Comparison of Different Fixed-bed Methanation Reactors for Renewable Natural Gas Production

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Overview

**TUM in numbers:**
- 14 departments
- 3 Integrative Research Centers
- 7 Corporate Research Centers
- 10,103 staff members
- 40,124 students
- 545 professors
- 172 degree programs
- 411 buildings
- 17 Nobel prizes
- 800 Start-ups
- Budget: 1,329 Mio. € / 285 Mio. € third-party

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Chair of Energy Systems, TUM

Head of Chair: Prof. Dr.-Ing. Hartmut Spliethoff

- Located at the TUM Campus Garching, north of Munich
- Campus Garching: 6,000 employees, 15,000+ students
- Department of Mechanical Engineering

- CES staff:
  - 45 Employees
  - 30 PhD students
  - 5 Postdocs

- Group leaders:
  - Sebastian Fendt
  - Annelies Vandersickel
  - Christoph Wieland
  - Stephan Gleis
  - Stefan DeYoung

Mission: Efficient and low emission renewable power generation
Research group: Biomass and Renewable Fuels

Research topics:
- Biomass pre-treatment
- Biomass gasification and combustion
- Power, heat and fuel production from biomass

Projects:
- Biofficiency (EU/H2020)
- BioCORE (BMBF)
- E2Fuels (BMWi)
- ReGasFerm (BMBF)
- PyroGas (BMWi)
- SynSOFC II (DFG)

Pilot-scale test rigs:
Motivation and wording

Biomass-to-Fuel (BtG, BtL, BtF → BtX) and Power-to-Fuel (PtG, PtL, PtF → PtX)

- Gasification
  - CO₂
  - H₂O, O₂
- Syngas upgrade
- Fuel synthesis
  - Fuel "X"

- Electrolysis
  - H₂O
- Fuel synthesis
  - CO₂

"X" can be RNG, MeOH, FT-diesel, …
Wind and solar, the drivers of PtX

System studies and review studies by CES

Variability of wind and solar power
An assessment of the current situation in the European Union based on the year 2014

A. Buttler et al., Energy 106 (2016) 147-161

Current status of water electrolysis for energy storage, grid balancing and sector coupling via power-to-gas and power-to-liquids: A review

A. Buttler et al., International journal of hydrogen energy 40 (2015) 38-50
Carbon source for fuel synthesis: EFG of biomass and biogenic waste

PiTER

→ Investigated fuels:
  ▪ Biomass: HTC coal, torrefied wood, beech wood
  ▪ Coal mixtures/blends

→ Operating conditions:
  \[ T = 1200-1600^\circ C, \ p = 1-40 \text{ bar}, \ O/C = 1, \ O_2/H_2O/CO_2/N_2 \]

BOOSTER (autothermal gasification)

→ Investigated fuels:
  ▪ HTC biomass (green waste, beech wood and compost)
  ▪ Torrefied wood (deciduous and coniferous wood)
  ▪ Beech wood
  ▪ Corn cob
  ▪ Grass waste

→ Operating conditions:
  \[ P_{\text{th}} = 70-150 \text{ kW}_{\text{th}}, \ p = 1 \text{ bar}, \ \lambda = 0.3-0.6, \ O_2/H_2O/Air \]
Motivation:
- Gas-solid fluidized beds play an important role in many industrial operations
- But: lack of knowledge of the processes inside the bed which impedes proper designing

Modeling:
- Numerical model in an Eulerian-Lagrangian framework (treats gas phase as a continuum and describes particle interactions with discrete element method (DEM))
- Numerical model includes: gas-solid momentum exchange, solids collisional behavior, heat and mass transfer, particle shrinkage and change in material properties, pyrolysis, and homogeneous and heterogeneous chemical reactions

Results:
- The results of numerical simulation agree well with experimental observations and literature correlations (e.g. bed pressure drop, gas composition, and conversion time).
- This indicates that the proposed model can make a significant contribution towards understanding and improving the internal processes in fluidized bed reactors for biomass gasification and combustion.

CFD-DEM simulation of biomass gasification in a fluidized bed reactor

P. Ostermeier et al., Fuel 255 (2019) 115790
Process modeling of innovative IGCC and polygeneration concepts

Detailed process analysis (techno-economic analysis)

Fuel flexibility:
- Impact of fuels and fuel mixtures on conversion and efficiency

Potential of innovative technologies:
- e.g. membrane reactor, chemical quench

Operational flexibility and excess power integration:
- Development and evaluation of new flexible IGCC concepts with electrolysis and polygeneration

Chemical storages:
- Analysis of different storage options (SNG, MeOH, DME)
RNG production from lignocellulosic biomass

Experimental investigation of RNG production under realistic conditions

Motivation:

- Inherent lack of H₂ for RNG production from woody biomass
- At the same time: PtG concepts needs a renewable CO₂ source.
- The two processes fit well together for a sustainable solution
- But: Main technological obstacles have not been addressed sufficiently so far
RNG production from lignocellulosic biomass (BFB)

