</tr>
<tr>
<td>Iran</td>
<td>37 tcm</td>
<td>41 tcm</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Saudi Arabia</td>
<td>36 tcm</td>
<td>38 tcm</td>
<td>39 tcm</td>
<td>NA</td>
</tr>
<tr>
<td>Australia</td>
<td>5 tcm</td>
<td>13 tcm</td>
<td>26 tcm</td>
<td>28 tcm</td>
</tr>
<tr>
<td>Qatar</td>
<td>26 tcm</td>
<td>27 tcm</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Argentina</td>
<td>2 tcm</td>
<td>3 tcm</td>
<td>25 tcm</td>
<td>NA</td>
</tr>
<tr>
<td>Mexico</td>
<td>3 tcm</td>
<td>4 tcm</td>
<td>22 tcm</td>
<td>NA</td>
</tr>
<tr>
<td>Canada</td>
<td>4 tcm</td>
<td>6 tcm</td>
<td>18 tcm</td>
<td>22 tcm</td>
</tr>
</tbody>
</table>

**tcm:** trillion cubic meters

**Israel** (Tamar: 0.25 TCM; Leviathan: 0.5 TCM; Levant: 3.4 TCM)
European Shale Gas

639 TCM
More than 30 billion tonnes of CO₂ per year released into the atmosphere!

About half the CO₂ emissions accumulate in the atmosphere

Presently around 15 billion tonnes per year
Ocean Acidification is a Bigger Problem!
Daily usage of fossil fuels

- 85 Million Barrels of Oil is consumed!
- 8 Billion $m^3$ of Natural Gas
- 16 Million Tonnes of Coal

> 30 billion tonnes of CO$_2$ released into the atmosphere per year
Contributing to greenhouse effect – Global Warming

Ethanol economy: in the US, 13.9 billion gallons of ethanol is produced per year (~330 million barrels) from corn. Equivalent to 225 million barrels of oil: 2.5 days supply!

In Brazil, 5.57 billion gallons of ethanol from sugar cane is produced

Biodiesel a lot smaller: requires more land
Biomass

CO₂ fixation by photosynthesis (carbon neutral)

**CO₂ Fixation by Photosynthesis (carbon neutral)**

\[
\text{nCO}_2 + \text{nH}_2\text{O} \xrightarrow{\text{Chlorophyll}} \text{Sunlight} \quad \text{n(CH}_2\text{O)} + \text{nO}_2
\]

Biofuels- Ethanol, butanol, vegetable oils (biodiesel) - a small % of the energy mix.

* Land availability and use

* Water resources- Irrigation

* Food security vs Energy security

* Fertilizer use (nitrogen fertilizers from NH₃ (N₂ and H₂ (syngas))

* Processing technologies, energy use

* Overall energy balance

Sun is the source of most energy on Earth- **past, present and future**

130,000 TW continuous- A reliable nuclear fusion reactor!
Alternative Energies?

Hydropower
Geothermal energy
Wind energy
Solar energy
Biomass
Ocean energy (waves, tides, thermal)
Nuclear energy

Why don’t we use more alternative energies?
- Mainly a problem of cost
- Fossil fuels are still the biggest bargain
- Most renewable energies are intermittent
- They produce mostly electricity
- Difficult to store
(storage in the form of Hydrogen, methanol, etc)
## Electric Energy Generated in Industrial Countries by Non-Fossil Fuels (%, 2004)

<table>
<thead>
<tr>
<th>Country</th>
<th>Fossil Fuels</th>
<th>Hydroelectric</th>
<th>Nuclear</th>
<th>Geothermal, Solar, Wind, Wood and Waste</th>
<th>Total Non-Fossil</th>
</tr>
</thead>
<tbody>
<tr>
<td>France</td>
<td>9.4</td>
<td>10.9</td>
<td>78.6</td>
<td>1.1</td>
<td>90.6</td>
</tr>
<tr>
<td>Canada</td>
<td>25.7</td>
<td>58.0</td>
<td>14.7</td>
<td>1.6</td>
<td>74.3</td>
</tr>
<tr>
<td>Germany</td>
<td>61.9</td>
<td>3.6</td>
<td>27.5</td>
<td>6.9</td>
<td>38.1</td>
</tr>
<tr>
<td>Japan</td>
<td>62.2</td>
<td>9.2</td>
<td>26.4</td>
<td>2.2</td>
<td>37.8</td>
</tr>
<tr>
<td>South Korea</td>
<td>62.8</td>
<td>1.2</td>
<td>35.9</td>
<td>0.1</td>
<td>37.2</td>
</tr>
<tr>
<td>United States</td>
<td>71.0</td>
<td>6.7</td>
<td>19.8</td>
<td>2.4</td>
<td>29.0</td>
</tr>
<tr>
<td>United Kingdom</td>
<td>75.5</td>
<td>1.3</td>
<td>20.0</td>
<td>3.2</td>
<td>24.5</td>
</tr>
<tr>
<td>Italy</td>
<td>81.1</td>
<td>14.1</td>
<td>0.0</td>
<td>4.8</td>
<td>18.9</td>
</tr>
</tbody>
</table>

