INDUSTRIAL SYNTHESIS OF METHANESULFONIC ACID
Index

1. Overview Grillo-Werke AG

2. Functionalisation of Methane as an example of a successful R&D project in industry
GRILLO GROUP
HEADQUARTERS IN DUISBURG, GERMANY.
THE GRILLO GROUP

ONE OF THE MOST IMPORTANT MANUFACTURERS OF ZINC PRODUCTS AND PRODUCERS OF SULPHUR CHEMICALS

1,550 EMPLOYEES

€750M TURNOVER

EXPORT RATE 40 %

6 PLANTS IN GERMANY AND WESTERN EUROPE

SUBSIDIARIES AND DISTRIBUTION COMPANIES IN 30 COUNTRIES ON ALL CONTINENTS

100 % FAMILY OWNED AND MANAGED THROUGHOUT 5 GENERATIONS (SINCE 1842)
METAL DIVISION
OUR PRODUCTS

Strips

Wire

Anodes

Powder

ZAMAK®

KKS-Beton

ZEP®
ZINC OXIDE DIVISION
RANGE OF PRODUCTS

Raw materials
Rubber articles and tyres
Feed additives
Chemicals
Cosmetics and pharmaceuticals
Glass and ceramics
Paints and varnishes
Electronics
TEC series
TEC
RHEINZINK DIVISION
AREAS OF APPLICATION

Façade

Roof

Roof drainage

Indoor applications
CHEMICALS DIVISION
RANGE OF PRODUCTS

Sulfur dioxide
Sodium bisulfite
Sodium pyrosulfite
Oleum
Recycling
Sulfuric acid
Sodium bisulfate
Dimethyl ether
Dimethyl sulfate
Zinc sulfate
Grillo’s R&D Team Chemical Division

- Dr. Ingo Biertümpel (Head of R&D and IMS Chemical Division)
- Dr. Timo Ott (Head of Product- & Process-Development, Laboratory and Pilot Plant Manager)
- 4 permanent Technicians (3 x „Chemielaborant“, 1x „Chemikant/ Meister“)
- 1 Postdoc (PhD-Chemist, 1-2 years)
- 10 industrial worker for pilot-plant (24/7) („Laboranten, Chemikanten, Chemiejungwerker, Industriemachniker“)
- Students (Master, Bachelor, „Pflicht-Praktikum“)
Typical work of the R&D Department:

- Support/Optimisation Production Plants
- Chemical Consulting for all Divisions
- Customer Support
- IP-Management Chemicals Division
- Scale Up and Piloting
- Ideas for new Processes and Products

*Typical* work of the R&D Department:

1. **Support/Optimisation Production Plants**
2. **Chemical Consulting for all Divisions**
3. **Customer Support**
4. **IP-Management Chemicals Division**
5. **Scale Up and Piloting**
6. **Ideas for new Processes and Products**
Typical work of the R&D-Department:

- IDEAS FOR NEW PROCESSES AND PRODUCTS
- SUPPORT/OPTIMISATION PRODUCTION PLANTS
- SCALE UP AND PILOTING
- IP-MANAGEMENT CHEMICALS DIVISION
- CHEMICAL CONSULTING FOR ALL DIVISIONS
- CUSTOMER SUPPORT
CHEMICALS DIVISION
“LANDSCAPE” OF SULFUR-PRODUCTS: “NOTHING THAT SMELLS”

[Diagram of sulfur products with chemical reactions and compounds]
CHEMICALS DIVISION
METHANESULFONIC ACID (MSA) IS AN INTERESTING PRODUCT
Methanesulfonic Acid (MSA)

Properties\(^1,2\)
- Biodegradable
- Non-oxidant
- Low vapour pressure

\(^1\text{Janney, Green Chem. 1999, 1, 13111,}\)
\(^2\text{OECD Guideline 301 A and Janney, Green Chem. 1999, 1, 13111}\)

- Current multi-step industrial production

\[
\text{2CH}_3\text{OH} + H_2 + 2S \xrightarrow{\text{cat}} H_3\text{CS-SCH}_3 + 2\text{H}_2\text{O}
\]
\[
H_3\text{CS-SCH}_3 + 5/2\text{O}_2 + \text{H}_2\text{O} \xrightarrow{\text{cat}} 2\text{CH}_3\text{SO}_3\text{H}
\]

McCoy, \textit{C&EN 2016, 26, 10}
Methanesulfonic Acid (MSA)

FAST GROWING MARKETS FOR GREEN ACIDS

Properties\(^1,^2\):
- Biodegradable
- Non-oxidant
- Low vapor pressure

Current multi-step industrial production method

\[ 2\text{CH}_3\text{OH} + \text{H}_2 + 2\text{S} \rightarrow \text{H}_3\text{CS-SCH}_3 + 2\text{H}_2\text{O} \]

\[ \text{H}_3\text{CS-SCH}_3 + 5/2\text{O}_2 + \text{H}_2\text{O} \xrightarrow{\text{cat}} 2\text{CH}_3\text{SO}_3\text{H} \]

