METHANOL SYNTHESIS: EFFECTS IN ONCE-THROUGH AND RECYCLE OPERATION

Peter Kolb, Torsten Kaltschmitt, hte GmbH

DGMK Conference

Dresden, October 9 - 11, 2017

DISCLAIMER

- The document is incomplete without reference to, and should be viewed solely in conjunction with the oral briefing provided by hte.
- Certain statements that are included in this presentation are forward-looking in nature. There are associated risks and uncertainties inherent in such statements and actual results may differ materially from those expressed or implied by the forward-looking statements.
- hte does not assume any liability for those statements. There is no requirement or obligation for hte to update these forward looking statements.

THE HIGH THROUGHPUT EXPERIMENTATION COMPANY

hte

Worldwide leading provider of technologies and services for enhanced catalysis R&D

- Founded in 1999
- Operative focus on catalysis
- Center for independent competitor catalyst testing
- Largest (high throughput) catalysis laboratory worldwide with > 50 reactor systems
- Financially sound and a reliable ownership structure with BASF
- Staff > 300
- International blue-chip customer base
- Facilities located in Heidelberg, Germany

WHY METHANOL SYNTHESIS ?

- Large-scale chemical (> 100 MT/y)
- Pivotal hydrocarbon feedstock
  - [Carbon raw material] → Synthesis gas → MeOH
  - MeOH → MTP/MTO/Acetic acid/Formaldehyde/FC/..
- Not as simple as it seems
  - Role of water and CO_2 cofeed
  - Optimum pressure level (equilibrium vs. practicability)
  - Optimum temperature level (kinetics vs. thermodynamics)

$$2\,H_2 + CO \rightarrow CH_3OH$$

$$3\,H_2 + CO_2 \rightarrow CH_3OH + H_2O$$

$$H_2O + CO \rightarrow H_2 + CO_2$$

$$\Delta n = -2$$

$$\Delta H_r = -91\ [\mathrm{kJ/Mol}]$$

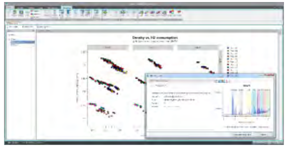
hte EXPERTISE IN METHANOL SYNTHESIS

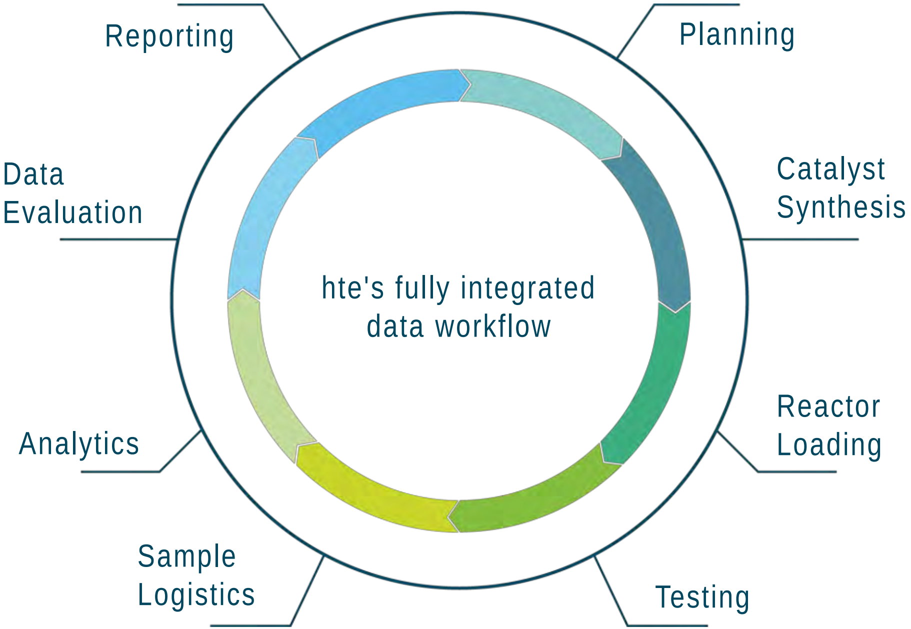
- Competitive catalyst testing: Ranking, Influence of process parameters
- Catalyst Preparation + screening: Influence of catalyst synthesis parameters
- DOE: Discover correlations between process variables