Source: Energy Information Administration, International Energy Annual 2007, World Net Electricity Generation by Type, 2004
Hydrogen economy (clean fuels, fuel cells)

- Hydrogen is not a primary energy carrier, b.p. = -253 °C
- Tied up in water and fossil fuels
- Incompatible with 20% oxygen in the air
- Liquid hydrogen has 1/3 Volumetric energy density of gasoline
- 2 grams occupy 22.4 liters of volume at NTP (high pressurization is required)
- Infrastructure is very expensive (hydrogen diffuses easily)
- Highly flammable (colorless flame)
The Methanol Economy
The Methanol Economy: Methanol as a fuel and feed-stock

- **In Internal Combustion Engines**
  - High octane ($ON = 100$)
  - Clean burning fuel, 15.8 MJ/liter.
  - M-85 Fuel

- **In Direct Methanol Fuel Cells**

- **Dimethyl Ether (Diesel and Household Fuel)**
  - $CH_3OCH_3$, high cetane clean burning diesel fuel, LNG and LPG substitute.

- **Conversion to olefins-gasoline, diesel, etc.**

$CH_3OH$
Methanol (methyl alcohol, wood alcohol) is an excellent internal combustion engine/turbine fuel. It is a liquid (b.p 64.7 °C).

- Methanol has a high octane number (~100)- used in Race cars.
- M85- used in Flex-Fuel vehicles (similar to E-85).
- Half the volumetric energy content of gasoline (15.8 MJ/liter), but more efficient and cleaner burning.
- Methanol can be blended into Biodiesel (Esterification). Converted to dimethyl ether and dimethyl carbonate.
- Methanol is an excellent hydrogen carrier - easily reformed to H₂ (syngas) at modest temperatures.
Methanol in ICE

- Octane number 100- fuel/air mixture can be compressed to smaller volume-results in higher compression ratio
- Methanol has also has higher “flame speed”- higher efficiency
- Higher latent heat of vaporization (3.7 times higher than gasoline)- can absorb heat better- removes heat from engine- air cooled engines
- Methanol burns better- cleaner emissions
- Safer fuel in fires than gasoline
- Methanol can be dispensed in regular gas station requiring only limited modifications
- Compatible with hybrid (fuel/electric) system
- New Generation Spark-Ignition Heavy Duty Engines (40% smaller than the Diesel Engines)
Diesel-Like Efficiency And Torque (Daniel Cohn- MIT)

• Methanol provides exceptionally strong suppression of engine knock, especially when it is directly injected

• Higher allowed turbocharging pressure than gasoline or natural gas

• Spark ignition methanol engine could provide around 1.5 X more torque/liter than diesel
Potential Spark Ignition Methanol Operation In Modified Diesel Engine (e.g. 9 Liter engine)

<table>
<thead>
<tr>
<th>Diesel</th>
<th>Methanol Engine size (liter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>9</td>
</tr>
</tbody>
</table>

| Torque (lb-ft) | 1300 | 2000 |

Size of diesel engine with same torque as methanol engine 15 liter
Methanol as marine fuel

Availability, distribution and storage

Engine technology and adjustment to the ship

Environment and cost benefit

Safety and regulations
Drawbacks

- Methanol is miscible in water - corrosive for Al, Zn, Mg
  Solution: use compatible materials - Flexfuel vehicles

- Methanol has low vapor pressure at low temperatures
  Solution: spike it with gasoline- M85 (M15, M5)

- Ingestion > 20 mL can be lethal - Dispensing should not be a problem

- Spillage - very safe to the environment
  methanol used in water treatment plants for denitrification
Flex-Fuel Conversion Kit
Methanol (M70) Based Gardening Tools
Methanol (M70) Based Portable Generators
Fully-Automated Methanol/Gasoline Fueling Station
Fuel Choice for American Prosperity

RECOMMENDATIONS TO THE NATION ON OPENING THE TRANSPORTATION FUEL MARKET TO COMPETITION

United States Energy Security Council

Anne Korin and Gal Luft
Co-Directors, Institute for the Analysis of Global Security (IAGS)

