Syngas Technologies at thyssenkrupp: from **Biomass** to **Jetfuel** to **Propane** to **Acrylonitrile**

Karsten Radtke  
President  
Process Technologies  

thyssenkrupp Industrial Solutions (USA), Inc.  
engineering.tomorrow.together.
206 Years of Corporate History

thyssenkrupp - on 1 slide

> 2,200 production sites, offices and service locations all over the world

€778mn R&D spending

~156,000 employees

€39,263mn Sales

~2,000 industrial property rights in reporting period

~18,000 patents in total

Present in ~80 countries

Fiscal Year 2015/16
From Biomass to Jetfuel
Overview Syngas Technologies

- PSG
- PDQ
- PRENFLO®
  Entrained-Flow Gasification
- HTW
  Fluidized Bed Gasification
- SMR
  Steam Methane Reforming
- ATR
  Autothermal Reforming
Fluidized-Bed Gasification: High-Temperature Winkler

- HTW especially suited for biomass, wastes and low-rank, high-ash coals with high ash melting points
- HTW has strong reference basis through full commercialization over 3 decades
PRENFLO is a slagging gasifier that operates above the ash melting point

- high carbon conversion, high efficiency
  - for coal and petcoke
  - for biomass, if pre-treated

40 years of experience

Largest Reference: Elcogas IGCC, Puertollano/Spain

Newest PRENFLO application: BioTfueL, Dunkirk/France
The BioTfueL Project - a multinational cooperation of topic leaders

R&D

Technology Providers

Fuel Producers

BioTfueL Plant

Bio-Jetfuel
Bio-Diesel

BioTfueL partnership to realize a complete B-XTL process chain
BioTfueL Dunkirk

2 demo plants located in Dunkirk and Venette in France for torrefaction and gasification/FT:

- to generate scale-up data
- to validate various schemes/configurations
Principle PDQ Features

- dry powder feed (coal/biomass)
- multiple horizontal co-annular burners
- membrane wall
- direct water quench
- operation pressure flexible to requirements (25 - 42 bar)
- raw gas temperature outlet of quench (200 - 250 °C)
- compact gasification system with low plant investment
BioTfueL Gasification Plant: Ready for Start-up (RFSU) Achieved 28 August 2017
The BioTfueL objectives are to develop, demonstrate and commercialize a full B-XTL chain.

One key target is to demonstrate the multi-feedstock ability in one single PDQ gasification reactor.

The BioTfueL project combines the expertise of 6 companies.

The BioTfueL project demonstrates the complete chain from biomass to jet fuel and diesel.

Gasification and Fischer-Tropsch are proven technologies and allow maximum feedstock flexibility.
U.S. Advanced Bio-Fuels in Hawaii: turning waste wood into ultraclean jetfuels

Courtesy: Hawaiian Legacy Hardwoods, 91 Coelho Way, Honolulu, HI 96817
U.S. Advanced Bio-Fuels in Hawaii: turning waste wood into ultraclean jetfuels

- Making use of **abundant waste wood** derived from invasive species impact ⇒ **sustainable feedstock supply**
- **Reforestation** of new native species through **Hawaiian Legacy Reforestation Initiative**
- **Jetfuel situation today:** long-haul and intrastate take-offs and landings require the import of liquid hydrocarbons by ship to Hawaii to refuel the **increasing daily airplane traffic**
- **Task:** conversion of waste wood via **gasification** and **Fischer-Tropsch synthesis** to jetfuels through locally generated, environment-friendly **bio-jetfuel**

Courtesy: Hawaiian Legacy Reforestation Initiative
From Propane to Acrylonitrile: the STAR process®
Converting Raw Materials to Propylene and Derivates

- Gas
- Condensate
- Oil
- Coal

- Steam Cracker
- Methanol + MTO / MTP
- Olefin Interconnection
- Propylene

- PDH (STAR process®)
- Catalytic Pyrolysis

- LPG / Propane
- Naphtha / Gas Oil
- Fuel Oil / Residues

- PP
- PO
- Cumene
- ACRN
- Acrylic Acid
- Oxo-Alcohol
STAR process®: Brief History & References

since 1960s: Development by Phillips Petroleum, Bartlesville, OK
1992: Commissioning of first commercial STAR plant, Coastal Chem, WY
1994: Commissioning of second commercial STAR plant, PBA, Ensenada, Argentina
1999: Acquisition of STAR technology and catalyst IP by thyssenkrupp Industrial Solutions
2000-2003: Enhancement of technology in Ennigerloh, Germany
2007-2017: first commercial PDH plant based on STAR process® EPPC/Egypt, followed by 3 new licenses