- Full gas recycle: Process development

hte´s FULLY INTEGRATED WORKFLOW

"THE LAB 4.0" FOR HETEROGENEOUS CATALYSIS



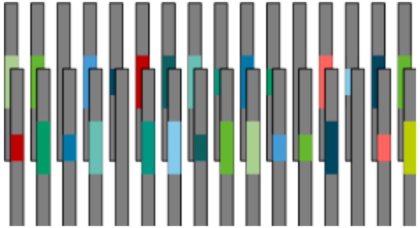


METHANOL SYNTHESIS IN PARALLEL FIXED BED REACTORS

- Classical Catalyst screening

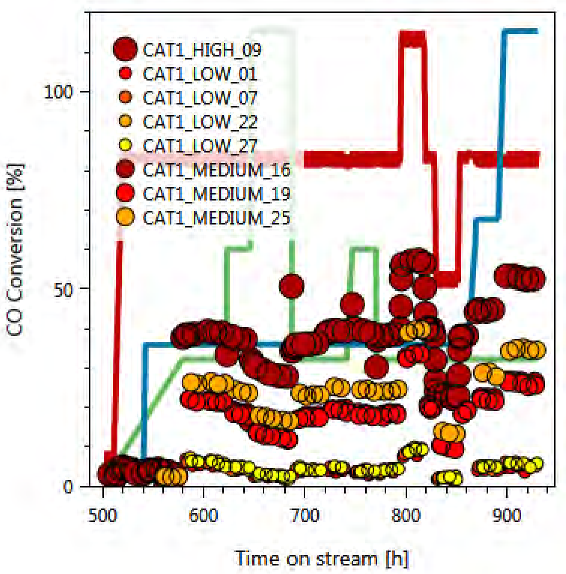
METHANOL CATALYST SCREENING
TEST RIG, LIBRARY LAYOUT, AND PROCESS PARAMETERS

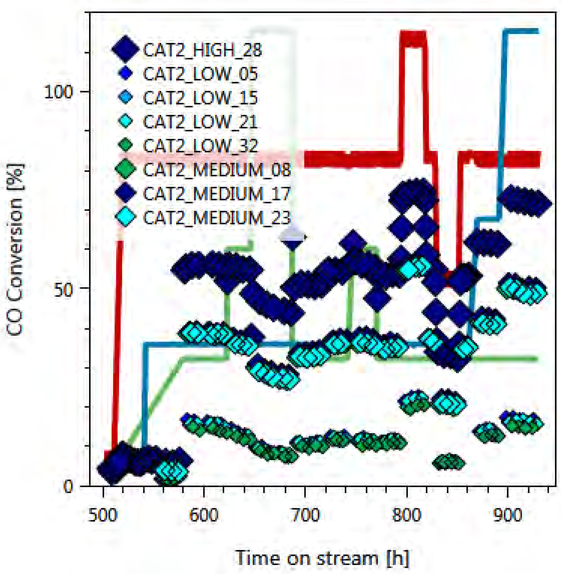
- Parallel reactor system with 32 channels
- Two reactor blocks with independent heating, each for 16 liners
- Common pressure control
- Common feed supply



- Library of commercial and hte prepared catalysts
- Variation of catalyst amount → different GHSV at identical liner flow

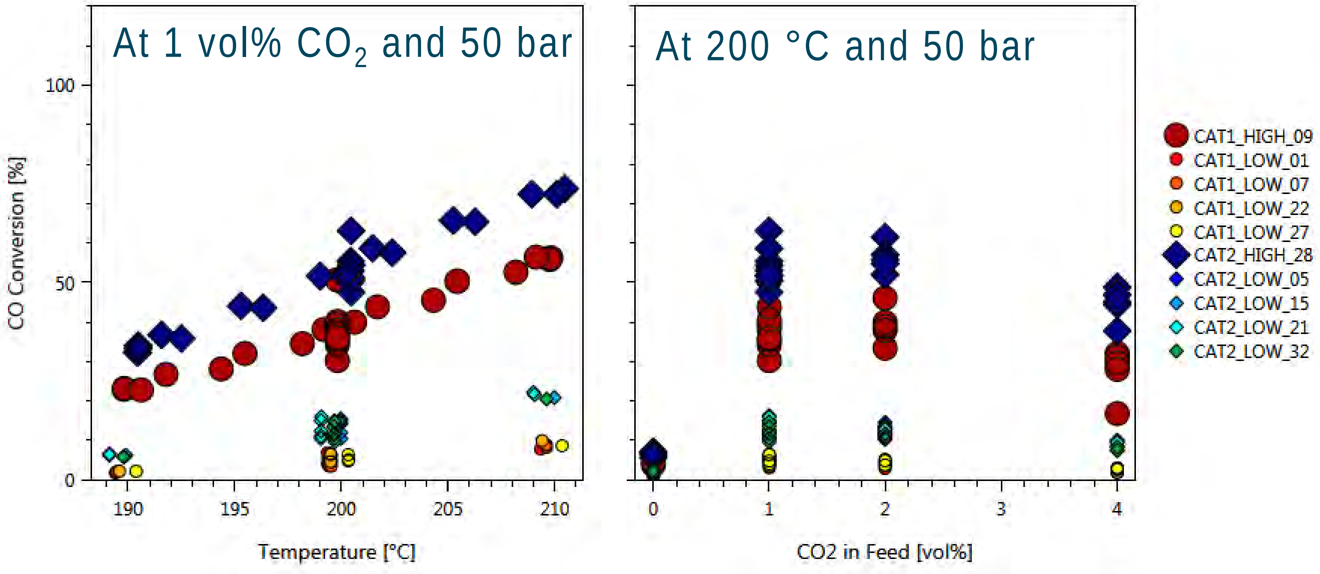
AN OVERVIEW: TIME-ON-STREAM DATA





- Two catalysts: CAT1 and CAT2
- Process variables: temperature (red), CO_2 concentration (green), pressure (blue)
- Good reproducibility between identical fillings
- Catalyst 2 better than catalyst 1