2013
<table>
<thead>
<tr>
<th>Fuel</th>
<th>Volume Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Gas</td>
<td></td>
</tr>
<tr>
<td>CNG</td>
<td>4.8 – 5.9</td>
</tr>
<tr>
<td>LNG</td>
<td>1.57</td>
</tr>
<tr>
<td>Propane (LPG)</td>
<td>1.29</td>
</tr>
<tr>
<td>Hydrogen (LH2)</td>
<td>3.93</td>
</tr>
<tr>
<td>Reformulated Gasoline</td>
<td>1.01</td>
</tr>
<tr>
<td>Methanol</td>
<td></td>
</tr>
<tr>
<td>M100</td>
<td>2.03</td>
</tr>
<tr>
<td>M85</td>
<td>1.76</td>
</tr>
<tr>
<td>Ethanol</td>
<td>1.53</td>
</tr>
<tr>
<td>Competing Fuel</td>
<td>Price at Pump (GGE) ($3.82 for gasoline and $3.70 for diesel as of October 2012)</td>
</tr>
<tr>
<td>----------------------</td>
<td>---------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Corn Ethanol (E85)</td>
<td>$4.91</td>
</tr>
<tr>
<td>Methanol (M85)</td>
<td>$3.29</td>
</tr>
<tr>
<td>CNG</td>
<td>$2.12</td>
</tr>
<tr>
<td>LNG</td>
<td>$2.00</td>
</tr>
<tr>
<td>Biodiesel (B20)</td>
<td>$3.82</td>
</tr>
<tr>
<td>Biodiesel (B100)</td>
<td>$4.32</td>
</tr>
<tr>
<td>Electricity</td>
<td>$2.64 for full charge</td>
</tr>
</tbody>
</table>
FINDING
The potential for natural gas to reduce oil dependence could be increased by conversion into room temperature liquid fuels that can be stored at atmospheric pressure. Of these fuels, methanol is the only one that has been produced for a long period at large industrial scale. Methanol has the lowest cost and lowest GHG emissions, but requires some infrastructure modification and faces substantial acceptance challenges. Natural gas derived gasoline and diesel have the advantage of being drop-in fuels, but carry a higher conversion cost.
Dimethyl ether (DME)

\[
2\text{CH}_3\text{OH} \xrightarrow{- \text{H}_2\text{O}} \text{CH}_3\text{OCH}_3
\]

b.p. -24.8 °C; m.p. -141 °C

- Excellent diesel fuel substitute with a cetane number of 55-60 (45-55 for regular diesel) and very clean burning
- Already used in spray dispenser
- Non-toxic, Safe and does not form peroxides
- Substitute for LNG and LPG
- Easy to produce, ship and dispense
- Sootless flame for glass blowing
Advanced methanol-powered fuel cell vehicles

On-board generation of hydrogen through methanol reforming

\[
\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{Reforming Catalyst} \rightarrow \text{H}_2 + \text{CO}_2 \rightarrow \text{Proton Exchange membrane (PEM) Fuel cell} \rightarrow \text{H}_2\text{O}
\]

Methanol has no C-C bonds: reforming at low temperatures (250-300 °C)

Avoids the problem of on-board hydrogen storage under high pressure or in cryogenic liquid form (-253 °C)
Direct oxidation methanol fuel cell (DMFC) USC, JPL - Caltech

**Anodic Reaction:**

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \xrightarrow{\text{Pt-Ru (50:50)}} \text{CO}_2 + 6 \text{H}^+ + 6 \text{e}^- \]

**Cathodic Reaction:**

\[ \frac{3}{2} \text{O}_2 + 6 \text{H}^+ + 6 \text{e}^- \xrightarrow{\text{Pt}} 3\text{H}_2\text{O} \]

**Overall Reaction:**

\[ \text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{electricity} \]

\[ E^\circ = 0.006 \text{ V} \]

\[ E^\circ = 1.22 \text{ V} \]

\[ E_{\text{cell}} = 1.214 \text{ V} \]

Direct Methanol Fuel Cell
Advantages

- Methanol, 5 kWh/Liter – Theoretical (2 X Hydrogen)
- Absence of Pollutants
  \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) are the only byproducts
- Direct reaction of methanol eliminates reforming
  Reduces stack and system complexity
  Silent, no moving parts
- Capable of start-up and operation at 20 °C and below
  Thermally silent, good for military applications
- Liquid feed of reactants
  Effective heat removal and thermal management
  Liquid flow avoids polymer dryout
  Convenient fuel storage and logistic fuel

**Smart Fuel Cells (SFC), Germany**
70 Wh to 3 kWh Portable Devices
Methanol as a fuel and feedstock

* Electricity production by combustion in existing gas turbines

* Electricity generation through fuel cells
  Fuel cells not limited by weight and space: other types of fuel cells can be used; PAFC, MCFC and SOFC

* Use of methanol as cooking fuel in developing countries
  Much cleaner burning and efficient than wood

* Methanol is a feed for single cell proteins- as a feed for animals
World Consumption of Methanol in 2010: 48 million tonnes

- Formaldehyde
- MTBE & TAME
- Acetic acid / Acetic anhydride
- Direct fuel uses
- Chloromethanes
- Solvents
- Methylamines
- Methyl methacrylate
- Others

