DEVELOPMENT OF INTENSIFIED REACTORS FROM LAB TO BENCH SCALE

NEO-CARBON ENERGY 7th RESEARCHERS’ SEMINAR

Johanna Kihlman 24.1.2017
CARBON DIOXIDE METHANATION

- Reduction of CO₂ emissions
- CO₂ capture and fixation + Renewable energy
- SNG
DIRECT AIR CAPTURE

ELECTRICITY

CO₂

H₂

SYNTHESIS

INTESIFIED REACTOR DEVELOPMENT FOR CO₂ METHANATION

NATURAL GAS

ELECTROLYSIS
\[ \text{CO}_2 + 4\text{H}_2 \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H_{278K} = -165.1 \text{ kJ/mol} \]
INTENSIFIED REACTORS

- Surface area
- Mass Transfer

- Compactness
- Temperature Control

- High surface area
- Production efficiency
Intensified reactors 1/2

Conventional packed-bed reactors

Well known technology
High surface contact area
Mass/Heat transfer limitations
Pressure drop

Intensified reactors

Size reduction
High heat transfer rate
Temperature control
Low pressure drop
Costs decrease
Development effort
Microchannel reactors: Metallic sheets with etching microchannels in which the catalyst particles are deposited.

Structured reactors: Metallic or ceramic fixed arrangements coated with catalytic material.

Figure 3. Microchannel plates (Kiwi-Minsker, 2005).

Figure 4. (a) Honeycomb monoliths, (b) and (c) open-cell foams (Tronconi, 2014).

Development of heat exchanger reactors
How to deposit the catalyst?

- VTT has 10 years of experience in depositing the catalyst on ceramic surfaces by washcoating.
- In washcoating the substrate material is dipped into catalyst slurry.
  - After drying and calcination, a thin, solid layer of catalyst is coating the surface.

**Challenges in washcoating:**
- Adhesion of washcoat on metallic surfaces of intensified reactors.
- Stability of the catalyst in long test runs.
- Durability of the washcoat.

Development of washcoating method

**Serious problems due to washcoat flake-off in real conditions**

**Slurry optimization resulted in durable washcoat**
Development process

Vast VTT in-house know-how on catalytic coatings developed during previous decade.

30 years of experience on steam reforming catalysts and reactors.

STAGE 1 & 2
Development of methanation HEX reactor

STAGE 3
Testing of bench scale washcoated HEX reactor for steam reforming

STAGE 4
Testing of bench scale washcoated HEX reactor for methanation

RESULTS
Validated manufacturing and operation method for catalytic HEX methanation reactor.

TEKES Research Benefit application with Finnish industry

2014-2016
2016
2017
2017 >
STAGE 1: WASHCOATED TUBE REACTORS

Development of methanation HEX reactor
Experimental Set up

Inner surface of the tubes was washcoated with nickel catalyst.

Testing in typical CO2 methanation conditions.
Tube reactor results

RESULTS:
+ Equilibrium conversion almost reached.
+ Stable activity of the catalyst.
- Poor temperature control!
  ➢ Development for better temperature control in STAGE 2
STAGE 2: WASHCOATED TUBE REACTORS WITH ADVANCED HEAT CONTROL

Development of methanation HEX reactor
Experimental set-up

The temperature control was improved by developing a lab scale HEX reactor.

- Tube reactors with nickel/ruthenium catalyst washcoat.
- Plenty of technical difficulties, but successful results in the end.

1st version: Huber oil bath
  + Easy to operate
  - Temperature too low (< 270 °C) for the initiation of the reaction.

2nd version: Huber Unistat
  + Temperature up to 330 °C
  - Problematic operation
  - Leaking of the thermal oil

3rd version: Solar salt
  + Temperature up to 550 °C
  + Easy to operate
  - Slow to heat up and quick to cool down
Results with lab scale HEX reactor

**RESULTS:**
+ Equilibrium conversion reached.
+ Excellent temperature control with solar salt.
+ Validation of catalyst

➢ Bench scale HEX manufacturing for STAGE 3
STAGE 3: WASHCOATED HEAT EXCHANGER REACTOR

Testing of bench scale washcoated HEX reactor for steam reforming
Experimental Set up

- EU-project STAGE-SOFC: Proof-of-concept of SOFC system with 5 kW electricity production capacity
- Fuel: Natural gas 55 NLPM
- Manufactured bench scale, plate type HEX reactor with washcoated steam reforming catalyst.
RESULTS:
+ Successful manufacturing, installation and operation of HEX reactor.
+ Equilibrium conversion almost reached.
+ Stable activity of the catalyst.

➢ Feasibility validated for STAGE 4: Methanation HEX reactor
CONCLUSIONS & FUTURE RESEARCH
What has been achieved?

**STAGE 1 & 2**
- Development of methanation HEX reactor
- Novel washcoating method for metal substrates
- Stable and active catalyst composition
- Validation of both washcoat and catalyst in laboratory scale tests.
- Equilibrium conversion to methane in HEX reactor

**STAGE 3**
- Testing of bench scale washcoated HEX reactor for steam reforming
- Successful manufacturing of bench scale HEX reactor.
- Successful operation of the HEX reactor with almost equilibrium conversion.
- Bench scale HEX validated
What next?

- In NeoCarbon spin-off project SOLETAIR, a plate type HEX reactor for methanation will be manufacture in late 2017 and installed as part of VTT Mobile Synthesis Unit.
- This will conclude the development work for methanation started in NeoCarbon.

- TEKES Research Benefit project on catalytic heat exchanger reactors is currently in preparation stage.
- The project partners will include VTT and Finnish industry.
- The aim of the project is to develop catalytic HEX reactors further.
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