McCoy, *C&EN* 2016, 26, 10
CHEMICALS DIVISION
BEST AND EASIEST PROCESS WOULD BE CH4-SULFONATION
METHANESULFONATION
100% ATOM ECONOMIC/ NO BY-PRODUCTS

Sulfur trioxide
SO₃

Methane, CH₄
(natural gas,
Bio-gas or CO₂/H₂-based)

CH₃ SO₃ H
INDUSTRIAL METHANE CHEMISTRY

Making methane into more than fuel

Different commercialization pathways for methane, including the new process by Díaz-Urrutia and Ott. Commercial demand for products that would use the amount of methane that is flared exists only for compounds usable as fuels (methanol or higher hydrocarbons).

<table>
<thead>
<tr>
<th>REACTION</th>
<th>INITIAL PRODUCT</th>
<th>END PRODUCT</th>
<th>COMPANIES</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Classical, large-scale commercial</strong></td>
<td>H₂O, (O₂), heat</td>
<td>Synthesis gas</td>
<td>Methanol</td>
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<td></td>
<td></td>
<td></td>
<td>Higher hydrocarbons</td>
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<td></td>
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<td>Several worldwide</td>
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<tr>
<td><strong>Commercialization phase</strong></td>
<td>O₂, catalyst</td>
<td>Ethylene</td>
<td>Higher hydrocarbons</td>
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<td></td>
<td></td>
<td></td>
<td>Siluria</td>
</tr>
<tr>
<td><strong>Previous commercialization attempts</strong></td>
<td>Pt catalyst, SO₃, in oleum</td>
<td>Methylbisulfate</td>
<td>Methanol</td>
</tr>
<tr>
<td></td>
<td>Metal bromide, regenerated by bromine</td>
<td>Methylbromide</td>
<td>Higher hydrocarbons</td>
</tr>
<tr>
<td></td>
<td>H₂S₂O₈ (initiator), SO₃</td>
<td>Methanesulfonic acid</td>
<td>Methanol or hydrocarbons</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Catalytica</td>
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<td>GRT</td>
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<td>Methion</td>
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</table>

METHANE VALORISATION

- Natural gas contains >87% of CH₄
- Emissions of CH₄ are a large contributor to climate change
- Much bigger resources of natural gas than crude-oil
- Liquefaction of CH₄ requires harsh conditions
- Until now no single process using methane as a direct feedstock to a high-value product known

**Partial oxidation to Synthesisgas**

\[ \text{CH}_4 + \text{H}_2\text{O} \xrightarrow{\text{catalyst}} \text{CO} + 3\text{H}_2 \]

Source: Satellite-Detected Natural Gas Flaring for Jan 1, 2018 from skytruth.org
METHANESULFONATION

HANDLING PURE SULFUR TRIOXIDE IS DIFFICULT

- Intermediate sulfuric acid prod.
- Handling is difficult
- Special Equipment necessary
- Extremely Corrosive
- High vapour pressure
- Builds fumes of conc. sulfuric acid
- Boiling point: 44°C
- High melting point: Polymerization starts below 32.5°C
OVERVIEW SULFONATION REACTIONS

25 YEARS OF RESEARCH – BUT NO INDUSTRIAL PROCESS, WHY?

\[
\text{CH}_4 + \text{SO}_3 \xrightarrow{\text{radical init.}} \text{CH}_3\text{SO}_3\text{H}
\]

- Peroxodisulfates or Marshall’s Acid (H₂S₂O₈) as Initiator
- Poor yields (1-20%)
- Poor selectivity
- Limitations in reproducibility
- By-products (radical recombination)
- Addition of precious metals (e.g. Rh)
- Purification of MSA not investigated:
  - possible to separate MSA?
  - What happens to alkali- and precious metals?

Bell et al., *ACIE* **2003**, *42*, 2990
Sen et al., *JACS* **1996**, *118*, 13111
INDUSTRIAL PROCESSES
BEYOND CHEMISTRY

- (Modern) Production-Process
  - Equipment/Engineering/Scalability
  - Materials/Corrosion
  - Intellectual Property
  - Ecology/Energie
  - Waste-Management
  - Authorisation
  - Safety
  - Market
  - Economy/Competition
  - ... etc
INDUSTRIAL PROCESSES
BEYOND CHEMISTRY

(Modern) Production-Process

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- … etc
INDUSTRIAL PROCESSES
BEYOND CHEMISTRY

- Low Yields
- IP-Situation not clear
- Toxic By-products
- Initiator not stable!
- No stable materials found
- Gas evolution Initiator
- Ecology/Energie
- Equipment/Engineering/Scalability
- Materials/Corrosion
- Waste-Management
- Authorisation
- Safety
- Intellectual Property
- Growing Market
- Market
- Economy/Competition
- Plant set-up not economic
- Growing Market
- … etc

(Modern) Production-Process

By-products

Toxic By-products

Low Yields

No stable materials found

Gas evolution Initiator

Initiator not stable!