Source: SRI Consulting

MTBE: Methyl tert-butyl ether
TAME: Tertiary-amyl methyl ether
METHANOL AS HYDROCARBON SOURCE

\[ 2\text{CH}_3\text{OH} \xrightarrow{-2\text{H}_2\text{O}} \text{CH}_2=\text{CH}_2\left(\text{CH}_3-\text{CH}=\text{CH}_2\right) \]

Zeolites or bifunctional catalysts

HYDROCARBON FUELS AND PRODUCTS
(Gasoline, Diesel, etc.)
2013-2018 Chinese Coal (methanol) to Olefins Capacity (mt/a)

Source: ASIACHEM Database and Analysis
CH$_3$OH Sources

Industrial Production
- Syn-gas (from coal or natural gas)
- Direct Methane Conversion
- Biomass Gasification
- Carbon Dioxide Reduction

Natural Sources
- From Wood (wood alcohol)
- Recently discovered enormous galactical methanol clouds (460 billion km in diameter near nascent stars)
CH₃OH from syn-gas

Syn-gas is a mixture of H₂, CO and CO₂

\[
\begin{align*}
CO & + 2H₂ & \rightleftharpoons & CH₃OH & \Delta H_{298K} = -21.7 \text{ kcal/mol} \\
CO₂ & + 3H₂ & \rightleftharpoons & CH₃OH & + H₂O & \Delta H_{298K} = -11.9 \text{ kcal/mol} \\
CO & + H₂O & \rightleftharpoons & CO₂ & + H₂ & \Delta H_{298K} = -9.8 \text{ kcal/mol}
\end{align*}
\]

\[
S = \frac{\text{moles H}_2}{\text{moles CO}}
\]

S=2 ideal for methanol

Syn-gas can be produced from any source of carbon: natural gas, petroleum, coal, biomass, etc.

However, not all give an ideal S ratio for methanol synthesis
**CH₃OH from methane**

- **Syn-gas from natural gas – steam reforming**
  \[ \text{CH}_4 + \text{H}_2\text{O} \overset{\text{Ni Cat.}}{\rightleftharpoons} \text{CO} + 3\text{H}_2 \quad \Delta H_{298K} = 49.1 \text{ kcal / mol} \]  
  Excess H₂ generally used for ammonia (NH₃) production

- **Partial oxidation of methane**
  \[ \text{CH}_4 + 1/2 \text{O}_2 \rightleftharpoons \text{CO} + 2\text{H}_2 \quad \Delta H_{298K} = -8.6 \text{ kcal / mol} \]  
  \[ \text{CO} + 1/2 \text{O}_2 \rightleftharpoons \text{CO}_2 \quad \Delta H_{298K} = -67.6 \text{ kcal / mol} \]  
  \[ \text{H}_2 + 1/2 \text{O}_2 \rightleftharpoons \text{H}_2\text{O} \quad \Delta H_{298K} = -57.7 \text{ kcal / mol} \]

- **Dry reforming with CO₂**
  \[ \text{CO}_2 + \text{CH}_4 \overset{\text{Ni Cat.}}{\rightleftharpoons} 2\text{CO} + 2\text{H}_2 \quad \Delta H_{298K} = 59.1 \text{ kcal / mol} \]  
  \[ S=1 \]

**Reactions occur at high temperatures (at least 800-1000 °C)**
Bireforming of Methane

Steam Reforming \[2\text{CH}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{CO} + 6\text{H}_2 \quad \Delta H_{298K} = 98.4 \text{ kcal / mol}\]

Dry Reforming \[\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H_{298K} = 59.1 \text{ kcal / mol}\]

Bireforming \[3\text{CH}_4 + 2\text{H}_2\text{O} + \text{CO}_2 \rightarrow 4\text{CO} + 8\text{H}_2 \quad \Delta H_{298K} = 157.5 \text{ kcal / mol}\]

Metgas

\[\downarrow\]

\[4\text{CH}_3\text{OH}\]

The production of methanol is generally conducted at pressures of 30 to 100 bars. Conducting the steam and dry reforming or the bireforming at higher pressure would therefore be also advantageous to avoid the need for compression of the syn-gas.

Bireforming allows the use of natural gas resources containing CO₂ without need for separation.

