Renewable feedstocks supplying the petrochemical industry

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- Why is CO2 utilization important?
- What is DNV GL doing about it?
- What are the barriers?
- Ways to overcome the barriers – current status
- Going forward
We are a global classification, certification, technical assurance and advisory company

OUR PURPOSE

TO SAFEGUARD LIFE, PROPERTY AND THE ENVIRONMENT
Only by connecting the details can we impact the bigger picture

- We classify, certify, verify and test against regulatory requirements, rules, standards and recommended practices
- We develop new rules, standards and recommended practices
- We qualify new technologies and operational concepts
- We give expert advice to enhance sustainable business performance
Global reach – local competence

150 years
350 offices
100 countries
15,000 employees
Why is CO₂ utilization important?

- The world will continue to rely mainly on fossil fuels and fossil-fuel based chemicals
- CCS is unlikely to meet its targets at least for the foreseeable future, but there could be large concentrations of CO₂ available
- Significant increases in renewable energy will require mechanisms to store excess electrical energy
- CO₂ utilization is capable of unlocking the vast innovation potential of society

From Fossil to CO₂ Economy
There are many ways to utilize CO₂

Input Energy & Chemicals
- Solar
- Wind
- Geothermal
- Tidal
- Hydro
- Waste heat
- Nuclear
- Water
- Hydrogen
- Other chemicals

Conversion/Recycling
- Chemical
- Biochemical
- Photochemical
- Electrochemical

Non-conversion use
- Solvent
- Working fluid
- Heat transfer

Energy Storage
- Renewable fuels
- Syngas, methane, etc.
- Formic acid, methanol, DME

Feedstock
- Carboxylates & lactones
- Carbamates
- Urea, isocyanates
- Inorganic & organic carbonates
- Biodegradable polymers

Enhanced oil recovery (EOR)
- Super critical CO₂
- Geothermal fluid
- Beverages & microcapsules

Non-conversion use
- Waste heat conversion
- Syngas, methane, etc.
Advantages of Electrochemical Route over Other Processes

- Different Products: Formic Acid, Formate Salt, CO, Methanol, Ethylene, Methane
- Scalable & Intermittent
- Portable
- Alternate Fuels
- Flexible Power Sources
- Chemical Feedstock
- Energy Storage

**CO₂ Utilization**

- Wind Solar
- Waste Grid
- 25°C 14.420

DNV GL © 2013
Energy for CO₂ conversion can be modest

<table>
<thead>
<tr>
<th>Product</th>
<th>Gibbs Free energy, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water to hydrogen</td>
<td>237</td>
</tr>
<tr>
<td>Iron ore to iron</td>
<td>740</td>
</tr>
<tr>
<td>Silica to silicon</td>
<td>798</td>
</tr>
</tbody>
</table>
CO₂ utilization provides value added products

Total CO₂ produced worldwide = 30 GigaTon/yr

- >0.4 Gt/y potential
  - U.S. produces about 40 Mt/y ethanol

- >0.3 Gt/y potential
  - Total urea use of CO₂: 112 Mt/y

- >0.4 Gt/y potential

- Potential for 1.6 Gt/y. Currently, one plant operates at 700 t/y

> 1000 Gt total capacity possible; 12 plants: 25 Mt/y in 2013

Total CO₂ produced worldwide = 30 GigaTon/yr
Why Formic Acid? Highest energy eff. & potential profitability

Formic acid (and CO) had highest selectivity and lowest energy consumption.

Market price of Formic acid offered most favourable price gap.
**Electrochemical Reduction of Carbon Dioxide to Formic Acid (ECFORM)**

**Cathode Reactions**
- \( \text{CO}_2(aq) + H^+ + 2e^- \rightarrow \text{HCOO}^- (aq) \)
- \( \text{CO}_2(aq) + 2H^+ + 2e^- \rightarrow \text{CO}(g) \)
- \( +H_2O \ 2H^+ + 2e^- \rightarrow H_2(g) \)

**Anode Reaction**
- \( 4\text{OH}^- \rightarrow 2H_2O + O_2 + 4e^- \) (alk.)
- \( 2H_2O \rightarrow 4H^+ + O_2 + 4e^- \) (acidic)
**DNV GL Efforts in CO₂ Utilization**