Coastal Chemicals
- Wyoming, USA
- Commissioning in 1992
- 100,000 t/a Isobutylene

Formosa Plastics Corporation
- Texas, USA
- Basic Engineering completed
- Commissioning in 2019
- 545,000 t/a Propylene

EPPC
- Egypt
- LSTK
- Commissioning in 2010
- 350,000 t/a Propylene

MEPEC
- MENA
- Basic Engineering completed
- Commissioning in 2019
- 425,000 t/a Propylene

Polybutenos
- Argentina
- Commissioning in 1994
- 40,000 t/a Isobutylene

SFPC
- MENA
- Basic Engineering completed
- Commissioning in 2019
- 425,000 t/a Propylene
STAR process®: Uhde Steam Reforming Technology

- Fixed bed reactor
- More than 70 steam reformers since 1966
- Simple, reliable and robust in operation
- Uhde reformers operate over a wide range:

<table>
<thead>
<tr>
<th>Product</th>
<th>Pressure Range</th>
<th>Temperature Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>40 bar</td>
<td>780 - 820 °C</td>
</tr>
<tr>
<td>Methanol</td>
<td>20 - 25 bar</td>
<td>850 - 880 °C</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>20 - 25 bar</td>
<td>880 °C</td>
</tr>
<tr>
<td>Oxogas</td>
<td>9 - 12 bar</td>
<td>900 °C</td>
</tr>
<tr>
<td>Olefins (STAR)</td>
<td>5 - 6 bar</td>
<td>570 - 590 °C</td>
</tr>
</tbody>
</table>
Main reactions

- \( \text{C}_3\text{H}_8 \iff \text{C}_3\text{H}_6 + \text{H}_2 \) \quad \text{Propane to Propylene}
- \( \text{C}_4\text{H}_{10} \iff \text{C}_4\text{H}_8 + \text{H}_2 \) \quad \text{Butane to Butylene}

By-products

- \( \text{CH}_4, \text{C}_2\text{H}_4, \text{C}_2\text{H}_6, \text{CO}_2 \)

Coke formation

- \( \text{Cracking of hydrocarbons (HC)} \)

Coke conversion

- \( \text{C} + \text{H}_2\text{O} \iff \text{CO} + \text{H}_2 \)
- \( \text{C} + 2 \text{H}_2\text{O} \iff \text{CO}_2 + 2 \text{H}_2 \)
PDH / PP: Conventional Concept

Propane → PDH Plant → Propylene → PP Plant → Polypropylene

Offsites/Utilities
Building Block Approach: SynSTAR process® combined with PP
Building Block Approach: SynSTAR process® combined with Ammonia Production

1. Propane → SynSTAR PDH Plant → Hydrogen
2. Hydrogen → Ammonia Synthesis Plant → Ammonia
3. Propylene
4. Offsites/Utilities
SynSTAR process® for Propylene with Ammonia Export

Building Block Approach: SynSTAR process® combined with Acrylonitrile+ Production

- Propane feeds STAR PDH Plant to produce Propylene, which is fed to ACRN Plant to produce ACRN and other products.
- Ammonia Synthesis Plant uses Hydrogen to produce Ammonia, which is directed to STAR PDH Plant.
- Offsites/Utilities support the overall process.

Products:
- ACRN
- AS
- ACEN
- HCN
What is Acrylonitrile (ACRN)?

Acrylonitrile is a monomer, colorless, liquid, organic compound formed from the catalytic ammoxidation of propylene utilizing technology invented by Sohio in 1957.

\[
\text{CH}_2=\text{CH-CH}_3 + \text{NH}_3 + \frac{3}{2} \text{O}_2 \rightarrow \text{CH}_2=\text{CH-CN} + 3\text{H}_2\text{O}
\]

Propylene  Ammonia  Oxygen  Acrylonitrile  Water
Applications for Acrylonitrilie (ACRN)

- **ABS** 37%
- **Acrylic fibers** 32%
- **Amides** 13%
- **Adiponitriles** 8%
- **NBR** 7%
- **Carbon Fiber** 2%
- **Other** 4%

**Applications**
- Automotive, electronics, appliances, construction
  *Competing products: Polycarbonate, PVC, PP*
- Garments, carpets, fabric
  *Competing product: Polyesters*
- Water treatment, EOR, fracking
  *Competing product: Specialty Water Treatment*
- Nylon 6,6 (carpet, automotive)
  *Competing product: Polyester or PP*
- Automotive Rubber
  *Competing product: Natural Rubbers*
- Aerospace, automotive, wind
  *Competing product: Aluminum/Steel*
- Automotive, mining, Reinforced plastics (PAN)
  *Competing products: PVC, PP*
Thank you for your attention.