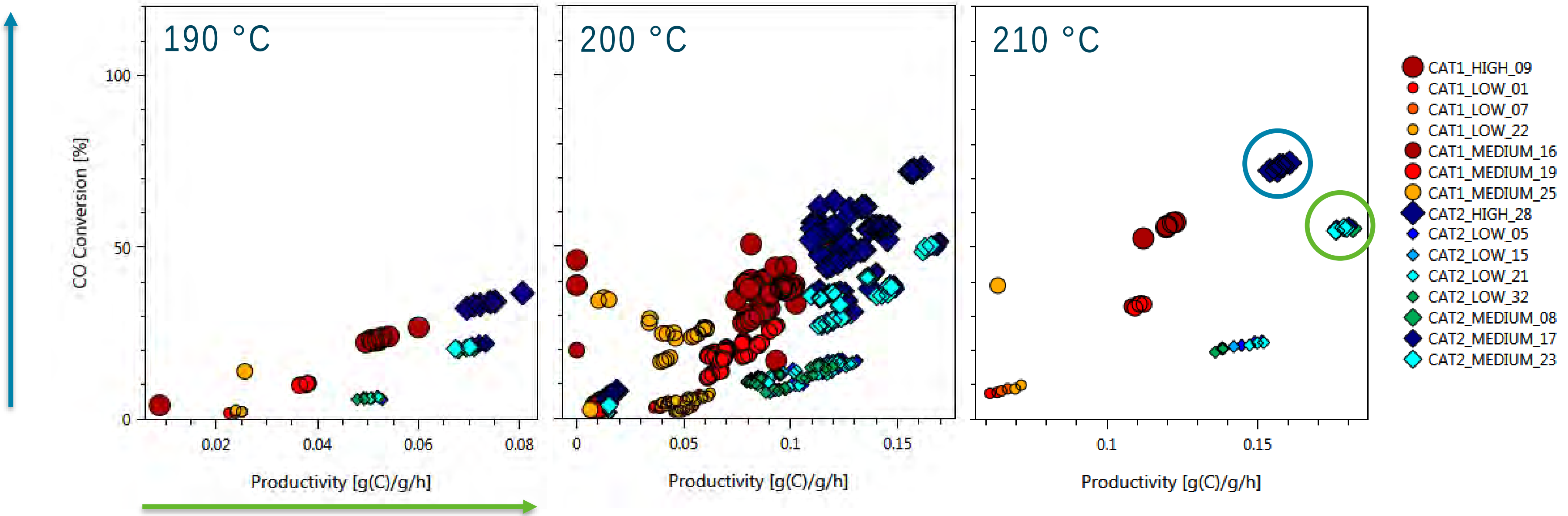
EFFECT OF TEMPERATURE AND CO_2 COFEED



- Increasing activity with increasing reactor temperature
- Considerable increase in activity after introduction of 1 vol% CO_2
- Change from 1 to 2 vol% CO_2 without effect
- Change from 2 to 4 vol% CO_2 detrimental

CO CONVERSION VERSUS PRODUCTIVITY

Effective gas utilization

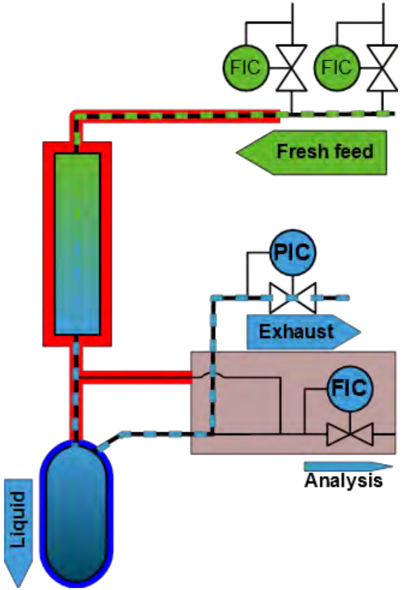


Effective utilization of catalyst mass and reactor volume (STY)

