Redefine FCC catalyst testing for advanced technical service support in new markets

Dr. Marius Kirchmann, Dr. Alfred Haas
10. December 2020
MDU: an enabling technology to FCC catalyst testing

- FCC Introduction
- Catalyst Testing
- Catalyst Deactivation
- Analytics / Workflow / Lab 4.0
- Kinetic Modelling
- Case Studies
Fluid Catalytic Cracking (FCC)
Overview

• 500 FCC units worldwide
• Main conversion technology for bottom of the barrel (VGO / Resid)
• Main products are gasoline, distillates and LPG
• Catalyst market of ~ 3$ billion
Fluid Catalytic Cracking (FCC)
Lab test requirements
Fluid Catalytic Cracking (FCC)
Lab test requirements
FCC catalyst testing
Overview on lab methods

<table>
<thead>
<tr>
<th>CRU</th>
<th>MDU</th>
<th>ACE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>30-150 g (dep. on C/O)</td>
<td>7g</td>
</tr>
<tr>
<td>Feed</td>
<td>&lt;10 ml</td>
<td>&lt;10 ml</td>
</tr>
<tr>
<td>Cracking count / day</td>
<td>Up to 18</td>
<td>Up to 18</td>
</tr>
<tr>
<td>3-5 kg</td>
<td>2-3</td>
<td></td>
</tr>
<tr>
<td>~30l / day</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
FCC catalyst testing
Overview on lab methods

- CRU
  - Entrained flow

- MDU
  - Entrained flow

- ACE
  - Fixed-fluidized bed
FCC catalyst testing
Contact time

- CRU
  - Time on feed: Continuous
  - Contact time gas: 1.5-5s
  - Contact time catalyst: 1.5-5s + slip factor

- MDU
  - Contact time gas: 0.5-4s
  - Contact time catalyst: 0.5-4s – slip factor

- ACE
  - Contact time gas: 30-60s
  - Contact time catalyst: 2s
  - Contact time: 30-60s
FCC catalyst testing

Temperature

- CRU
  - Temperature gradient
  - Implications
  - 700°C → ROT

- MDU
  - 700°C → DOT (ROT)

- ACE
  - Isothermal
FCC catalyst testing
Coke gradient

CRU
- Coke CoC during feed contact
- Gradient
- Constant (fresh)

MDU
- Gradient
- Constant (fresh)

ACE
- Fully back-mixed
- Increases during TOS
- Activity changes / averaging
FCC catalyst testing
Coke profiles

**Coke Accumulation vs. Time on Stream**

- Catalyst A
- Catalyst B

<table>
<thead>
<tr>
<th>Coke on Catalyst, wt%</th>
<th>Time on Stream, sec</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8%</td>
<td>0</td>
</tr>
<tr>
<td>0.7%</td>
<td>15</td>
</tr>
<tr>
<td>0.6%</td>
<td>30</td>
</tr>
<tr>
<td>0.5%</td>
<td>45</td>
</tr>
<tr>
<td>0.4%</td>
<td>60</td>
</tr>
<tr>
<td>0.3%</td>
<td>75</td>
</tr>
<tr>
<td>0.2%</td>
<td>90</td>
</tr>
</tbody>
</table>

- **Entrained flow**
- **Fully back-mixed**
- **Increases during TOS**

Lucas Dorazio, Jian Shi, James Fu, Junmei Wei, CP Kelkar, Abstract NAM 2018
Micro Downflow Unit (MDU)
Technology
MDU
New generation

- Up to 18 C/O measurements per day
- Flexible feedstocks:
  - VGO / Resid with CRC’s 0-10% (15%)
  - Crude Oil
  - Lighter feeds (naphtha, gas)
- C/O: 3 to 50 (100)
- Pressure: 0.5 to 3.5 barg
- Reactor temperature: up to 700°C
- Catalyst temperature: up to 900°C
- Variable stripping efficiency
- Cost effective (operation, catalyst, feedstock)
- Fully automated lab system
MDU
Simplified process scheme

Feed dosage
- Precise dosage of broad range of feedstocks

Liquid recovery
- Fast exchange of 6 traps

Gas recovery
- Volume collection
- Online GC

Particle recovery
- Fast exchange of 6 catalyst containers

Particle dosage
- Thermal reservoir
- Variable catalyst

Downflow reactor
- Multiple heating zones
- Short contact time 0.5-4s
MDU
Temperature control

CatT = 700°C
ROT = 530°C

TOS (s)
1 2 3 4 5 6 7 8 9 10 15 20 25 30 35 40 45 50 55 60
MDU
Temperature control

CatT = 900°C

ROT = 530°C
MDU
Summary

• "Nothing is constant in FCC"

• Gradients exist in temperature, partial pressure, coke, ...