US Patent, 7,909,559, March 15, 2011
US Patent, 8,440,729, March 14, 2013
Oxidative Bi-reforming and Methanol Synthesis

Methane combustion

\[ \text{CH}_4 + 2 \text{ O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} \quad \Delta H_{298K} = -191.9 \text{ kcal/mol} \]

After admixing fresh methane, bi-reforming is carried out

\[ 3\text{CH}_4 + 2\text{H}_2\text{O} + \text{CO}_2 \rightarrow 4\text{CO} + 8\text{H}_2 \quad \Delta H_{298K} = 157.5 \text{ kcal/mol} \]

Methanol synthesis

\[ 4\text{CO} + 8\text{H}_2 \rightarrow 4\text{CH}_3\text{OH} \quad \Delta H_{298K} = -86.8 \text{ kcal/mol} \]

Overall reaction

\[ 4\text{CH}_4 + 2 \text{ O}_2 \rightarrow 4\text{CH}_3\text{OH} \quad \Delta H_{298K} = -121.2 \text{ kcal/mol} \]

Dry reforming side reactions

\[
\begin{align*}
\text{CO}_2 + \text{H}_2 & \rightarrow \text{CO} + \text{H}_2\text{O} \text{ (RWGS)} \\
\text{CO}_2 + 4\text{H}_2 & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \text{ (CO}_2/\text{H}_2 \text{methanation)} \\
\text{CO} + 3\text{H}_2 & \rightarrow \text{CH}_4 + \text{H}_2\text{O} \text{ (CO/\text{H}_2 \text{methanation)} }
\end{align*}
\]

Carbon forming side reactions:

\[
\begin{align*}
2\text{CO} & \rightarrow \text{C} + \text{CO}_2 \text{ (CO disproportionation)} \\
\text{CH}_4 & \rightarrow \text{C (coke)} + 2\text{H}_2 \text{ (Carbon deposition)} \\
\text{CO} + \text{H}_2 & \rightarrow \text{C} + \text{H}_2\text{O} \text{ (CO/\text{H}_2 \text{reduction)} }
\end{align*}
\]
Dry reforming of methane at 100 psi

**TR-81 Dry reforming on catalyst 1, 100 psi**

**Conversion**

- CH4 Conversion
- CO2 Conversion

- CO2/CH4 1.06/1

**Time (hour)**

- Graph showing conversion percentages over time.

**H2/CO ratio**

- Graph showing H2/CO ratio over time.

Equations:
- \[ y = 2E-05x + 83.962 \]
- \[ y = 0.0018x + 77.615 \]
- \[ y = -6E-05x + 0.7965 \]
Bi-reforming of methane at 100 psi

**TR-74-Bireforming on catalyst 2, 100 psi**

*Conversion*

- CH4 Conversion
- CO2 Conversion

*H2/CO ratio*

- Time (hour)
- H2/CO ratio

Equation:
\[ y = -0.0042x + 74.902 \\
\[ y = -0.0033x + 74.777 \]
TR-69 Bireforming on catalyst 1
CH₄ conversion as a function of water and CO₂ content in the gas feed at 100 psi

CH₄ conversion (%)

- (CO₂ + H₂O)/CH₄ 2.3/1: 88.5%
- (CO₂ + H₂O)/CH₄ 1.2/1: 71.4%
CH₃OH from coal
A proven technology

\[
\begin{align*}
3C & + 3/2 O_2 \xrightarrow{\text{Catalysts}} 3CO \\
2CO & + 2H_2O \rightarrow 2CO_2 + 2H_2 \\
CO & + 2H_2 \rightarrow CH_3OH \\
3C & + 2H_2O + 3/2 O_2 \rightarrow 2CO_2 + CH_3OH
\end{align*}
\]

China is currently adopting this approach on a massive scale based on its large coal reserves
100 plants in construction or planned!

Due to the low H/C ratio of coal: a lot of CO₂ is produced!
CH₃OH through methane halogenation

Overall reaction: \[ \text{CH}_4 + \frac{1}{2} \text{O}_2 \rightarrow \text{CH}_3\text{OH} \]
CH₃OH through intermediates other than syn-gas

CH₄ + 2H₂SO₄ $\xrightarrow{\text{Homogeneous catalyst}}$ Pt, Hg, Au based CH₃OSO₃H + 2H₂O + SO₂

CH₃OSO₃H + H₂O $\rightarrow$ CH₃OH + H₂SO₄

SO₂ + 1/2 O₂ + H₂O $\rightarrow$ H₂SO₄

CH₄ + 1/2 O₂ $\rightarrow$ CH₃OH (Overall reaction)

Advantage: low temperature reaction (180-250 °C), much lower than syn-gas generation (800-1000 °C)

Inconvenient: need to recycle concentrated and corrosive H₂SO₄

R. Periana, H. Taube and others
Biomass includes any type of plant or animal material: Wood, wood wastes, agricultural crops and by-products, municipal waste, animal waste, aquatic plants and algae, etc.

Transformed to methanol by gasification through syngas- very efficient

\[ \text{Biomass} \rightarrow \text{Syn-gas} \rightarrow \text{Methanol} \]

\[ \text{CO} + \text{H}_2 \]

Any biomass is fine to make methanol

Large amount of biomass needed- can convert biomass to biocrude and it can be shipped.

