INDUSTRIAL SYNTHESIS OF METHANESULFONIC ACID

Fachforum Ressourcen 2019
Dr. Timo Ott

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1. Overview Grillo-Werke AG

2. Functionalisation of Methane as an example of a successful R&D project in industry

GRILLO GROUP

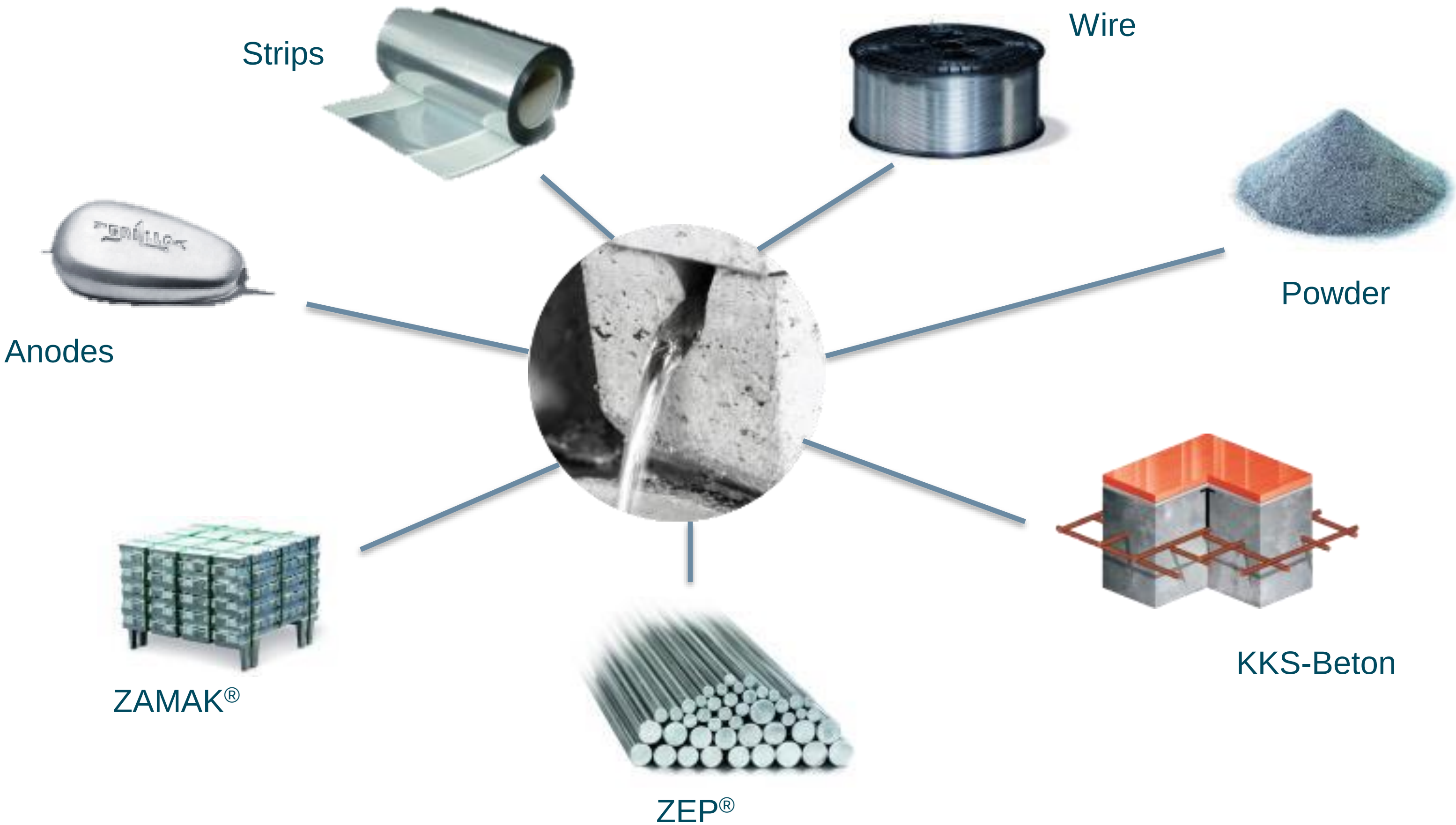
HEADQUARTERS IN DUISBURG, GERMANY.

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



ZINC OXIDE DIVISION

RANGE OF PRODUCTS

RHEINZINK DIVISION

AREAS OF APPLICATION

Façade

Roof

Roof drainage

Indoor applications

CHEMICALS DIVISION

RANGE OF PRODUCTS

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")

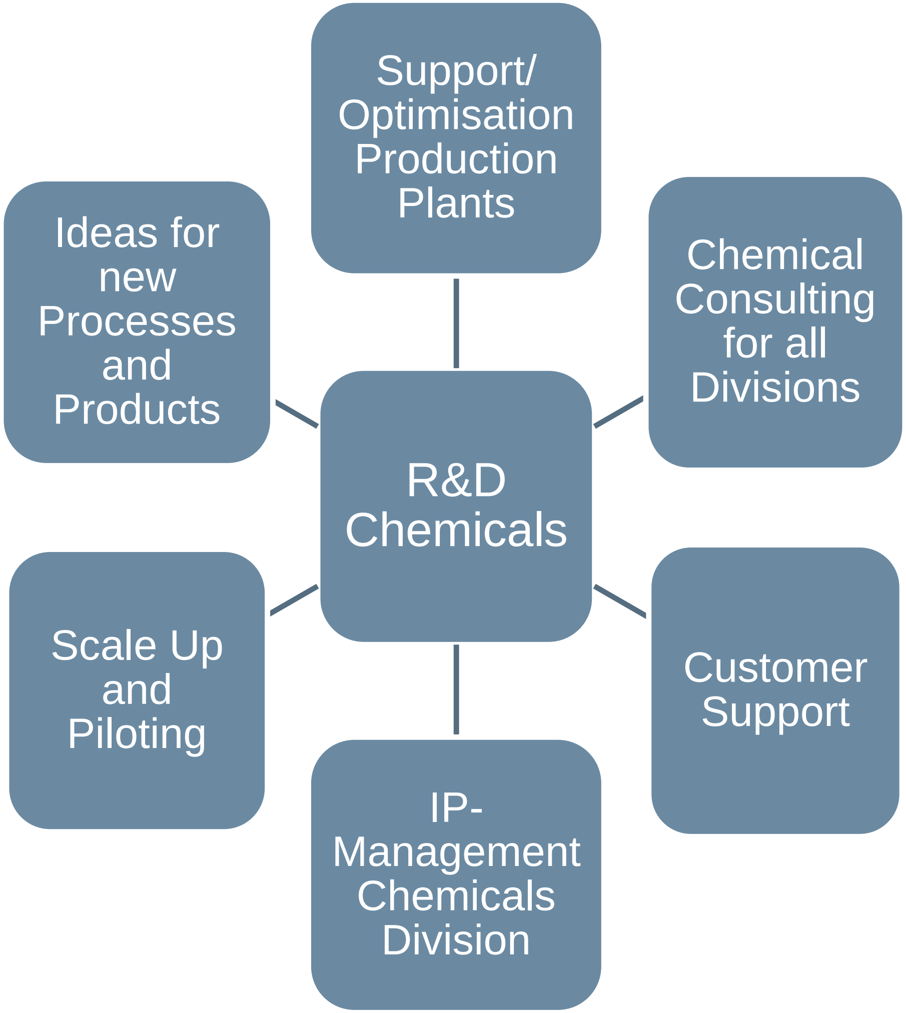
- 1 Postdoc (PhD-Chemist, 1-2 years)

- 10 industrial worker for pilot-plant (24/7)