• Entrained flow reactors (CRU, MDU) resemble the commercial process

• MDU
  • Cost efficient and fast testing in laboratory scale
  • Flexibility to access broad parameter space and feeds
MDU
Applications

Classical FCC
- Catalysts / additives
- Process optimization
- Feed testing

Petrochemicals
- Catalysts / additives
- Process optimization
- Pyrolysis (CPP)
- Alternative feeds
  - Naphtha (Petroriser)
  - Resid
  - Propane (PDH)
  - Methanol

Crude Oil to Chemicals
- Catalysts / additives
- Process optimization
- Pyrolysis

Sustainable Processes
- Biogenic feeds
- Sugar conversion
- Pyrolysis oil (i.e. co-processing)
- Circular economy
- Plastics
- Pyrolysis

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2 picture © Aunging/shutterstock
3 picture © Thalvire/shutterstock
4 picture © kram-9/shutterstock
FCC
Process / test requirements

Products

Feed

Catalyst Testing

Feed Ni, V

Products

steam

~20% steam

Fresh Cat Make-up

Fresh Cat

Cat the Deactivation

ECat

DCat

FCC

Process / test requirements

products

feed

catalyst testing

feed Ni, V

products

steam

~20% steam

fresh cat make-up

fresh cat

catalyst deactivation

ecat

dcat

fbbtc mena & me-cat 2020, 8-10 december 2020, kirchmann et al.

hte-company.com
FCC
Process / test requirements
Catalyst deactivation
Options to deactivate fresh FCC catalysts

- **Hydrothermal Steaming (HT)**
  - No metals impregnation
  - Hydrothermal steaming

- **Cyclic Propylene Steaming (CPS)**
  - Metals deposition by separate impregnation step (MM / SI)
  - Redox-cycles with SO$_2$ / C3=
  - Hydrothermal steaming

- **Cyclic Metals Deactivation (CMD)**
  - Metals deposition by cracking spiked VGO on catalyst (crack-on)
  - Redox-cycles with Air
  - Hydrothermal steaming

1United States Patent Application 20190134589
3picture © sandsun/shutterstock
4picture © Przemysław Ceynowa/shutterstock
5picture ©NikolayN/shutterstock
The majority of the oil refining companies are using only CMDU to accurately deactivate catalysts and predict closer the commercial performance.

<table>
<thead>
<tr>
<th>Method</th>
<th>Metals deposition / distribution</th>
<th>Deactivation / conditioning</th>
<th>Metals activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>MM + HT</td>
<td>×</td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td>MM + CPS</td>
<td>×</td>
<td>✓</td>
<td>×</td>
</tr>
<tr>
<td>SI + CPS</td>
<td>✓</td>
<td>✓</td>
<td>×</td>
</tr>
<tr>
<td>CMD</td>
<td>✓</td>
<td>✓</td>
<td>✓ (✓)</td>
</tr>
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</table>

MM: Mitchell method (wet impregnation), HT: Hydrothermal (steaming), SI: Spray Impregnation, CMD: Cyclic Metals Deactivation
Catalyst deactivation
Large scale deactivation unit

- Joint development and construction of multi-purpose deactivation unit with BASF
- Up to 5 kg of catalyst / batch
- Hydrothermal steaming, CPS or CMDU
- Dual-vessel design (patent pending)\(^1\)
- Continuous age distribution method (CADM)\(^2\)

\(^1\)United States Patent Application 20190134589
Catalyst deactivation
Medium scale deactivation unit

• Scale-down of multi-purpose deactivation unit
• Up to 1 kg of catalyst / batch
• Hydrothermal steaming, CPS or CMDU
• Dual-vessel design (patent pending)\(^1\)
• Continuous age distribution method (CADM)\(^2\)

\(^1\)United States Patent Application 20190134589
Catalyst deactivation
Full workflow from catalyst deactivation to catalyst testing
Catalyst deactivation
Full workflow from catalyst deactivation to catalyst testing

- Same process control (hteControl4) with high flexibility
- Same database (myhte4)
  - Deactivation parameters / procedures
  - Catalyst characterization data
  - Performance data
- Easy calculation and visualization of structure-performance relationships
Analytics
Methods for FCC product analysis