**2008**
- Lab studies
  - Cu catalyst, CH₄, C₂H₄

**2009**
- Small reactor studies
  - Sn catalyst, HCOOH

**2010**
- Demo reactor, 1 Kg/d
  - Self powered trailer

**2011**
- Improve process chemistry, catalyst life

**2012**
- Establish external partnerships to demonstrate value chains
  - Interactions with other technology developers

**2013**
- Value chain analyses
  - Berkeley workshop
  - Supported other networks

**2014**
**2015**

**2008-2015**
- Start of larger internal project
- Focus on formic acid
- Other conversion processes
- Energy analyses

**Position paper on CO₂ utilization**
Barriers for adoption – CO₂ Utilization

**Technology Barriers**
- High energy and chemical consumption
- Cost and energy requirements of CO₂ capture
- Long-term performance
- Carbon balance

**Financial Barriers**
- Competition with fossil fuels and chemicals
- Market saturation due to high CO₂ volumes
- Distributed production reducing scale advantage
- Long time horizon for return on investment

**Policy Barriers**
- Lack of sufficient carbon incentive
- Lack of subsidies, loans, and credits
- Lack of an industry voice
- Lack of inclusion of novel CO₂ utilization pathways in international policies
Overcoming Technology barriers

- Reduce activation energies through novel catalysts, chemistry, and biology
  - Energy and chemical inputs must be balanced
- Single technologies won’t be sufficient – leverage existing infrastructure and technologies
- Long-term demonstration – test centers
- Novel capture technologies
  - Traditional absorption-based capture too big and expensive
- The use of renewable power, energy harvesting will improve carbon balance and economics – LCA analysis
- Standards & guidelines
ECFORM
Novel Electrodes to Increase current density to reduce CAPEX

- **Current (rate of rxn)** directly influences the CAPEX (no. of reactors)

- **Selectivity for formate reaction** (Faradaic Efficiency) = 70 – 90%

- **Stability of current and FE over time** is key

<table>
<thead>
<tr>
<th>Catalyst - Electrode Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 solid Sn only</td>
</tr>
<tr>
<td>2 Sn - CFP</td>
</tr>
<tr>
<td>3 Nano Sn - CFP</td>
</tr>
</tbody>
</table>

![Bar Chart]

Catalyst – Electrode Type

- **current, mA/cm²**
- **% product selectivity**
- **stability, days**
ECFORM
Stable Performance – High Current density and formate selectivity

Nano-tin catalyst

Setup

Current density, mA/cm²

% Formate Product Selectivity

Time, days

3x reduction in reactors achieved, hence lower CAPEX
Technical Targets Achieved, Technology is ‘ready’ for scale-up

- High Current Density
  ~ 150 mA/cm²

- Long Electrode Life
  (1 – 2 years)

- High Catalyst Selectivity
  (FE > 75%)

- Low Energy Consumption
  (~ 5.5 MWh/ton)

- Low Chemical Consumption

Reduce corrosivity of chemicals

DNVGL has de-risked by tech. development & optimization.

Patents: 2 issued, 3 filed
Overcoming financial barriers

Financial Barriers

- Competition with fossil fuels and chemicals
- Market saturation due to high CO₂ volumes
- Distributed production reducing scale advantage
- Long time horizon for return on investment

- Establish niche markets, then expand
  - Government funding is essential to support long-term development
    - ARPA-e REFUELS project
  - Prize schemes may bring novel solutions
    - CCEMC
    - X-Prize
- Government support is still essential
- Intergovernmental collaborations
- Standards and guidelines can reduce financial risks
The Chlor Alkali Process – as a model for scale-up

- Three electrochemical processes (numbers from J. Appl. Elect., 2008)
  - Mercury (being phased out) – 3.1 to 3.4 MWh/t Cl₂
  - Diaphragm (asbestos and non-asbestos) – 3.2 to 3.8 MWh/t Cl₂
  - Membrane - 2.4 to 2.9 MWh/t Cl₂

- Long history
  - Over 100 years old
  - Energy reduction innovations occur even today (e.g., Oxygen depolarization cathodes)
  - Initial concept of ODC in 1950, but developn
Technology Advances = Reduce Energy/Increase Efficiency

NAFION® Cation Ion Exchange Membrane Employed

Mixed Metal Oxide Based Dimensionally Stable Anodes – long operating life

UHDE: Total supported: 20 MMtpy

Largest: 1 MMtpy

Optimized Single Cells

Modular – Skid Mounted Stacks of Single Cells

Operating data

<table>
<thead>
<tr>
<th>Current density</th>
<th>up to 7 kA/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power consumption</td>
<td>see graph</td>
</tr>
<tr>
<td>Cell temperature</td>
<td>88-90 °C</td>
</tr>
</tbody>
</table>

Service life

- anode coating: > 8 years
- cathode coating: 8 years
- membranes: > 4 years
- gaskets: > 4 years
- compartments: > 20 years
- Active area per element: 2.72 m²
Combined Electrochemical and Thermochemical routes

Net reaction: \( \text{CO}_2 + \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{HCOOH} \)
New Niche Markets: Electro-fuel Pathway