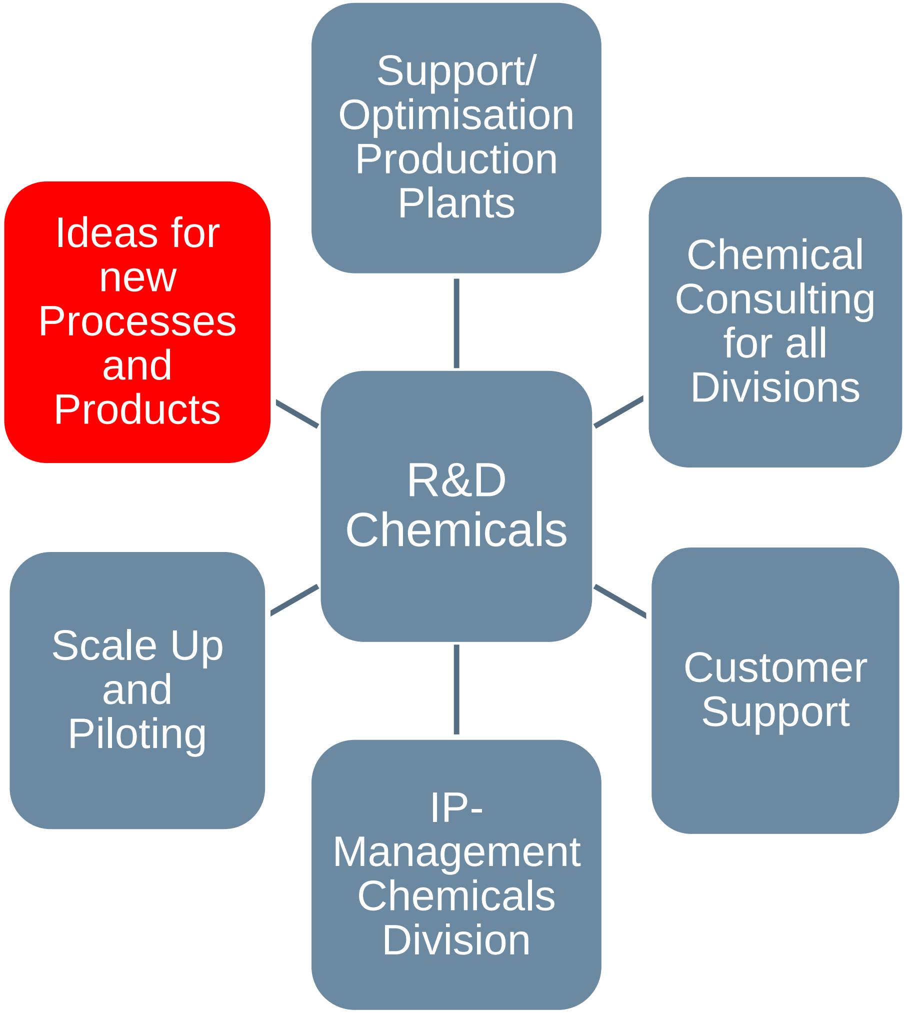
(„Laboranten, Chemikanten, Chemiejungwerker, Industriemechaniker")

- Students (Master, Bachelor, „Pflicht-Praktikum")

Typical work of the R&D Department:

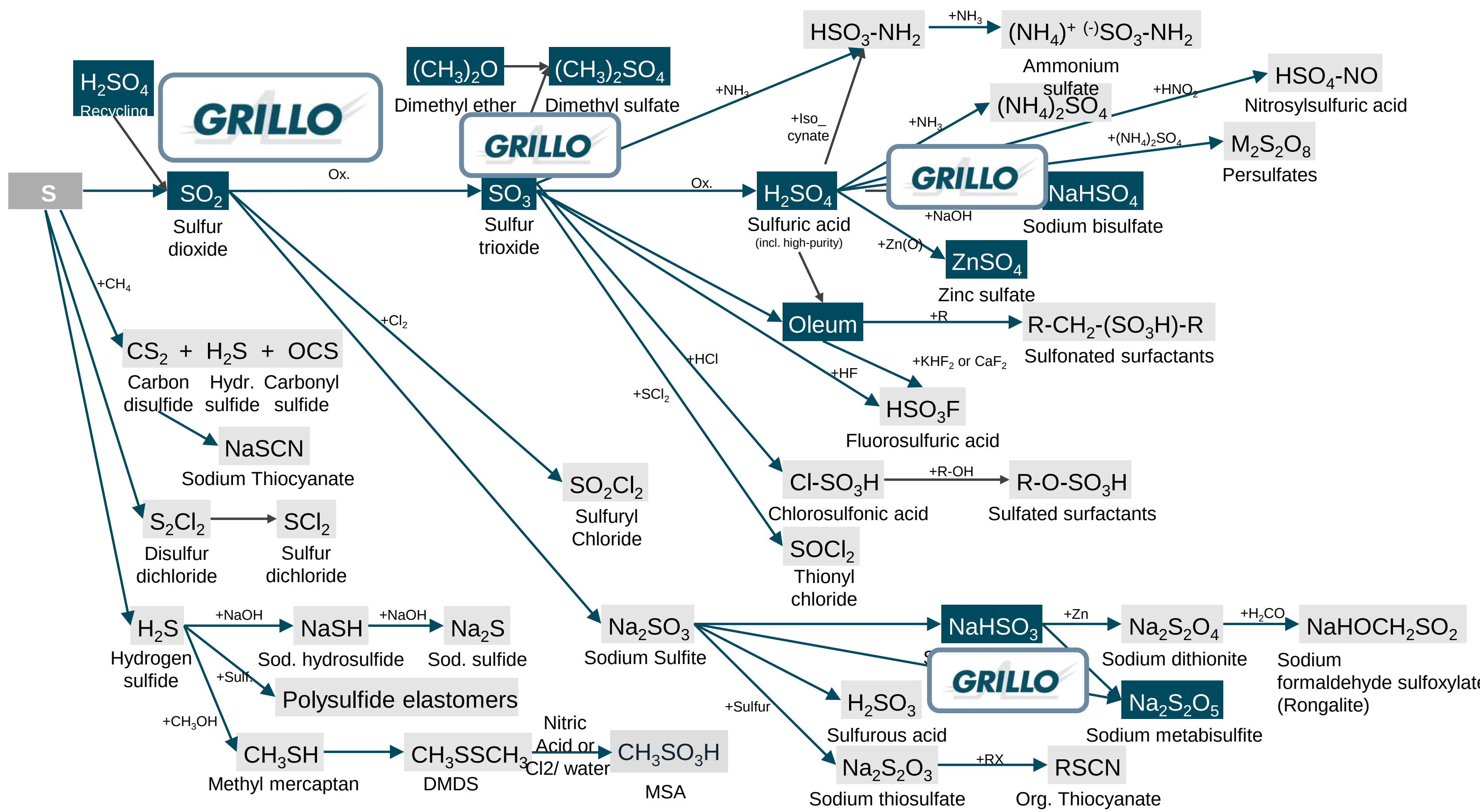


Typical work of the R&D-Department:



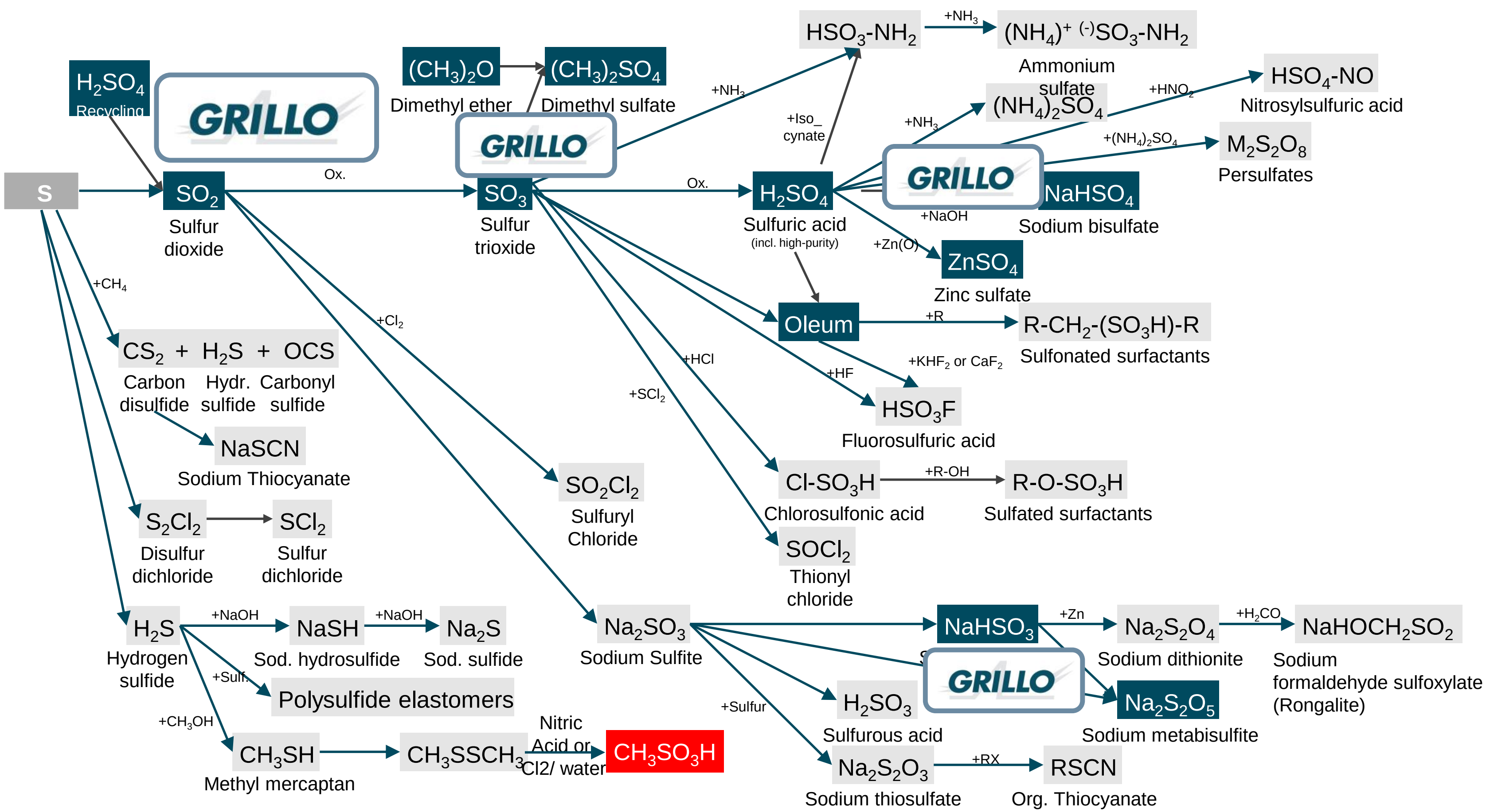
CHEMICALS DIVISION

“LANDSCAPE” OF SULFUR-PRODUCTS: “NOTHING THAT SMELLS”