Products
- VGO
- CCR
- FCC
- Educt

Base Analyses
- Drygas
- LPG
- Gasoline
- LCO
- HCO
- Coke
- Coke analysis

Add. Analysis
- Online GC < C7
- SimDist
- PIANO / RON

Development
- 2D-GC < 600°C

Temperature Ranges
- 30°C
- 220°C
- 350°C
- 750°C
Data evaluation
Integrated workflow / Lab 4.0
Floor 1: Catalyst testing
Lab 4.0 for fluid catalyst testing
Catalytic cracking modelling in MDU

Kinetic model

- Collaboration with A. Corma, ITQ
- 11 product lumps
- 39 parameters
- Non-isothermal
- Catalytic and thermal cracking
Catalytic cracking modelling in MDU
Parametric studies

Experimental data / DoE
Prediction by kinetic model
Catalytic cracking modelling in MDU
Parametric studies @ constant catoil
Catalytic cracking modelling in MDU

Summary

- 11 lump kinetic model for detailed yield calculation
- MDU to determine and validate kinetic constants and activation energies by well defined and flexible parameter space
- Kinetic model to optimize yield distribution
- Potential: kinetic input for computational particle fluid dynamic (CPFD) or reactor modelling
## Case studies

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<tr>
<td>MDU vs. ACE vs. CRU ECat Standard VGO / low CCR</td>
<td>MDU vs. DCR ECat / Additives Standard VGO / low CCR</td>
<td>MDU vs. Commercial RFCC ECat Resid / CCR = 4 wt%</td>
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BBTC MENA & ME-CAT 2020, 8-10 December 2020, Kirchmann et al.
Case studies

Case 1

MDU vs. ACE vs. CRU

ECat

Standard VGO / low CCR

- Parameter space

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BASF

We create chemistry
Case 1
Results vs. conversion

Yield distribution of CRU and MDU match well
Case 1
Results vs. conversion

Yield distribution of CRU and MDU match well at constant conv
Best condition identified by parameter variation
Case 1
Summary

- Yield distribution of CRU at constant conversion / coke closely resembled by MDU
- Same conditions as in CRU directly obtained the same yield pattern
- Broad C/O, conversion and coke range accessible
- Kinetic model by Corma describes the yields and parameter variations quite well

- Parameter space
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**BBTC MENA & ME-CAT 2020, 8-10 December 2020, Kirchmann et al.**
Case 2 w/ Phillips 66
MDU vs. DCR

- Comparison of MDU / DCR at same conditions → no optimization of MDU
- Delta conversion @ constant catoil = 7.5
- Delta yields @ constant conversion = 73%
Case 2 w/ Phillips 66
Overview

• „MDU tends to match pilot plant cracking conversions at higher CTO“

• „MDU yields closely resemble those of the DCR unit for the step changes in this study“
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BBTC MENA & ME-CAT 2020, 8-10 December 2020, Kirchmann et al.
Case 3
Overview

• Target
  • Achieve same yield distribution as RFCCU @ constant coke

• Feed
  • Atmospheric resid
  • 4 wt% CCR
  • 0.5 wt% sulfur
  • 13 wt% with BP > 745°C

• Catalyst
  • eCat

• Parameter space
Case 3
Yield distribution RFCCU

Yield distribution provided by customer at constant coke of 7.94 wt%
Case 3
Yield distribution RFCCU and MDU results

Accessible yield distribution in MDU by changing:
- Catalyst T
- Reactor T
- Pressure
- Residence time
- Dilution
Case 3
Yield distribution RFCCU and MDU results

Closest yield distribution
Catalyst T: 700°C
Reactor T: 560°C
Pressure: 1.86 bar
Residence time: 3.5 s
Case 3
Interpolation @ constant conversion / coke

@ Conversion = 68.2%  
@ Coke = 7.94wt%
Case 3
Summary

- Yield distribution of commercial RFCCU at constant conversion / coke closely resembled by variation of parameter space in MDU
- Higher reactor temperature needed to reach reaction progress to LPG at shorter reactor length
- Close reaction kinetics of bottoms to gasoline to LPG
- Thermal cracking / wall effects increase drygas yields

- Parameter space
Summary

MDU

- Provides laboratory test at reasonable costs
- Enables tech service support and supports R&D in multiple areas by offering:
  - Broad accessible parameter space
  - Flexible feed supply
  - Detailed product analysis
- Operates in a digital lab 4.0 environment
- Delivers input for kinetic modelling
- Simulates commercial yield distributions
People
FCC team
THANK YOU.