Methanol from Biogas (mixture of \( \text{CH}_4, \text{CO}_2 \))

Methanol through aquatic biomass- micro-algae

Biomass alone can not fulfill all our increasing energy needs
Biomass to Liquids (Methanol)

Lignocellulose

Fast Pyrolysis, 550 °C

Condensate + Char + Slurry, 90%

Gasification with Oxygen, 1200 °C

CO + H₂ Syngas, 78%

Methanol or other liquids
Bio-DME from Black Liquor

Paper manufacturing → Black liquor by-product → Syn-gas (CO + H₂) → DME

CHEMREC pilot plant in Sweden (4 t/day Bio-DME)
Bio-DME filling station
Volvo DME powered truck
Bio-Methanol from Glycerol

Vegetable oil → Biodiesel production → Biodiesel

Biodiesel by-product → Syn-gas CO + H₂ → Methanol
Methanol → BioMCN process

H₂ → Oxford University

BioMCN commercial methanol plant
with a 200 000 kT/year capacity
The Netherlands

Further expansions in steps of 200 000 kT capacity planned
Efficient Ways to Capture CO$_2$ and Its Electrochemical Conversion

Why Focus on Carbon Dioxide?

- Linear molecule
- Very stable
  - Difficult to efficiently reduce
- Trace gas
  - 0.040% of the atmosphere
  - Amount of CO$_2$ in the atmosphere is increasing
- With declining fossil fuel reserves, CO$_2$ will become the best source of carbon

*US Patent*, 7,605, 293, October, 20, 2009
*US Patent*, 7,608, 743, October, 27, 2009
Efficient capture from air remains challenging

Sources of CO₂

Geothermal Vents  Fossil Fuel Burning Power Plants
Fermentation Processes  Aluminum Plants
Natural Gas Wells  Air Itself
Cement Plants

CO₂ separation and Capture technologies

Absorption
  Chemical
    MEA, DEA, KOH, NaOH, MgO, Etc.
  Physical
    Sollex, Rectisol, Etc.

Adsorption
  Alumina
  Zeolite
  Activated carbon

Cryogenics
  Dry ice formation at low temperature

Membranes
  Polymer based
    Poly(phenylene oxide)
    Poly(ethylene oxide)
    Poly(ionic liquid)
  Inorganic membranes
    Ceramic based
    Zeolite based

Algal and microbial systems

Regeneration method
  Pressure swing
  Temperature swing
  Moisture swing
  And combination thereof
Structure of branched polyethylenimine (PEI)

Reaction of polyethylenimine (PEI) with CO$_2$

Polyethylenimine (PEI) + CO$_2$ $\rightleftharpoons$ Carbamate

Carbamate $\rightleftharpoons$ Bicarbonate + H$_2$O
Support characteristics
Fumed silica synthesis

Fumed silica: primary particle size ~ 7 nm, fluffy powder, very low density

<table>
<thead>
<tr>
<th>Absorbent support</th>
<th>Pore volume (cm$^3$/g)</th>
<th>Bulk tapped density (cm$^3$/g)</th>
<th>Volume between particles (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fumed SiO$_2$ (Aldrich)</td>
<td>0.961</td>
<td>~ 20</td>
<td>~ 19</td>
</tr>
<tr>
<td>Fumed SiO$_2$ (Aerosil 300)</td>
<td>0.714</td>
<td>~ 20</td>
<td>~ 19</td>
</tr>
<tr>
<td>Fumed SiO$_2$ (Aerosil 150)</td>
<td>0.426</td>
<td>~ 20</td>
<td>~ 19</td>
</tr>
<tr>
<td>Precipitated SiO$_2$ (Hi-Sil T-600)</td>
<td>0.704</td>
<td>~ 20</td>
<td>~ 19</td>
</tr>
<tr>
<td>Silica gel</td>
<td>1.094</td>
<td>2.55</td>
<td>~ 1</td>
</tr>
</tbody>
</table>

Presence of large volume mesopores and macropores to which PEI can easily access and still allow facile CO$_2$ diffusion
Support characteristics

TEM

Silica gel

Precipitated silica

Fumed silica

PEI / Fumed silica
Adsorption of CO$_2$ from the air at 25 °C on PEI/Fumed Silica
Inset: Desorption at 85 °C

Adsorption of CO₂ from the air at 25 °C on FS-PEI-50 (PEI/fumed silica 1/1)

Total CO₂ adsorption:
75 mg/g
1.71 mmol/g

Amount of catalyst : 2.72 g
Flow rate: 335 mL/min air

Adsorption of CO$_2$ from the air at 25 °C on FS-PEI-33. Effect of humidity

<table>
<thead>
<tr>
<th>Conditions</th>
<th>mg/g adsorbent</th>
<th>mmol/g adsorbent</th>
<th>mg/g PEI</th>
<th>mmol/g PEI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry</td>
<td>52</td>
<td>1.18</td>
<td>156</td>
<td>3.55</td>
</tr>
<tr>
<td>Humid</td>
<td>78</td>
<td>1.77</td>
<td>234</td>
<td>5.32</td>
</tr>
</tbody>
</table>

In the case of zeolites, humidity stops the adsorption of CO$_2$ almost entirely.