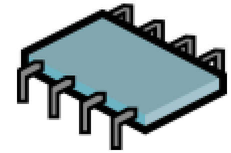
CHEMICALS DIVISION

METHANESULFONIC ACID (MSA) IS AN INTERESTING PRODUCT



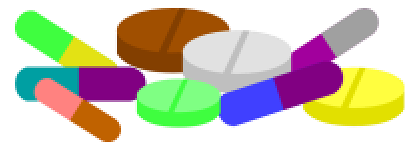
Methanesulfonic Acid (MSA)

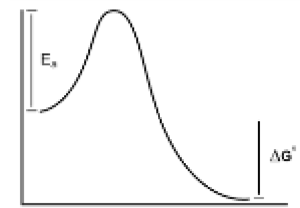
FAST GROWING MARKETS FOR GREEN ACIDS

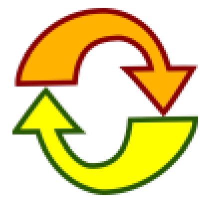


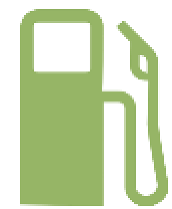
Properties[1,2]

- Biodegradable
- Non-oxidant
- Low vapour pressure









[1]Janney, *Green Chem.* **1999,** *1,* 13111,
[2]OECD Guideline 301 A and Janney, *Green Chem.* **1999,** *1,* 13111

- Current multi-step industrial production

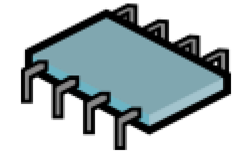
$$2CH_3OH + H_2 + 2S \xrightarrow{cat} H_3CS\text{-}SCH_3 + 2H_2O$$

$$H_3CS\text{-}SCH_3 + 5/2O_2 + H_2O \xrightarrow{cat} 2CH_3SO_3H$$

McCoy, *C&EN* **2016**, *26,* 10

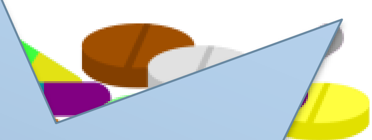
Methanesulfonic Acid (MSA)

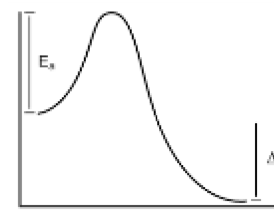
FAST GROWING MARKE TS FOR GREEN ACIDS



Properties[1,2

- Biodegrada
- Non-oxidant
- Low v





Idea: Producing a „green acid“ using a „green process“

[1]Janney, *Green Ch*
[2]OECD Guideli

- Current mu ... od

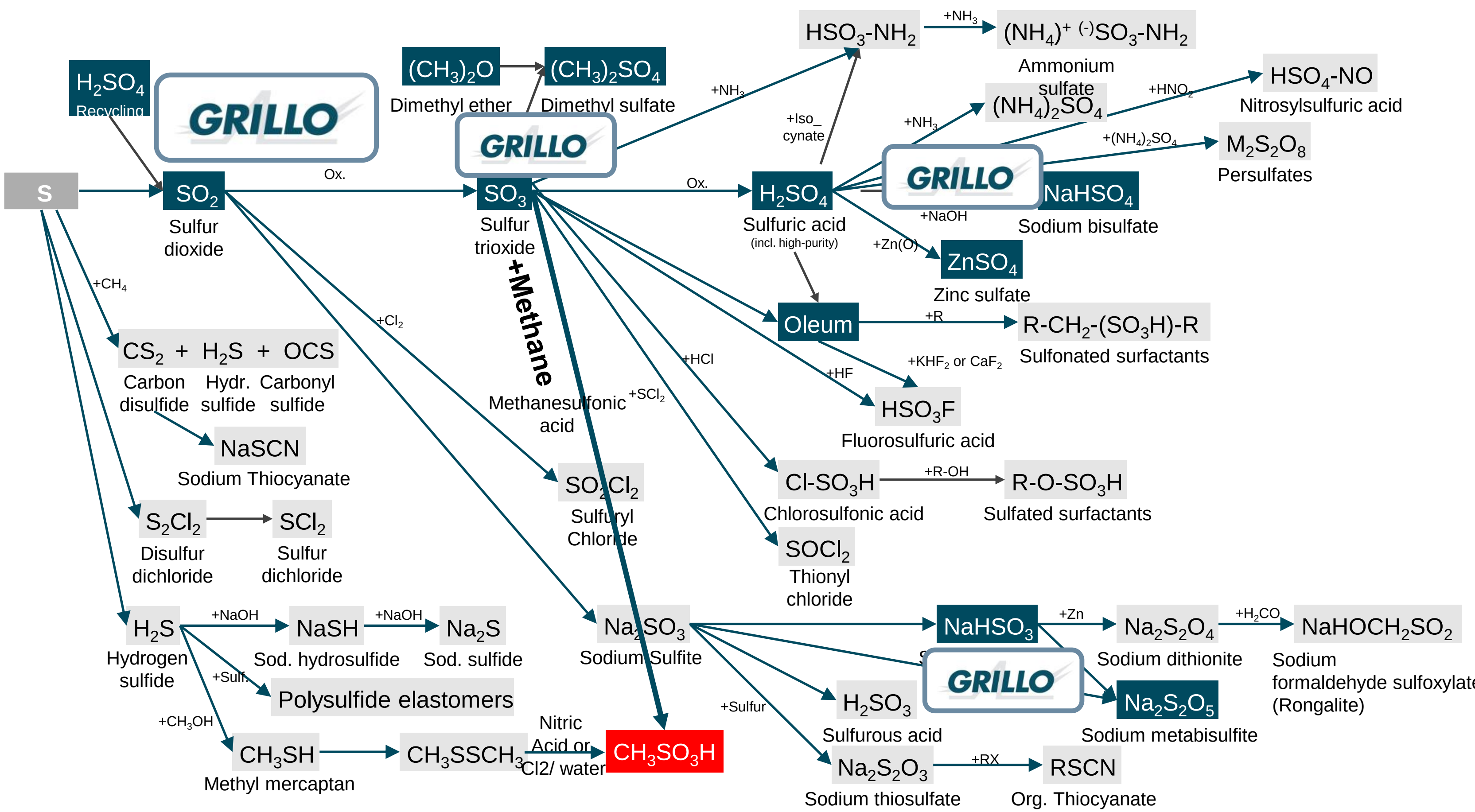
$2CH_3OH + H_2 \quad 2S \longrightarrow H_3 \quad -SCH_3 \quad 2H_2O$

$H_3CS\text{-}SCH_3 + 5/2O_2 + H_2O \xrightarrow{cat} 2CH_3SO_3H$

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
SO_3

Methane, CH_4
(natural gas,
Bio-gas or CO_2/H_2-based)

CH_3 SO_3 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).

	REACTION	INITIAL PRODUCT	END PRODUCT	COMPANIES
Classical, large-scale commercial	H_2O, (O_2), heat	Synthesis gas	Methanol Higher hydrocarbons	Several worldwide
Commercialization phase	O_2, catalyst	Ethylene	Higher hydrocarbons	Siluria
Previous commercialization attempts	Pt catalyst, SO_3, in oleum	Methylbisulfate	Methanol	Catalytica
	Metal bromide, regenerated by bromine	Methylbromide	Higher hydrocarbons	GRT
	$H_2S_2O_8$ (initiator), SO_3	Methanesulfonic acid	Methanol or hydrocarbons	Methion

Schüth, *Science* **2019**, *343*, 6433.