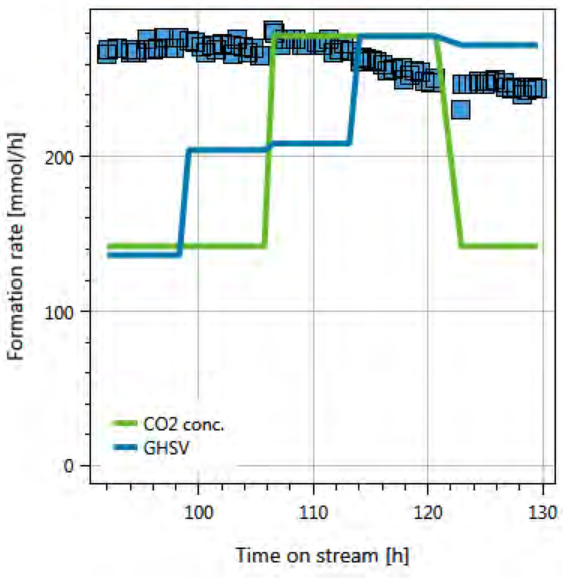
METHANOL SYNTHESIS IN A SUB-PILOT FIXED BED REACTOR IN ONCE THROUGH MODE

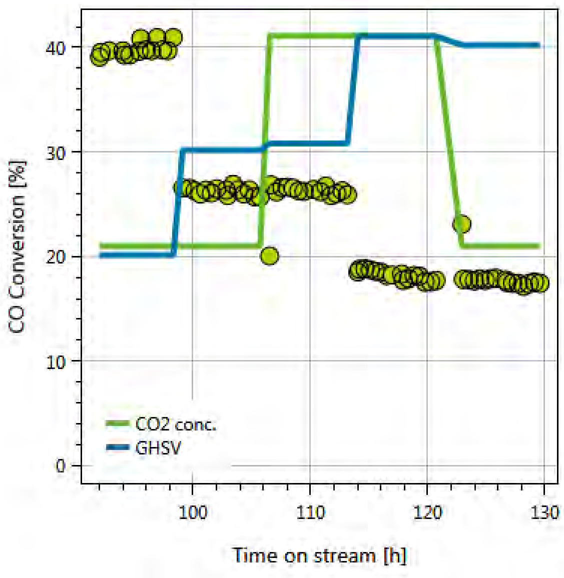
FEATURES OF THE REACTOR SYSTEM

- Sub-pilot scale: reactor ID up to 25 mm, length 106 cm, > 100 ml catalyst possible
- Six individually controllable reactor heaters
- Coolable condenser with level-controlled, continuous liquid drain-off into weighted, larger product vessels
- Flow-controlled release of the hot reactor effluent or the cold condenser off-gas to the online GC analysis
- Pressure controller in major off-gas pipe
- Large set of feed gas modules in the major feed pipe



EFFECT OF GHSV AND CO_2 CONCENTRATION
AT 220 °C



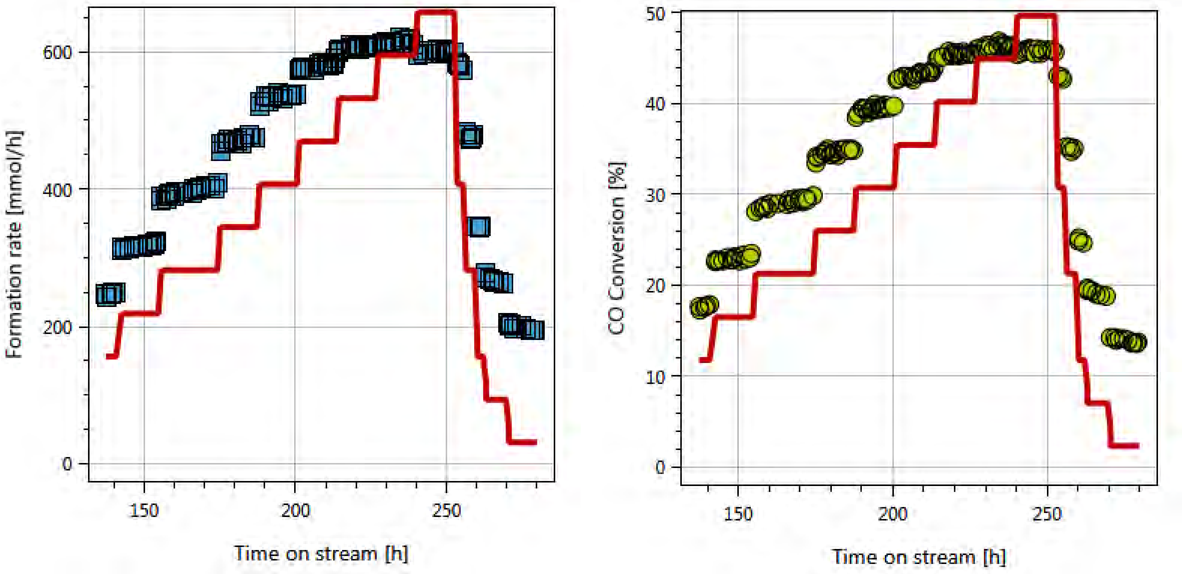


- Nearly constant MeOH formation rate between 2 and 4 vol% CO_2 and a GHSV between 3200-6500h^{-1}
- Activity mainly kinetically controlled
- Constant catalyst utilization
- CO conversion variable (~1/GHSV) → reduced feed gas utilization