- Greater energy efficiency (15-30%) vs. biofuel (3-8%) pathway
- Production de-coupled from the sun
- Land-use minimized / no limitation with geography
- No competition with food (corn, sugar)
- Flexibility in end fuel – butanol or diesel (depending on organism)
- Significant net reduction in CO₂ emission

Renewable power → CO₂ source → Saline/waste water → Electrochemical process → Bio-Engineered Bacteria

Product Eg. Formate/Formic Acid → Fuels

Product Eg. Formate/Formic Acid → Chemicals
Formic Acid As Feedstock

Formamide Synthesis

\[ \text{HCONH}_2 + \text{C}_2\text{H}_5\text{OH} + \text{NH}_3 \rightarrow \text{HCOONH}_4 + \text{R'}\text{OH} \]

Methanol synthesis

\[ 2 \text{CH}_3\text{OH} + 2 \text{H}_2 \rightarrow \text{HCOOCH}_3 + \text{CH}_3\text{OH} + \text{R'}\text{OH} \]

Increasing Alcohol Carbon length

\[ \text{R'}\text{C}-\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{R'}\text{C}-\text{COOR'} + \text{CO}_2 + \text{H}_2\text{O} + 2 \text{e}^- \]

Acetate Synthesis via esterification

\[ \text{R'}\text{COOR'} + \text{H}_2 \rightarrow \text{R'}\text{COOH} + \text{R'}\text{OH} \]

Larger Carboxylic Acids

\[ \text{R'}\text{COOH} \rightarrow \text{R'}\text{COOH} \]

Isomerization

\[ \text{HCOOH} \rightarrow \text{R'}\text{COOH} \]

Carboxylic Acids

\[ \text{HCOOH} \rightarrow \text{HCOOCH}_3 + 2 \text{H}_2 \]

Methyl formate
Renewable Feedstock to Basic Building Blocks

**Renewable feedstocks**

- CO₂
- Sugars
- Biomass
- Waste streams

**Simple Molecules**

- HCOOH
- Methyl Formate
- Methanol
- Alkyl Formate
- Alkali Formate
- Carboxylic Acid
- Formaldehyde
- Glycols
Large volume markets are Accessible

- Biomass → Sugars → HCOOH → CO₂

- Biodiesel
  - Glycerol → Formaldehyde
    - Ethylene Glycol → Ethylene Glycol
    - Propylene Glycol
  - Carboxylic Acid
    - Methanol
- Alkali Formate
- Methyl Formate
- Alkyl Formate
- ROH H₂
- CH₃OH H₂
- MOH
Overcoming policy barriers

- **Policy Barriers**

  - Consistent policy support is essential
    - Pew report: 74 to 96% drop in wind energy market when production tax credits expired
  - Improved communication to policy makers
    - Public polls on CCS show greater support to utilization
  - Inclusion in renewable fuels standards
  - An industry voice is needed to convince and hold policymakers
  - Influence IPCC and other intergovernmental bodies
  - Iowa Tax credit for bio-based Chemicals
  - ‘Skyfill’ – create a level playing field for alternative feedstocks

- Lack of sufficient carbon incentive
- Lack of subsidies, loans, and credits
- Lack of an industry voice
- Lack of inclusion of novel CO₂ utilization pathways in international policies
"I know you **CCU and biomass feedstock advocates** are taking it in the teeth out there. But the first guy through the wall, he always gets bloodied. Always. **This is Renewables are** threatening not just a way of doing business, but in their minds is threatening the game—**petrochemical establishment**. But what's really on their minds is that it is threatening their livelihood, threatening their jobs, threatening the **foundation of the chemicals industry** way they do things.

"And every time that happens, whether it is a government, or a way of doing business or whatever it is, the people who are holding the reins—**making energy and climate change policy decisions**, who have their hands on the switch, they go bat-shit crazy.

"I mean anyone who is not tearing down their team right now—**CCS and reversing their LNG import terminal plans** and rebuilding it using your model—**biomass**, they're **just burning dinosaurs**. They're sitting on their ass—**will be sweating their asses off** on the sofa **in 2050**. October watching the Boston Red Sox win the World Series."

By Ed Rode, DNV GL
'With apologies to the writers of 'Moneyball'
Summary

- Significant innovation and technical progress has been made, need to scale up to pilot
- Novel combinations of technologies to maximize the utilization potentials and derive critical economies and carbon balance
- The nexus between CO2 utilization and renewable energy must be better exploited
- We must communicate better to decision makers
- Standards and guidelines help in reducing financial risks and improve interoperability
Renewable feedstocks supplying the petrochemical industry

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