METHANE VALORISATION

Methane (natural gas)
CH_4

- Natural gas contains >**87%** of CH_4
- Emissions of CH_4 are a large contributor to **climate change**
- Much bigger resources of natural gas than crude-oil
- Liquefaction of CH_4 requires **harsh conditions**
- Until now <u>no single process</u> using methane as a direct feedstock to a high-value product known

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

<u>Partial oxidation to Synthesisgas</u>

$$CH_4 + H_2O \xrightarrow[> 1{,}000\ ^\circ C]{\text{catalyst}} CO + 3H_2$$

METHANESULFONATION

HANDLING PURE SULFUR TRIOXIDE IS DIFFICULT

Sulfur trioxide
SO_3

- 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?

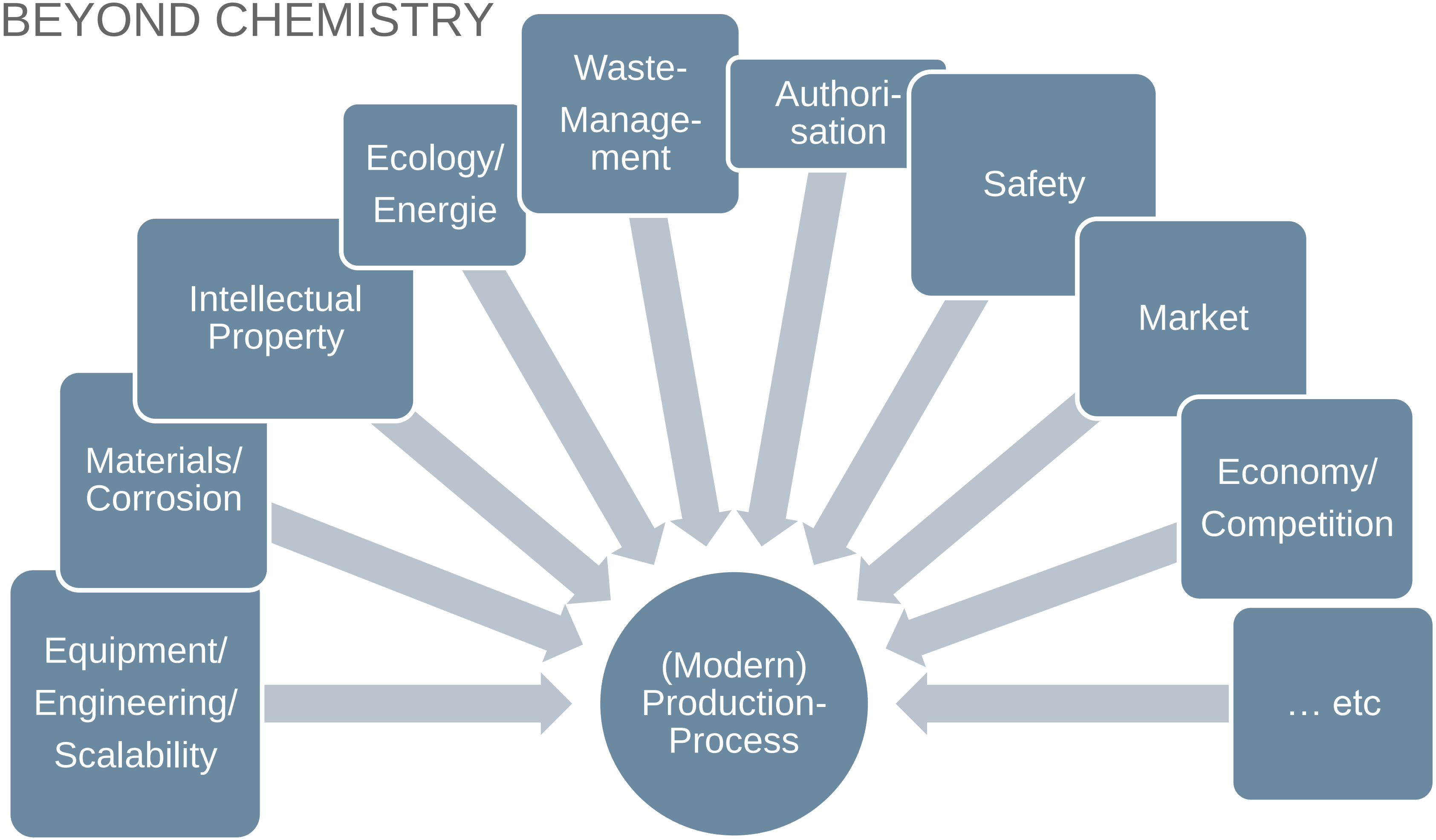
$$\boxed{CH_4 + SO_3 \xrightarrow{\text{radical init.}} CH_3SO_3H}$$

- Peroxodisulfates or Marshall's Acid ($H_2S_2O_8$) as Initiator
- Poor yields (1-20%)
- Poor selectivity
- Limitations in reproducibility
- By-products (radical recombination)
- Addition of precious metals (e.g. Rh)
- <u>Purification of MSA not investigated</u>:
  -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