EFFECT OF TEMPERATURE VARIATION

AT HIGH GHSV AND LOW CO_2 CONCENTRATION

On MeOH Formation and CO Conversion

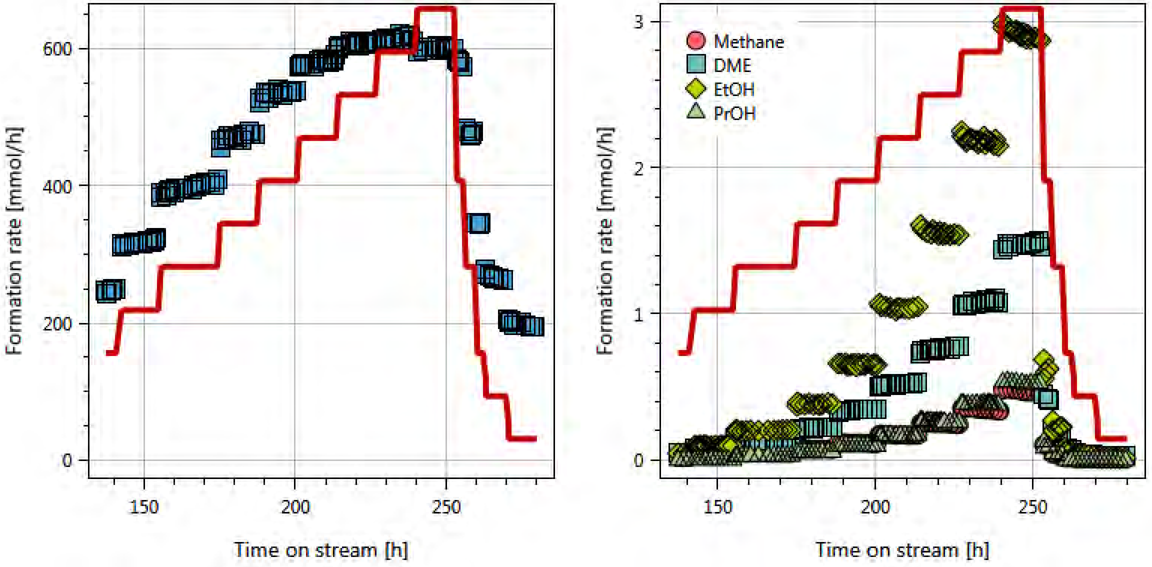


- Broad peak formation rate and CO conversion around 245 °C

EFFECT OF TEMPERATURE VARIATION

AT HIGH GHSV AND LOW CO_2 CONCENTRATION

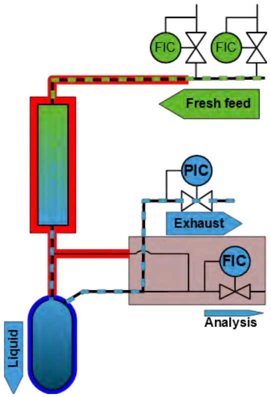
...and on formation of MeOH and side products



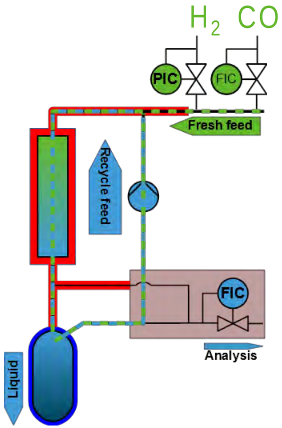
- Increasing formation of higher alcohols and DME at maximum MeOH formation rate
- Methanol selectivity > 99%

METHANOL SYNTHESIS IN A SUB-PILOT FIXED BED REACTOR IN RECYCLE MODE

ONCE THROUGH AND RECYCLE OPERATION

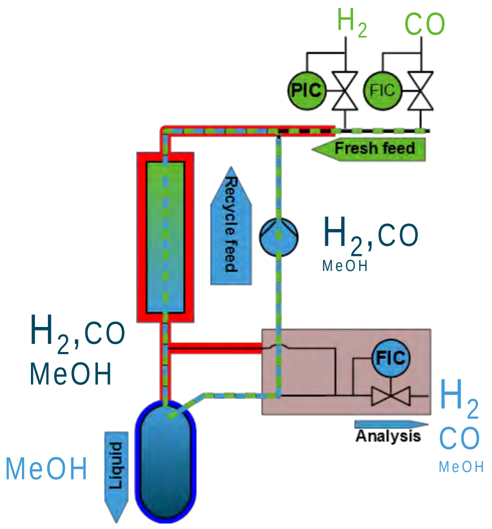


Once through	Parameter	Recycle
User defined heater temperatures + exotherm	Temperature	User defined heater temperatures + exotherm
By pressure controller in outlet	Reactor pressure	By pressure controller in H_2 feed module
Fresh feed only User defined flow rate for all feed gase modules	Feed composition and flow rate	Fresh and recycle feed User defined CO feed rate Process controlled H_2 feed rate User defined recycle flow rate Recycle gas composition influenced by catalyst activity