Consistent with the formation of bicarbonates.

Humid conditions: 67% relative humidity at 25 °C.
Adsorption of CO$_2$ from the air at 25 °C on PEI/Fumed Silica under dry and humid conditions

FS-PEI-50: 50% PEI in adsorbent
FS-PEI-33: 33% PEI in adsorbent

Electrochemical Reduction of CO₂ to Syngas and Formic Acid

Standard Electrochemical Reduction Potentials of CO₂ at pH=7, NHE, NTP Conditions

\[
\begin{align*}
\text{CO}_2 &+ \text{e}^- \rightarrow \text{CO}_2^{2-} \quad E^0 = -1.96 \text{ V} \quad (1) \\
\text{CO}_2 &+ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O} \quad E^0 = -0.53 \text{ V} \quad (2) \\
\text{CO}_2 &+ 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH} \quad E^0 = -0.61 \text{ V} \quad (3) \\
\text{CO}_2 &+ 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O} \quad E^0 = -0.48 \text{ V} \quad (4) \\
\text{CO}_2 &+ 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad E^0 = -0.38 \text{ V} \quad (5) \\
\text{CO}_2 &+ 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad E^0 = -0.24 \text{ V} \quad (6)
\end{align*}
\]

H₂O + CO \quad \leftrightarrow \quad \text{H}_2 + \text{CO}_2

HOC\text{H}_3

MeOH

H₂O + CO

A Fuel & Feed-stock

Direct Formic Acid Fuel Cell
Selected Experimental Data

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Membrane</th>
<th>Anolyte</th>
<th>Cell Potential (V)</th>
<th>Pressure (psig)</th>
<th>Current Density (mA/cm²)</th>
<th>Formate (%)</th>
<th>CO (%)</th>
<th>H₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 mesh Sn</td>
<td>Nafion-H</td>
<td>0.1 M LiOH</td>
<td>3.6</td>
<td>300</td>
<td>24.2</td>
<td>39.3</td>
<td>51.0</td>
<td>10.2</td>
</tr>
<tr>
<td>300 mesh Pb</td>
<td>Nafion-H</td>
<td>0.1 M LiOH</td>
<td>3.3</td>
<td>300</td>
<td>13.4</td>
<td>48.4</td>
<td>0.0</td>
<td>19.4</td>
</tr>
<tr>
<td>100 mesh Sn</td>
<td>Nafion-Na</td>
<td>0.1 M NaOH</td>
<td>3.6</td>
<td>300</td>
<td>132.4</td>
<td>11.9</td>
<td>11.3</td>
<td>77.8</td>
</tr>
<tr>
<td>100 mesh Sn</td>
<td>Nafion-Na</td>
<td>0.1 M NaOH</td>
<td>3.3</td>
<td>450</td>
<td>79.2</td>
<td>15.2</td>
<td>17.9</td>
<td>49.2</td>
</tr>
<tr>
<td>&lt;150 µm Sn</td>
<td>Nafion-H</td>
<td>0.1 M LiOH</td>
<td>3.3</td>
<td>450</td>
<td>78.3</td>
<td>10.9</td>
<td>11.7</td>
<td>54.5</td>
</tr>
<tr>
<td>100 mesh Sn</td>
<td>Nafion-Li</td>
<td>0.1 M LiOH</td>
<td>3.3</td>
<td>300</td>
<td>76.8</td>
<td>6.7</td>
<td>9.3</td>
<td>83.9</td>
</tr>
</tbody>
</table>

- Too much H₂ produced regardless of conditions
- Significant quantities of CO were produced on tin
  - Conditions apparently can significantly change the product distribution
- Nafion-Na and Nafion-Li gave much higher current density, but lower selectivity towards CO₂ reduction
- Larger surface area tin gave higher current density, but lower selectivity as well
M5: CO$_2$ Reduction to CO: Effect of Pressure and Flow on Gold

- Increased pressure at fixed cell potential increases CO$_2$ reduction efficiency
- Maximum efficiency appears limited to ~40% under standard conditions
- Increased CO$_2$ flow increases CO$_2$ reduction efficiency
  - Possibly a mass transport effect

**Conditions:** All experiments carried out galvanostatically at 30 mA/cm$^2$ for 1 hour, 0.5-0.8 µm Au on 10% Teflonized Toray paper cathode, Pt on non-Teflonized Toray paper anode, Nafion 117 membrane, indicated cell pressure, 30 mL/min CO$_2$ flow rate across the cathode, 2 mL/min 0.1 M NaOH flow rate across the anode, 40 °C. A fresh MEA was used for each data point.
Methanol from CO$_2$