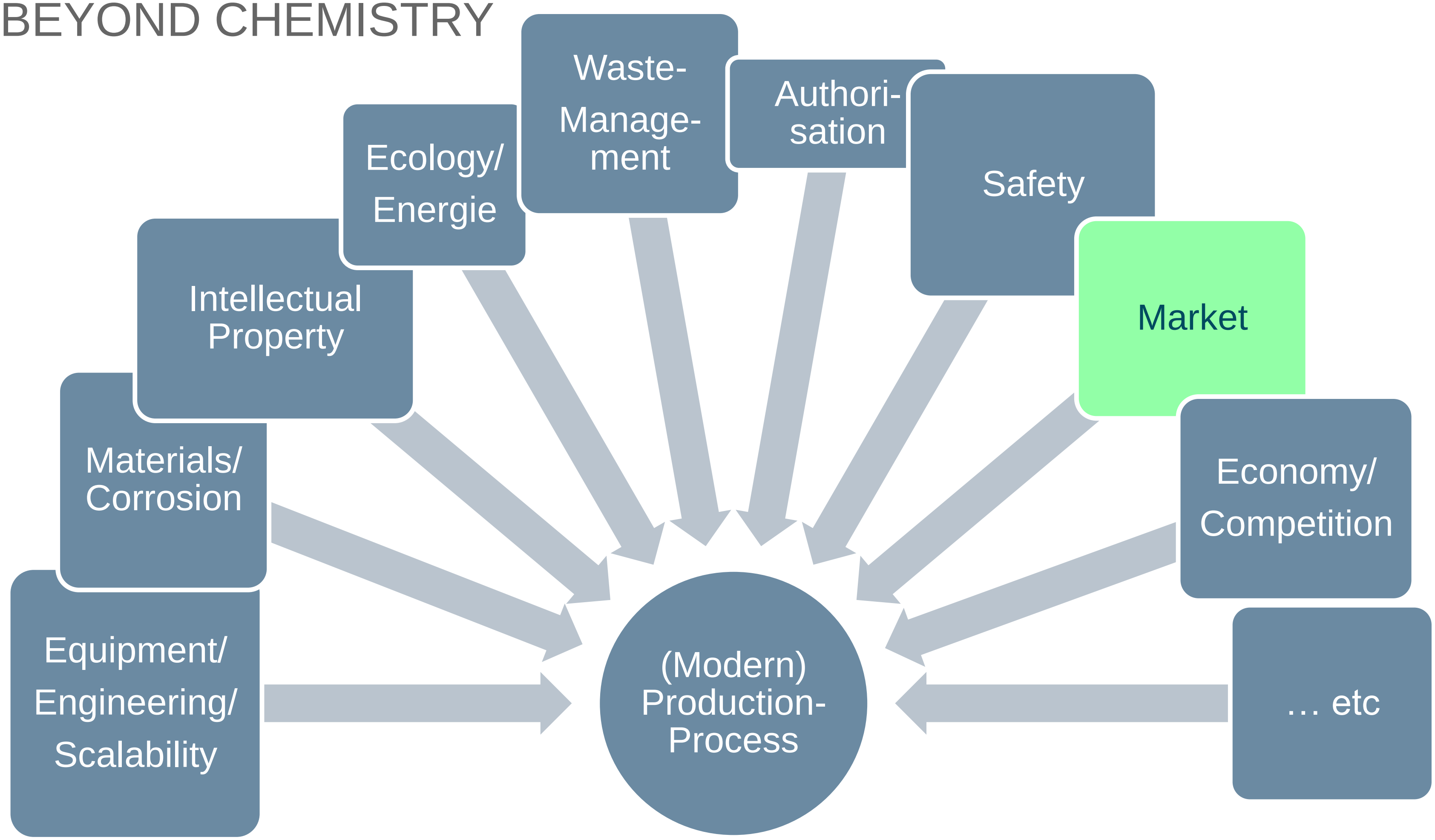
INDUSTRIAL PROCESSES

BEYOND CHEMISTRY



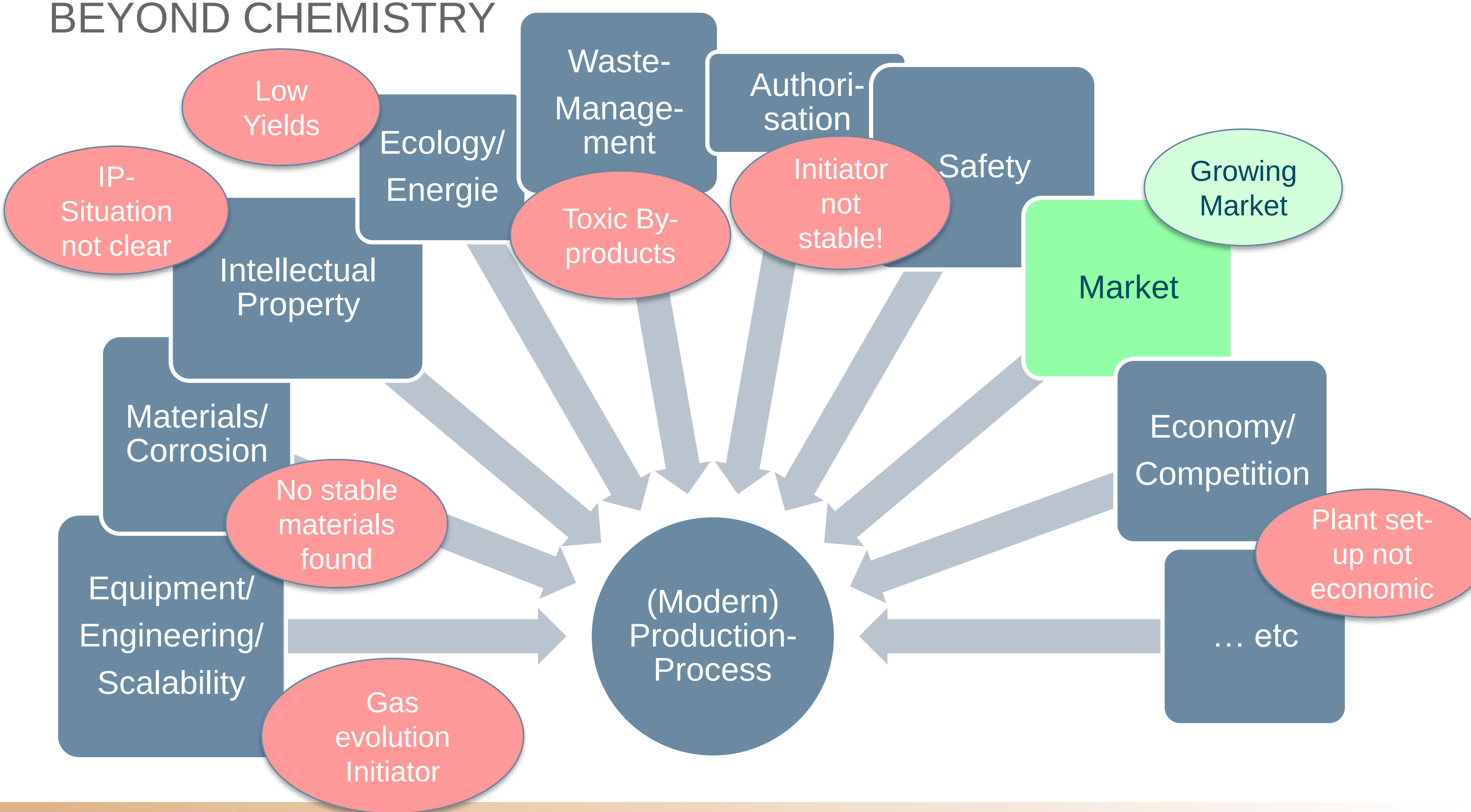
INDUSTRIAL PROCESSES

BEYOND CHEMISTRY



INDUSTRIAL PROCESSES

BEYOND CHEMISTRY



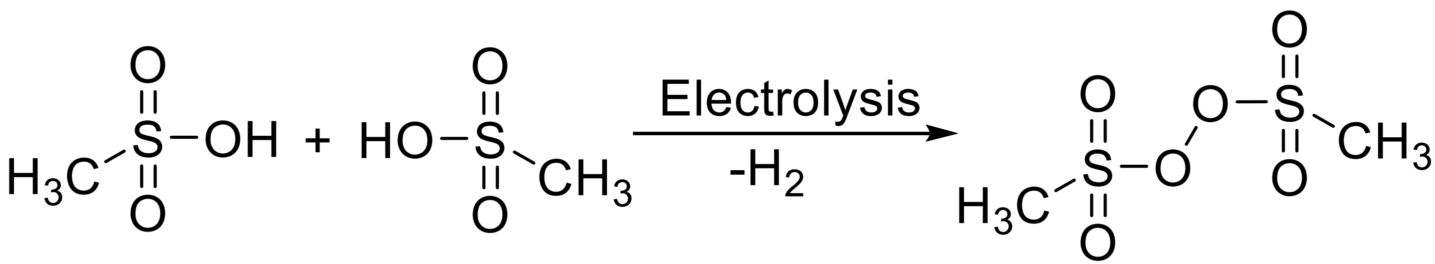
THE RADICAL DMSP PROCESS

INITIATOR (DMSP) BASED ON MSA

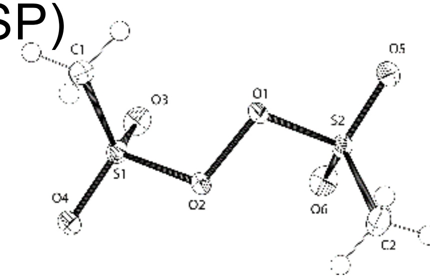
$$\boxed{CH_4 + SO_3 \xrightarrow{\text{radical init.}} CH_3SO_3H}$$

Development of a

scalable synthesis of stable and metal-free initiator:



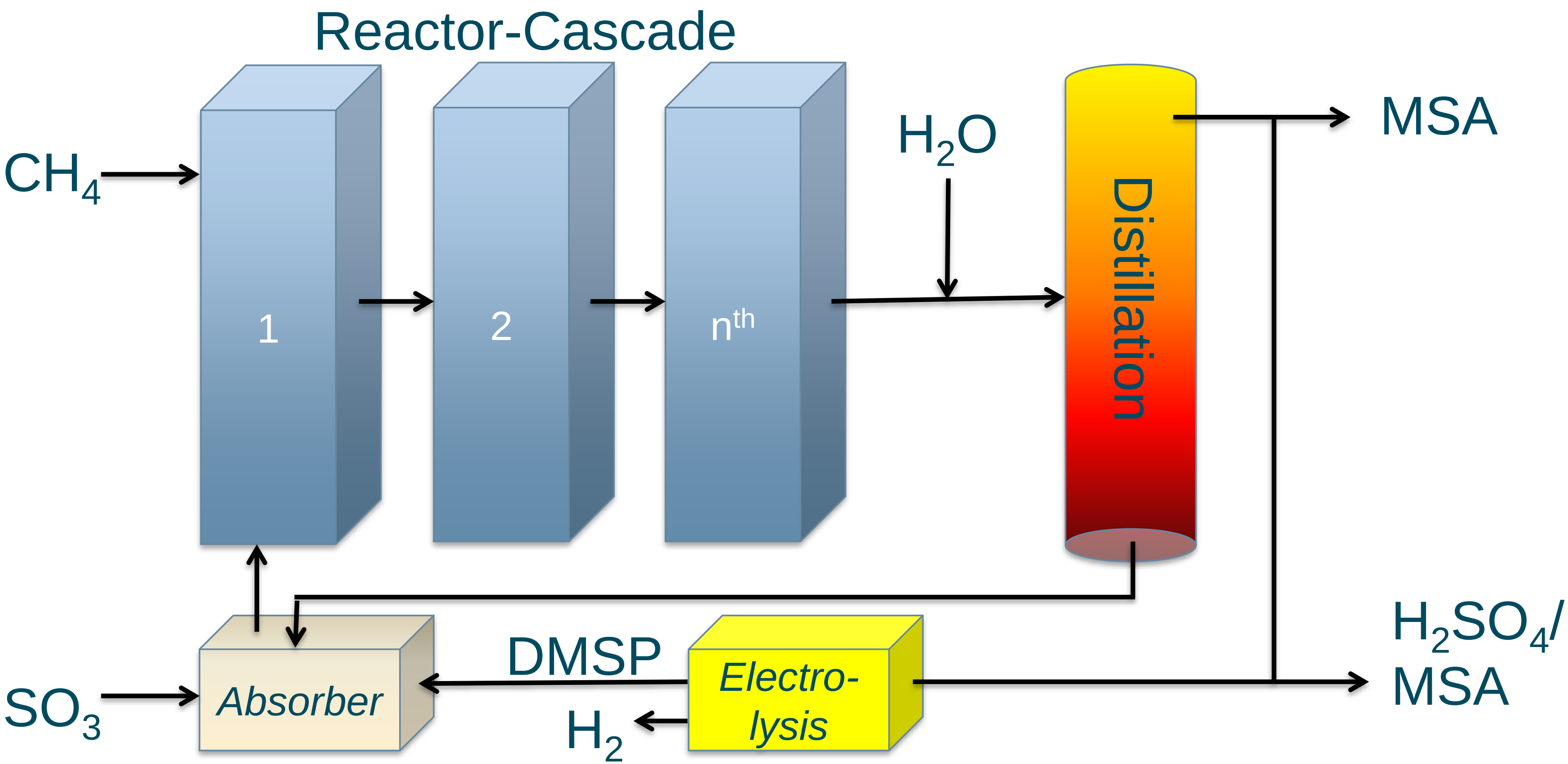
(DMSP)