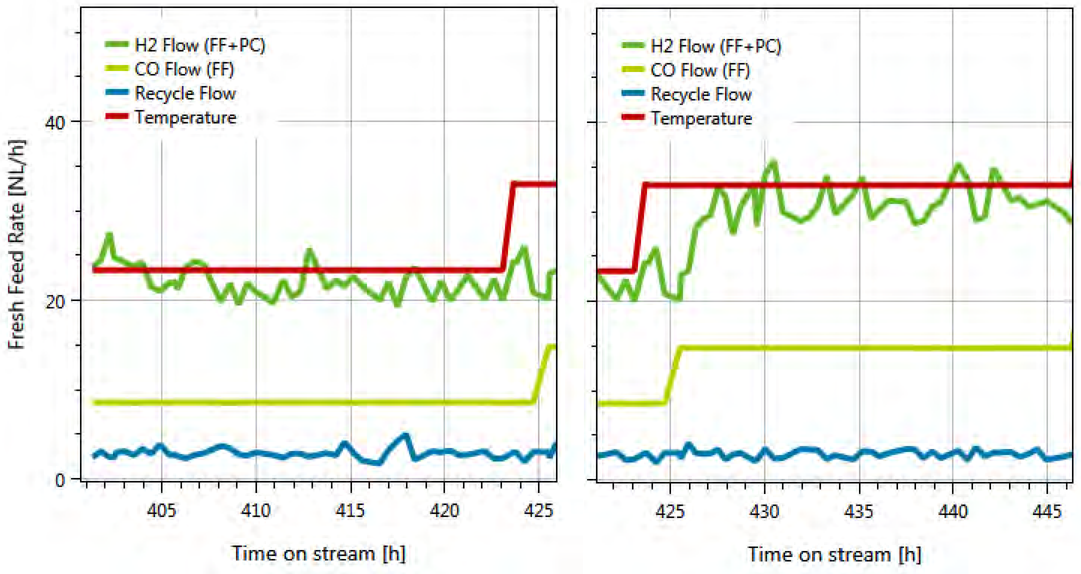


STEADY STATE CONDITIONS AND CRITERION

- Circulating gas stream with various input and output streams
- Input: fresh H_2 and CO
- Output
  - liquid MeOH drained off condenser
  - H_2, CO and gaseous MeOH purged to analytics
- Steady state inside loop: input and output streams balanced
- For CO: fresh CO feed rate = converted CO rate + purged CO rate
- Handle to adjust the CO conversion rate: temperature
- Adjust the temperature to achieve a methanol formation rate that matches the user defined CO flow rate

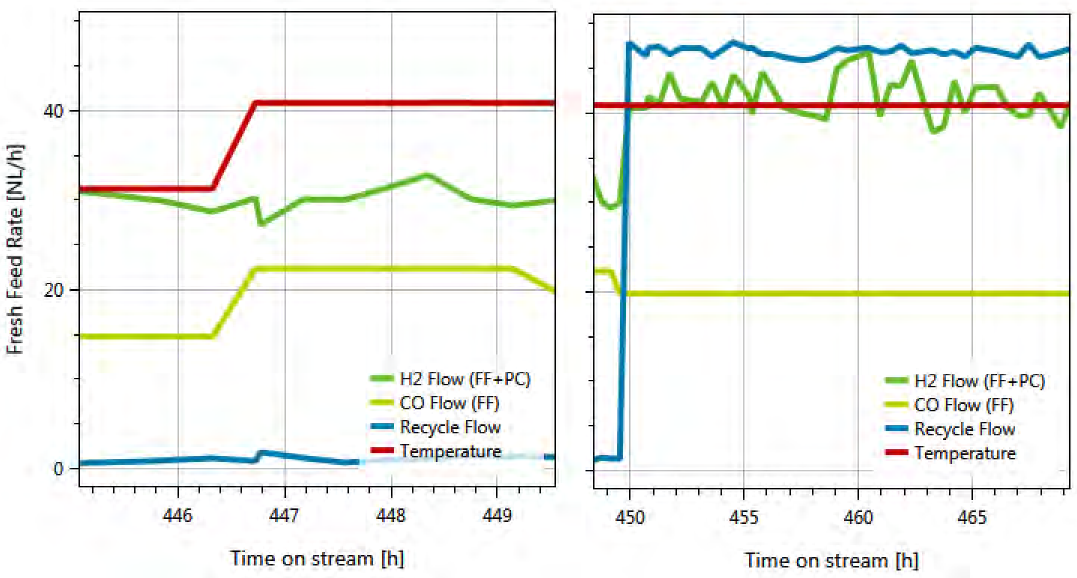


RECYCLE OPERATION – INITIAL RUNS



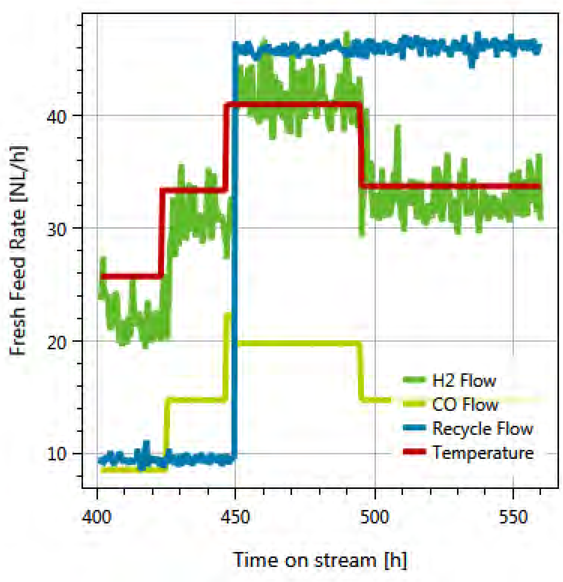
- First run: getting started
  - 220 °C, 8.5 NL/h CO fresh feed rate
  - H_2/CO consumption rate ratio: 2
  - Ratio of H_2 and CO fresh feed rates ~ 2.5
  - H_2/CO purge rate ratio: > 2
- Second run: increasing productivity
  - 230 °C, 15 NL/h CO fresh feed rate
  - Ratio of H_2 and CO fresh feed rates ~ 2.1
  - Purge rate constant, fresh feed ratio dominated by increased consumption ratio