Experimental investigation of RNG production under realistic conditions

- Gasification: Adaption of gas quality for later methanation
- Gas cleaning: Tar conversion (long-term testing)
- Methanation: Catalyst performance

Influence of parameter variation on syngas composition
Tar conversion under realistic conditions
Lab-scale tests on catalyst activity
Bio-RNG production from syngas – Fixed-bed methanation

Aims:
- Simple, optimized fixed-bed reactors for decentralized bio-based methanation
- Hot-spot control and reduction (→ catalyst life-time)
- Avoidance of sintering and carbon formation
- Model-based optimization of future designs → CFD
Methanation – Fundamentals

Influencing factors on CH₄-yield

- Temperature (highly exothermal, reaction kinetics)
- Pressure
- GHSV / CSV
- Inlet concentration (e.g. as H₂/CO)
- Catalyst (usually Ni-based)

Carbon Deposition Reactions

\[ 2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2 \]
\[ \text{CO} + \text{H}_2 \rightleftharpoons \text{C} + \text{H}_2\text{O} \]
\[ \text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2 \]
\[ \text{C}_n\text{H}_{2n} \rightleftharpoons n\text{C} + n\text{H}_2 \]
Investigation of different oil-cooled fixed bed reactors

- 3 geometries: 
  - a) Dented pipe (SR)
  - b) Standard pipe DN40 (GR)
  - c) Thinner pipe DN25 (GRth)

- 2 catalysts: 
  - Meth134: 25% Ni/Al\textsubscript{2}O\textsubscript{3}, spherical
  - Cat2: 40% Ni/Al\textsubscript{2}O\textsubscript{3}, cylinders
Reactor geometry influences hot spot $\rightarrow$ load changes
Hot spot reduction measures

Raschig rings, catalyst dilution using inert materials
Pseudo-homogenous reactor modeling

... enables time-efficient simulation of complex reactor geometries

**Approach:**

**Modeling of the kinetics**

Micro kinetic $r_{int}$

Mass transport limitation via Thiele modulus

→ Effectiveness factor: $\eta$

Macro kinetic $r_{eff} = r_{int} \times \eta$

(Rönsch, Koschany, Kopyscinski, …)

**Modeling of the fixed bed**
CFD model is capable of predicting temperatures for a broad variety of geometries and conditions

• Simulations are in good agreement with experimental results (not only regarding temperature profiles)
Excursus: Carbon formation running on syngas

Fixed-bed methanation with UC Davis bio-syngas

- Obvious carbon formation immediately detected if C₂H₄ is present
- Same conditions without C₂H₄: no further increase in diff. pressure

```
<table>
<thead>
<tr>
<th>Time in min</th>
<th>∆p (normalized to average)</th>
<th>T = 571°C</th>
<th>CH₄ = 27.8 vol%</th>
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<tr>
<td>0</td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>1.0</td>
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</tr>
<tr>
<td>30</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

w/o C₂H₄

T = 565°C
CH₄ = 27.5 vol%
```
Evaluation of dynamic operation (PtG plant)

Dimensioning and integration of electrolysis and methanation in the model

**Electrolysis:**

- Piece by piece interpolation of the characteristic curves for load-dependent H₂-production and efficiency

**Methanation:**

- Dimensioned to peak load of electrolysis
- Constant product gas composition
- $\eta_{HHV} = 78.2\%$

**Dynamic behavior:**

- Operation only if reactor warm
- Cool-down via half-life time (12 h)
- Different start types:
  - After long downtime: $26 \frac{\varepsilon}{MW}$
  - After e.g. 12 h of downtime: $14.2 \frac{\varepsilon}{MW}$
Resource scheduling for a PtG plant

Exemplary results for April 2017

Full Load Hours by Month

Distribution of Uptime

Cold Starts 47
Warm Starts 27
Hot Starts 129
Overall 203

Tumbling resource scheduling based on mixed integer linear optimization
Conclusion and Outlook

- Understanding methanation is crucial for the design of any RNG process (BtG and PtG)
- A holistic research approach from lab-scale kinetics to reactor design via modelling is extensive but needed → cooperation
- Different reactor technologies and process layouts might be suitable for different applications and scales
  → e.g. fluidized bed vs. fixed bed, multi-zone design, etc.
- Transferability of lab-scale results to full-scale reactor systems (integration of transport limitations in form of effectiveness factor to kinetic data sets) is crucial and needs still more work
- The findings might be transferrable to other highly exothermic reactions
- Heat management crucial for any methanation research

Outlook:
- Catalyst development and optimization ongoing → tests with „new“ catalysts
- Enhanced analysis of used catalysts regarding loss of activity, specific surface area, etc.
- Testing of different reactor geometries and catalyst systems in order to further optimize fixed bed methanation
- Develop new ideas and concepts, which might not be economic today, but show an increased potential efficiency and flexibility for the future
- Investigation of biological alternatives
Thanks…

… to my group and colleagues at CES
… to the German Federal Ministry for Economic Affairs and Energy
… to the Federal Ministry of Education and Research
… to BaCaTeC

… and thank you for the attention!

More information: http://www.es.mw.tum.de/