(Dimethylsulfonylperoxide, DMSP)

PRODUCTION PLANT SET-UP

THE DMSP PROCESS



Ott, Richards et al., WO2015071365

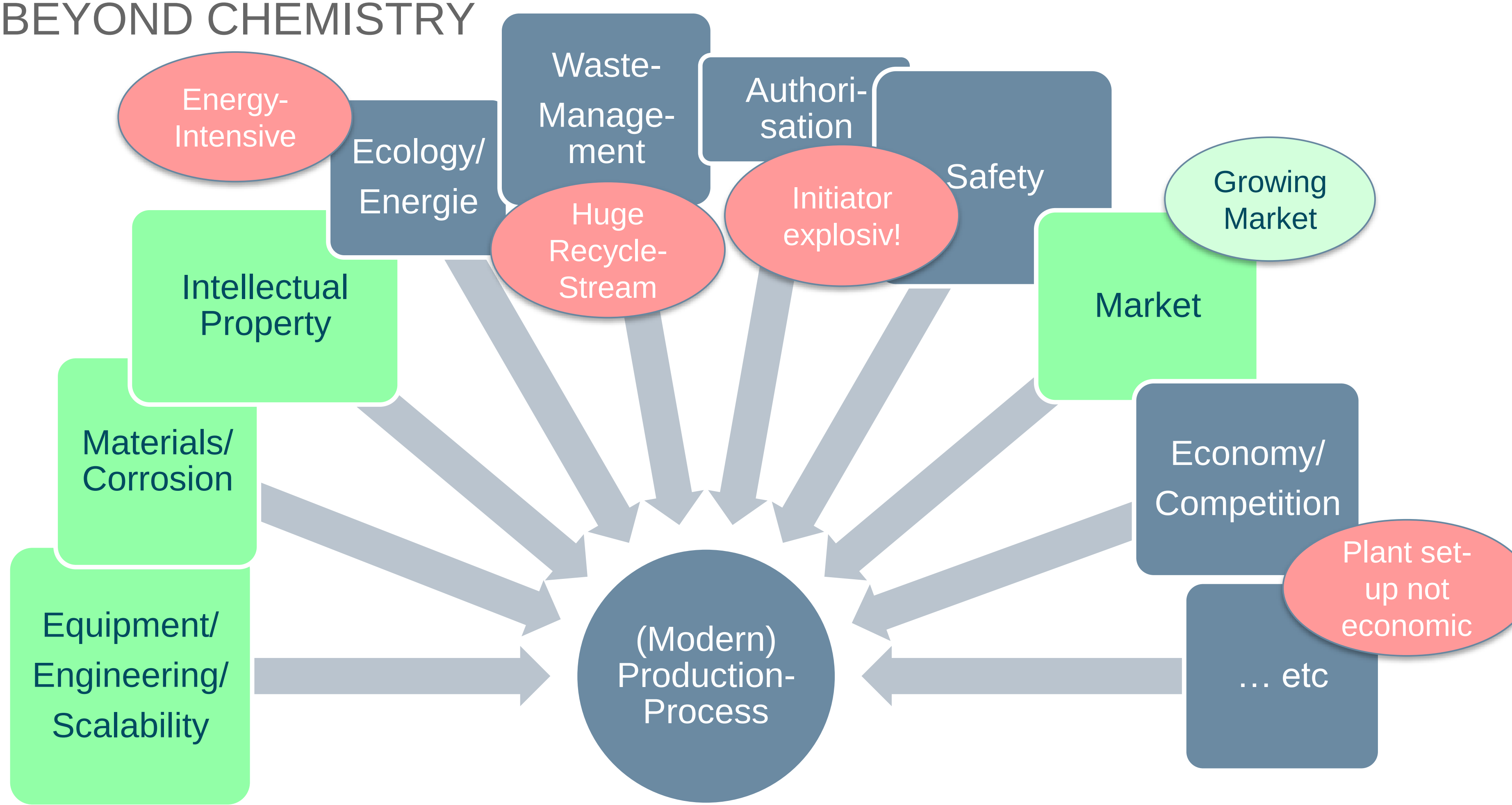
EVALUATION OF THE DMSP PROCESS

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



INVESTIGATION OF THE REACTION

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

- CO, O_2, and ethane show different degrees of deactivation

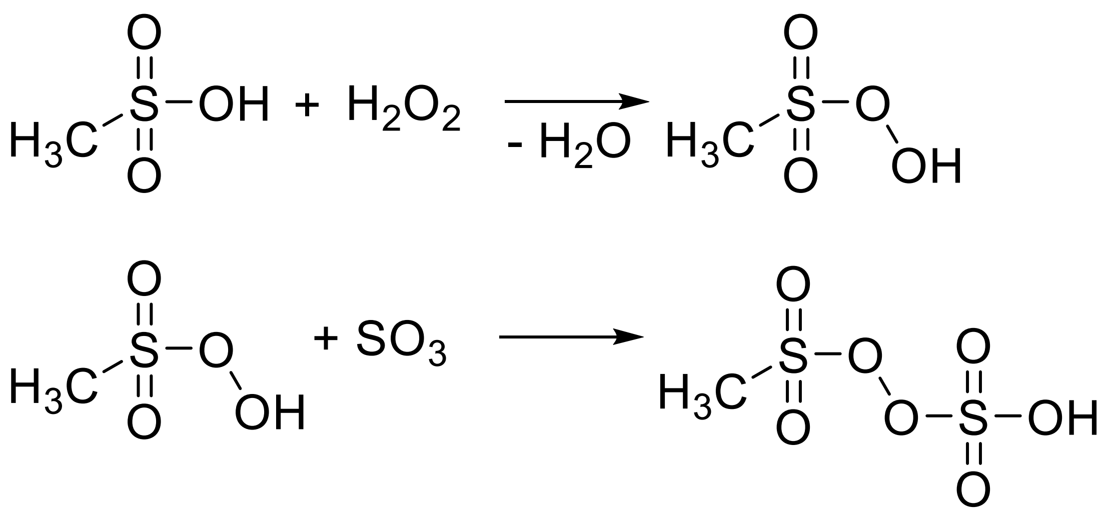
- Radical recombination products are **not** observed

Dr. Christian Diaz-Urrutia and Nicola Bloch

THE NEW INITIATOR (MMSP)

$$CH_4 + SO_3 \xrightarrow[50\ ^{o}C]{<\ 1\ \text{mol\% pre-cat}} CH_3SO_3H$$

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



Water-soluble white crystals

C. Diaz-Urrutia, T. Ott, *Science* **2019**, *363*, 1326-1329.

„NEW INITIATOR“ IS THE KEY!

$$CH_4 + SO_3 \xrightarrow[\substack{50\ ^{o}C \\ \textit{ca.}\ 100\ \text{bar} \\ \text{solv: } H_2SO_4}]{<\ 1\ \text{mol\% pre-cat}} CH_3SO_3H$$