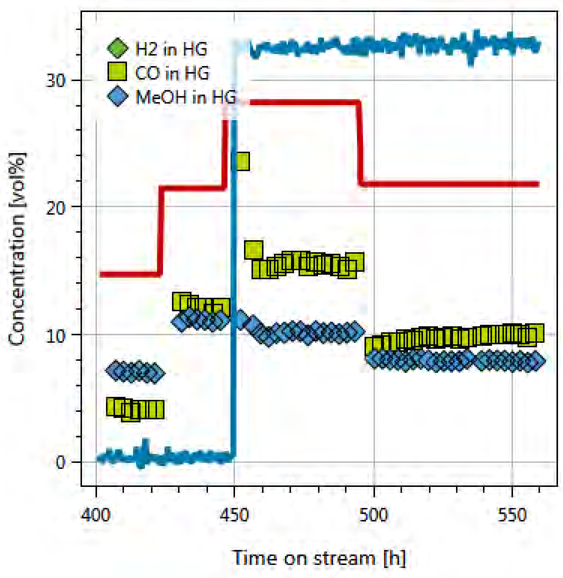
RECYCLE OPERATION – SUBSEQUENT RUNS



- Third run: maximizing productivity
  - 240 °C, 22 NL/h CO fresh feed rate
  - Ratio of H_2 and CO fresh feed rates ~ 1.5
  - CO input and output stream not balanced!
- Fourth run: stabilizing productivity
  - 240 °C, 20 NL/h CO fresh feed rate
  - Recycle rate increased from 110 to 170 NL/h
  - Ratio of H_2 and CO fresh feed rates ~ 2.1
  - CO input and output stream balanced

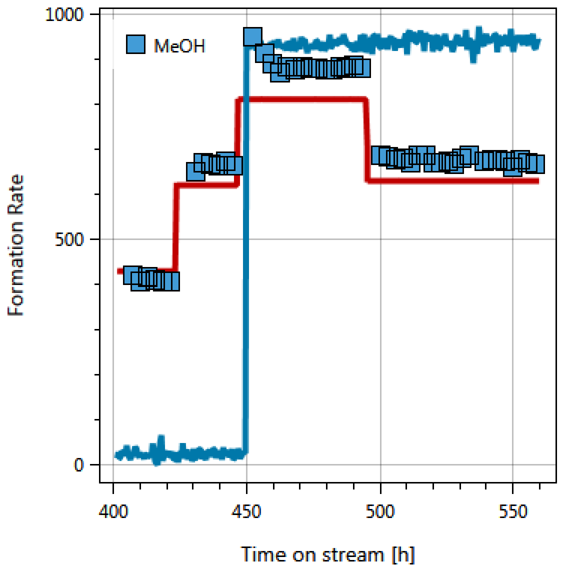
RECYCLE OPERATION – PROCESS DATA AND ONLINE HOT GAS GC ANALYSIS

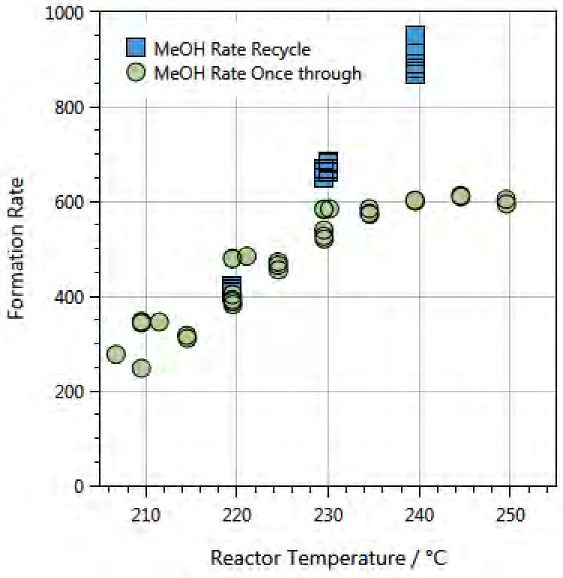




- CO enrichment during third run at 240 °C/20 NL/h CO
- Steady CO concentration after increase of recycle flow rate
- Little change in MeOH outlet concentration between third and fourth run → thermodynamic limit !
- Higher MeOH formation rate (CO consumption rate) possible by dilution with (MeOH free) recycle gas