Economic

Plant set-up not economic

Growing Market

Low Yields

IP-Situation not clear

Toxic By-products

Initiator not stable!

No stable materials found

Gas evolution Initiator

Economy/Competition

Plant set-up not economic

Growing Market

Low Yields
THE RADICAL DMSP PROCESS
INITIATOR (DMSP) BASED ON MSA

Development of a scalable synthesis of stable and metal-free initiator:

\[ \text{CH}_4 + \text{SO}_3 \xrightarrow{\text{radical init.}} \text{CH}_3\text{SO}_3\text{H} \]

(Dimethylsulfonylperoxide, DMSP)
PRODUCTION PLANT SET-UP
THE DMSP PROCESS

Ott, Richards et al., WO2015071365
EVALUATION OF THE DMSP PROCESS
METHANESULFONIC ACID (MSA)

- Scalable
- High investment (Electrolysis)
- High production costs
- Good yields (> 80% vs. SO$_3$)
- Long reaction times (> 15h)
- Safety issues with concentrated DMSP solutions (Cryst.)
DMSP PROCESS IS NOT ECONOMIC
BEYOND CHEMISTRY

- Energy-Intensive
- Ecology/Energie
- Intellectual Property
- Materials/Corrosion
- Equipment/Engineering/Scalability
- Waste-Management
- Huge Recycle-Stream
- Authorisation
- Initiator explosiv!
- Safety
- Market
- Economy/Competition
- Growing Market
- Plant set-up not economic
- ... etc

(Modern) Production-Process

BEYOND CHEMISTRY
DMSP PROCESS IS NOT ECONOMIC
INVESTIGATION OF THE REACTION

- UV irradiation does **not** trigger the sulfonation of methane in our system (new Initiator!)

- CO, O₂, and ethane show different degrees of deactivation

- Radical recombination products are **not** observed

Dr. Christian Diaz-Urrutia and Nicola Bloch
THE NEW INITIATOR (MMSP)

The reaction:

$$\text{CH}_4 + \text{SO}_3 \xrightarrow{< 1 \text{ mol}\% \text{ pre-cat}} \text{CH}_3\text{SO}_3\text{H}$$

$50 \degree \text{C}$

Invention of a **scalable synthesis for new and stable initiator:**

$$\text{H}_3\text{C}-\overset{\text{O}}{\text{S}}-\overset{\text{OH}}{\text{O}} + \text{H}_2\text{O}_2 \xrightarrow{-\text{H}_2\text{O}} \text{H}_3\text{C}-\overset{\text{O}}{\text{S}}-\overset{\text{O}}{\text{OH}}$$

$$\text{H}_3\text{C}-\overset{\text{O}}{\text{S}}-\overset{\text{O}}{\text{OH}} + \text{SO}_3 \xrightarrow{} \text{H}_3\text{C}-\overset{\text{O}}{\text{S}}-\overset{\text{O}}{\text{SO}}-\overset{\text{OH}}{\text{O}}$$


Water-soluble white crystals
„NEW INITIATOR“ IS THE KEY!

\[ \text{CH}_4 + \text{SO}_3 \xrightarrow{\text{< 1 mol\% pre-cat}} \text{CH}_3\text{SO}_3\text{H} \]

50 °C
ca. 100 bar
solv: H\textsubscript{2}SO\textsubscript{4}

- 99% conversion
- >99% yield
- 100% atom economy

Ott et al., WO2018096138; Ott et al., WO2015071455;
Bild der Wissenschaft 11/2017

- Life Cycle Analysis: The Grillo Process is More Sustainable
- Bio-methane: even better process

Seeger et al., *J. Cleaner Prod.* 2018, 202, 1179-1191
PRODUCTION PLANT SET-UP
THE DMSP PROCESS

Reactor-Cascade

CH₄ → Absorber → DMSP → Electrolysis → H₂O → Distillation → MSA

SO₃ → H₂ → DMSP

H₂SO₄/MSA
PRODUCTION PLANT SET-UP
“NEW INITIATOR”

CH₄ → Reactor-Cascade → H₂O → Distillation → MSA
SO₃

H₂O₂ → Static Mixer → H₂SO₄/MSA

MMSP-PROCESS IS VERY ECONOMIC
BEYOND CHEMISTRY
Pilot Plant: 80 Tons MSA per Year

• Continuous reactors allow for high conversion and selectivity
• Distillation affords high purity MSA
INORGANIC CHEMICALS

German firm claims new route to methanesulfonic acid
Grillo's direction reaction of methane and SO3 could open up market for unique acid

Grillo-Werke successfully converts methane into methanesulfonic acid
Acknowledgement:

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Dr. Matthias Vogt

Pilot Plant Team

Master Students/ Trainees