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

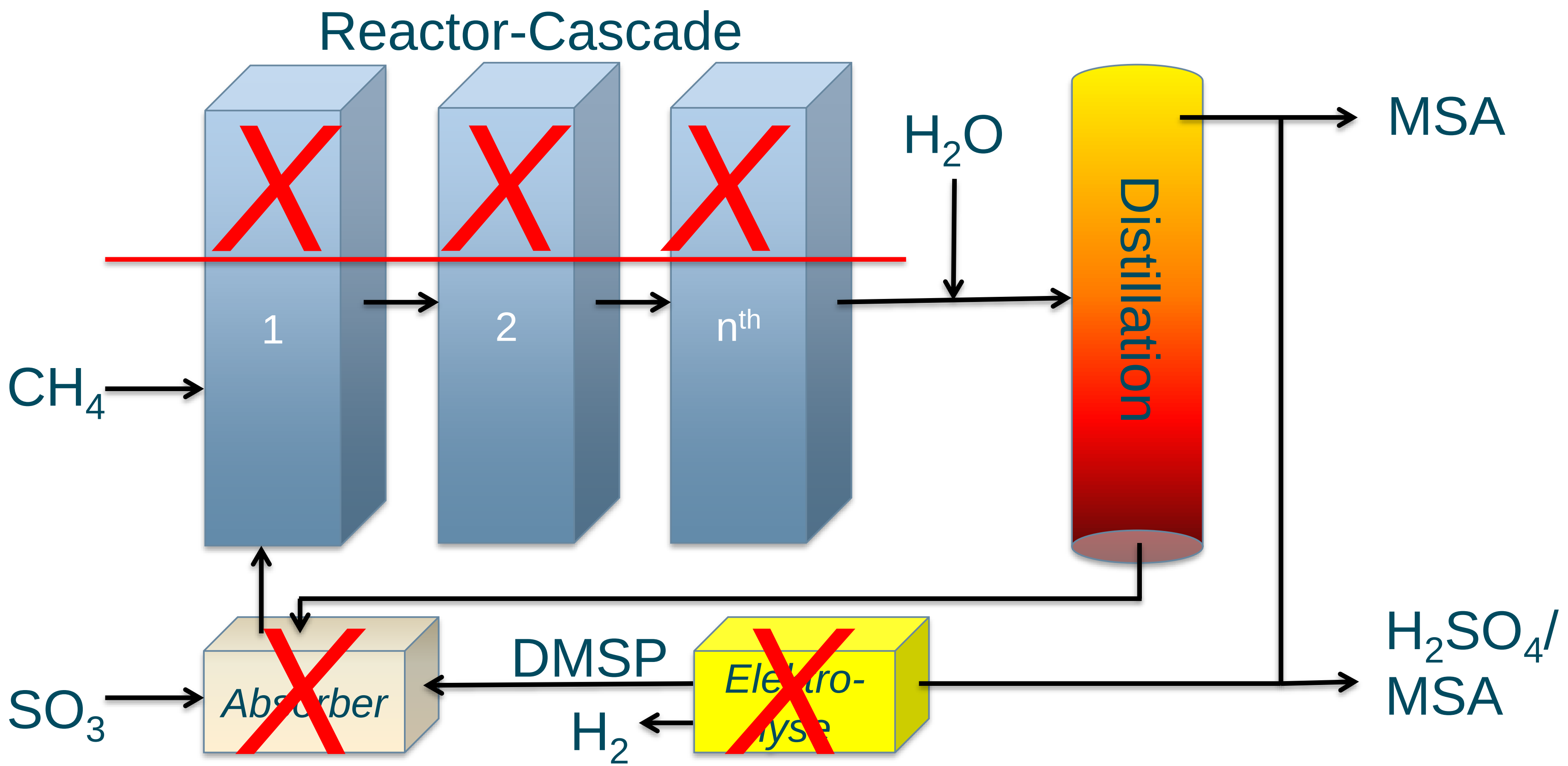
Ott *et al.*, WO2018096138; Ott *et al.*, WO2015071455; Bild der Wissenschaft 11/**2017**

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

Seeger et al., *J. Cleaner Prod.* **2018,** *202, 1179-1191*

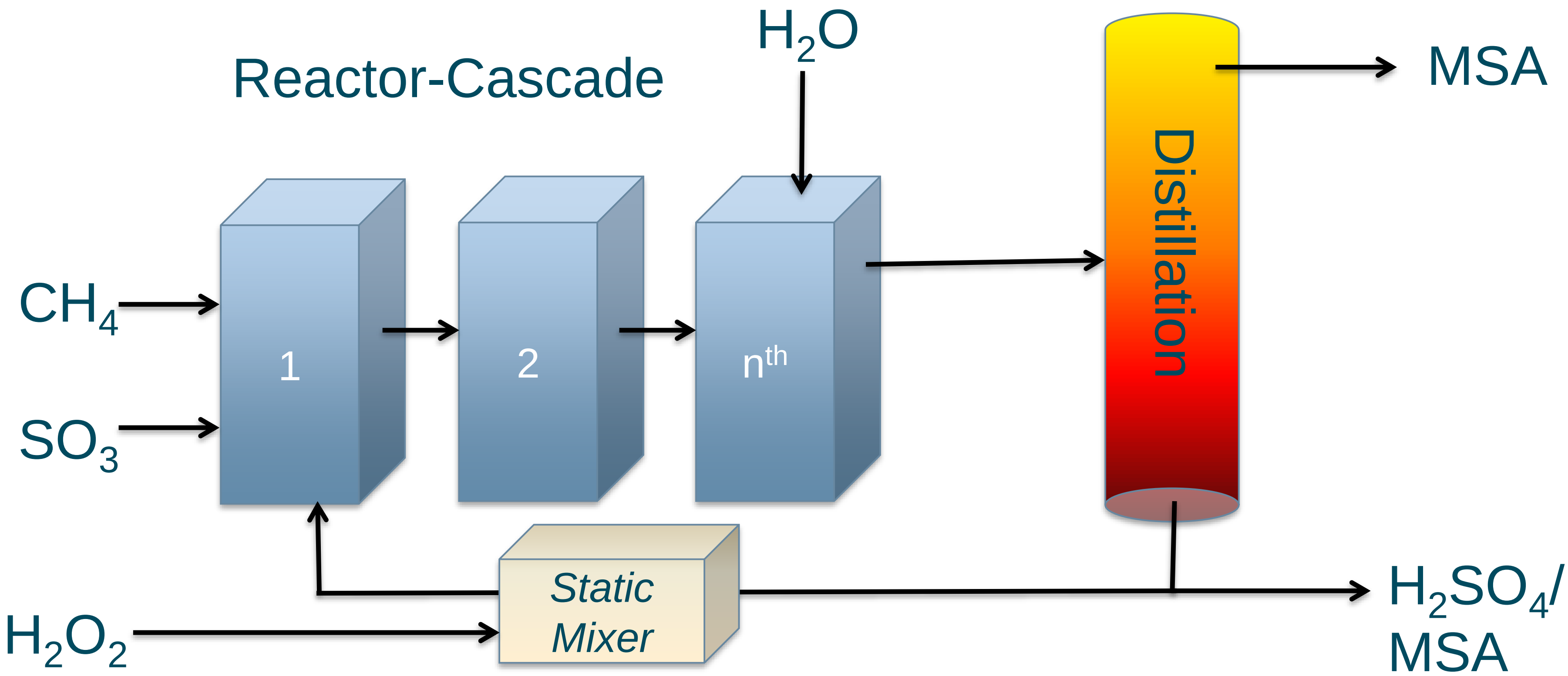
PRODUCTION PLANT SET-UP

THE DMSP PROCESS



PRODUCTION PLANT SET-UP

“NEW INITIATOR”