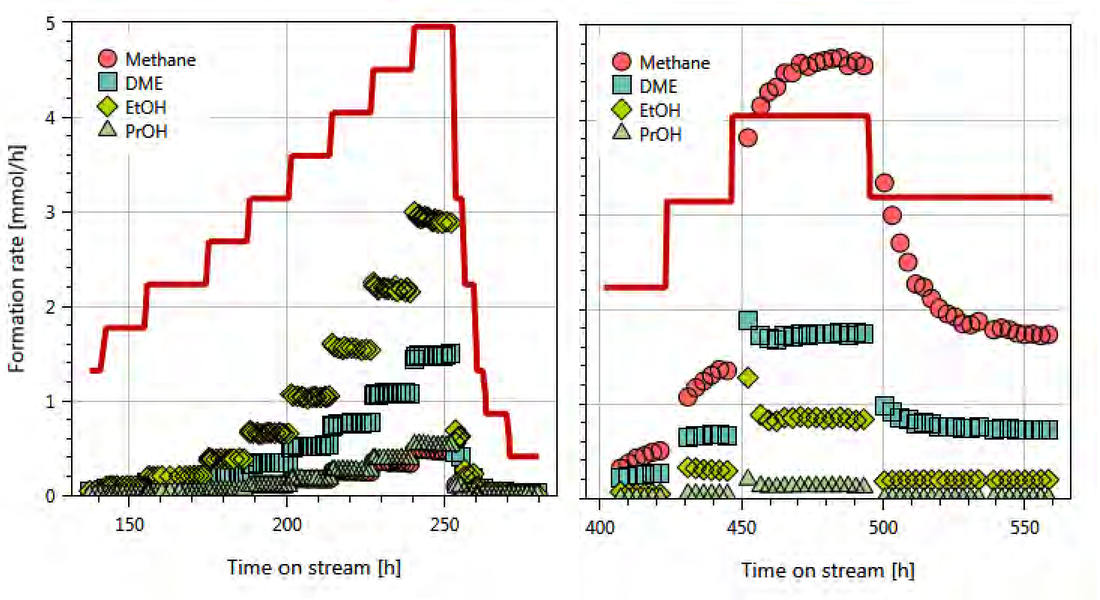
ONCE TROUGH VERSUS RECYCLE - METHANOL FORMATION





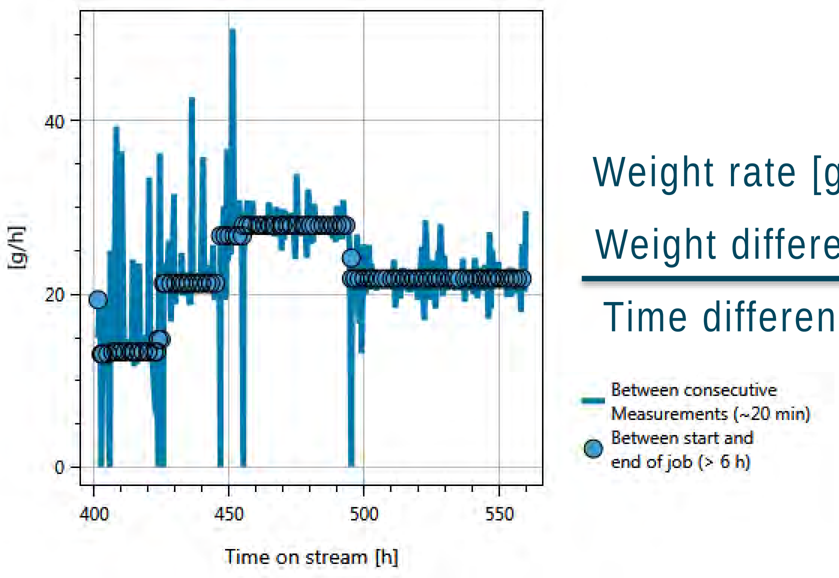
- MeOH formation rate of ~900 mmol/h
- High productivity achieved with little unconverted synthesis gas
- GHSV and fresh feed gas rates decoupled → high GHSV achieved by high recycle gas flow

ONCE TROUGH VERSUS RECYCLE - BYPRODUCT FORMATION

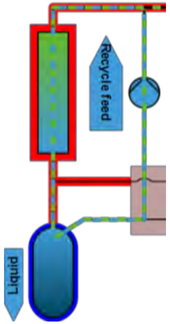


- Ethanol most important byproduct in once through
- Methane most important byproduct in recycle
- Ethanol: condensation and drain off
- Methane: transport to reactor inlet
- Methane enrichment until methane formation rate is balanced by methane output rate through purge

TRACKING OF LIQUID PRODUCT FORMATION



$$\text{Weight rate [g/h]} = \frac{\text{Weight difference [g]}}{\text{Time difference [h]}}$$



- Product container on balance
- Process data logged
- Good match between
  - Gravimetric Methanol formation rate of nearly 30 g/h
  - Methanol formation rate of 900 mmol/h by online GC
  - Fresh CO feed rate (20 NL/h)
- Generation of liquid samples for further offline analysis, inspection, specific tests, …

SUMMARY AND OUTLOOK

- Successful operation of a sub-pilot scale reactor system for methanol synthesis in once-through and recycle mode
- Recycle operation much more efficient than once through: high productivity combined with high gas utilization
- Observed activity most likely still thermodynamically limited, operation at even higher productivity (higher recycle flow, higher H_2 and CO fresh feed rates) well within capabilities of reactor system

- Starting point for more complex, multi-component reaction networks

THANK YOU FOR YOUR ATTENTION.