**imitating nature**

**Sources of carbon dioxide:**
- Industrial flue gases: Fossil fuel burning power plants, steel and cement factories, etc.
- The atmosphere itself (400 ppm)

**Hydrogenation of CO$_2$**

$$\text{CO}_2 + 3\text{H}_2 \xleftrightarrow{\text{Cu/ZnO}} \text{CH}_3\text{OH} + \text{H}_2\text{O}$$

**Electrochemical reduction of CO$_2$**

$$\text{CO}_2 + 2\text{H}_2\text{O} \xrightarrow{\text{Electrode catalyst}} \left\{ \text{CO} + 2\text{H}_2 \right\} + \frac{3}{2} \text{O}_2$$

Electricity needed to produce hydrogen or for the reduction can come from any renewable (wind, solar, etc.) or nuclear energy source

*US Patent, 7,704,369, April 27, 2010*
Water Electrolysis

\[ \text{H}_2\text{O} + \text{electricity} \rightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \]

39.4 kWh/kg \( \text{H}_2 \) needed at 100 % theoretical efficiency
In practice closer to 50 kWh/kg \( \text{H}_2 \)

At 4 \( \varphi \)/kWh the cost to produce \( \text{H}_2 \) is about $2.6 /kg

Main driver is cost of electricity
Capital and operating costs are a minor part of the cost

\[ \text{CO}_2 + \text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \]

1.375 kg \( \text{CO}_2 \) \hspace{1cm} 0.188 kg \( \text{H}_2 \) \hspace{1cm} 1 kg \( \text{CH}_3\text{OH} \) \hspace{1cm} 0.563 kg \( \text{H}_2\text{O} \)

At 4 \( \varphi \)/kWh the cost of producing methanol is estimated to be about $0.5 /kg or $1.8 per gallon

New Photochemical Processes are also being developed to split water
Methanol from Geothermal Sources

geothermal CO₂ + 3H₂ → H₂O + CH₃OH
3/2 O₂ → electrolysis using geothermal electricity
3H₂O

CRI Carbon Recycling International

“George Olah CO₂ to Renewable Methanol Plant”
HS Orka Svartsengi Geothermal Power Plant, Iceland
Production capacity: 10 t/day

About 40 kWh needed to produce one gallon of methanol
George Olah CO₂ to Renewable Methanol Plant” Groundbreaking
HS Orka Svartsengi Geothermal Power Plant, Iceland, October 17th 2009
Production capacity: 10 t/day, planned expansion to 100 t/day

geothermal CO₂ + 3H₂ → CH₃OH + H₂O

electrolysis using geothermal electricity

H₂O

US Patents 7,605,293 and 7,608,743
The “George Olah Carbon Dioxide to Renewable Methanol Plant”
of Carbon Recycling International in Iceland based on local geothermal energy
The first commercial carbon dioxide recycling plant operating in the world
K.C. Tran, CEO, Carbon Recycling International, Iceland
Solar Thermal Conversions

\[ \text{CO}_2 + 3 \text{FeO} \rightarrow \text{CO} + \text{Fe}_3\text{O}_4 \]

\[ \text{Fe}_3\text{O}_4 \rightarrow 3 \text{FeO} + \frac{1}{2} \text{O}_2 \]

Overall

\[ \text{CO}_2 \rightarrow \text{CO} + \frac{1}{2} \text{O}_2 \]

Sunshine to Petrol: Sandia National Laboratory Project
Ubiquitous Methanol as a Fuel and Feedstock

Natural (Shale) Gas (higher hydrocarbons)

Coal $\rightarrow$ CH$_3$OH $\leftarrow$ Biomass, waste or any carbon source

CO$_2$

Low Hanging Fruit

(KISS Principle, Bridge Fuel in the Short Term and Renewable Carbon Neutral fuel in the Long Term!)
The Methanol Economy

Anthropogenic Carbon Cycle

Carbon neutral cycle

Methanol CH₃OH

Direct methane oxidation

Synthesis H₂ + CO + CO₂

Synthetic hydrocarbons and their products

CO₂ chemical recycling
- Hydrogen by electrolysis of water
  H₂O → H₂ +½ O₂
- Followed by methanol synthesis
  CO₂ + 3H₂ → CH₃OH + H₂O
- Electrochemical reduction
  of CO₂ to methanol

Electricity

CO₂ sequestration

CO₂ capture

CO₂ from fossil fuel burning power plants and industries

Gasification

Sun energy

Atmospheric CO₂

Photochemical

CO₂ + H₂O

O₂ + Biomass

Fossil fuels
- Natural gas
- Petroleum
- Heavy oil
- Tar sands
- Shale oil
- Coal

Direct methane oxidation

Intermediates other than syn-gas

Renewable energy
- Solar
- Wind
- Hydro
- Geothermal
- Oceans

Atomic energy

Anthropogenic Carbon Cycle
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$$$$

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US Dept. of Energy
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