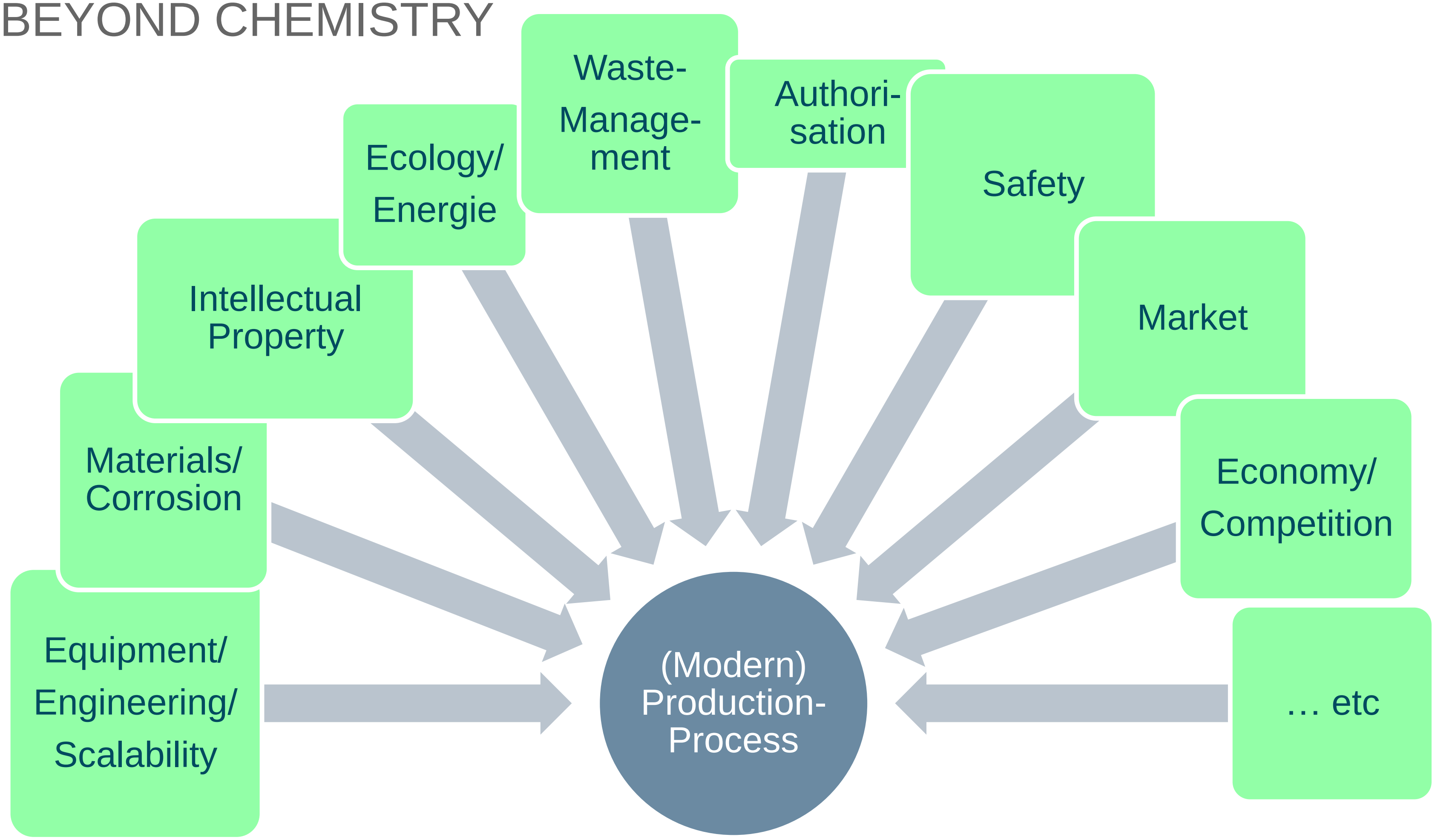
Ott *et al*, WO2018096138; Ott *et al*, WO2015071455; Ott,
Bild der Wissenschaft 11/**2017,** C. Diaz-Urrutia, T. Ott, *Science* **2019**, *363*, 1326-1329.

GRILLO

Progress as a Tradition

MMSP-PROCESS IS VERY ECONOMIC

BEYOND CHEMISTRY



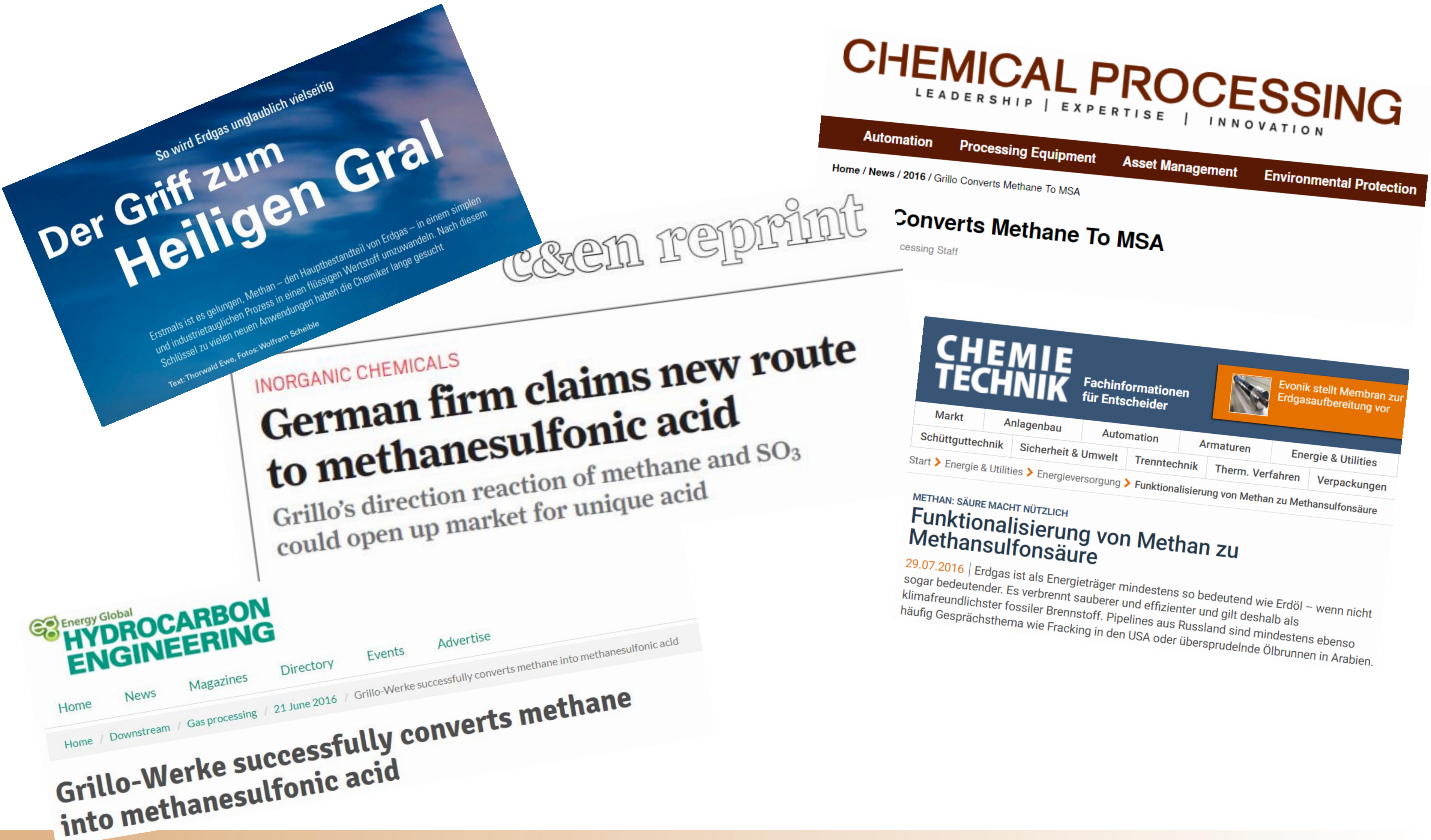
Pilot Plant: 80 Tons MSA per Year

- Continuous reactors allow for high conversion and selectivity
- Distillation affords high purity MSA

GRILLO

Progress as a Tradition

GRILLO IN THE PRESS:


So wird Erdgas unglaublich vielseitig

Der Griff zum Heiligen Gral

Erstmals ist es gelungen, Methan – den Hauptbestandteil von Erdgas – in einem simplen und industrietauglichen Prozess in einen flüssigen Wertstoff umzuwandeln. Nach diesem Schlüssel zu vielen neuen Anwendungen haben die Chemiker lange gesucht

Text: Thorwald Ewe, Fotos: Wolfram Scheible

CHEMICAL PROCESSING

LEADERSHIP | EXPERTISE | INNOVATION

Automation Processing Equipment Asset Management Environmental Protection

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Converts Methane To MSA

cessing Staff

c&en reprint

INORGANIC CHEMICALS

German firm claims new route to methanesulfonic acid

Grillo's direction reaction of methane and SO_3 could open up market for unique acid

CHEMIE TECHNIK

Fachinformationen für Entscheider

Evonik stellt Membran zur Erdgasaufbereitung vor

Markt Anlagenbau Automation Armaturen Energie & Utilities

Schüttguttechnik Sicherheit & Umwelt Trenntechnik Therm. Verfahren Verpackungen

Start > Energie & Utilities > Energieversorgung > Funktionalisierung von Methan zu Methansulfonsäure

METHAN: SÄURE MACHT NÜTZLICH

Funktionalisierung von Methan zu Methansulfonsäure

29.07.2016 | Erdgas ist als Energieträger mindestens so bedeutend wie Erdöl – wenn nicht sogar bedeutender. Es verbrennt sauberer und effizienter und gilt deshalb als klimafreundlichster fossiler Brennstoff. Pipelines aus Russland sind mindestens ebenso häufig Gesprächsthema wie Fracking in den USA oder übersprudelnde Ölbrunnen in Arabien.

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Home / Downstream / Gas processing / 21 June 2016 / Grillo-Werke successfully converts methane into methanesulfonic acid

Grillo-Werke successfully converts methane into methanesulfonic acid

Acknowledgement:

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Dr. Christian Diaz-Urrutia
Dr. Matthias Vogt

Pilot Plant Team

Master Students/ Trainees