Innovative ZoneFlow™ Technology Offers Breakthrough Solutions in Refinery Hydrogen Generation

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AFPM 2018 Annual Meeting New Orleans, USA; Mar 11-13
Presentation Outline

- Introduction
- Steam Reforming Pellet catalyst - status quo
- ZoneFlow™ (ZF) Reactor Technology - an innovative breakthrough
- ZF development status and validation programs
- Application of ZF Reactor Technology in hydrogen plants
  - ZF Single-Pass Reactors (ZF-SP)
  - Convective Pre-Reforming Reactors (ZF-CPR)
- ZF Bayonet for Recuperative reforming (for New SMRs)
Introduction: Refinery Hydrogen Intensification

- Leaner CR / Polyaromatics
- ULSD
- Diesel growth (HC)
- (E)HO + Shale Oil mix
- Min FO

Projected CAGR: 3-4% ~ 0.8 BCFD

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Hydrogen-for-Energy: Demand Projections (EJ)

Projected average investment in H2 based energy > $25 billion/year

1 Exa Joule (EJ) ~160 Mboe
2017: 9 EJ/y ~ 4 mbpd

Global energy demand supplied with hydrogen, EJ

Power generation, buffering
Transportation
Industrial energy
Building heat and power
New feedstock (CCU, DRI)
Existing feedstock uses

SOURCE: Hydrogen Council
Steam Reformer: Heart of Hydrogen Plant

Typical Overview

Values are Relative Energy units

Steam Reformer: Heart of Hydrogen Plant

Feed 10

Excess S/H steam 45

Air

Flue gas 15

150 °C

1100 °C

870 °C

330 °C

Syngas 30

Steam

180 °C

Reforming duty 100

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Steam Reforming Catalyst - Status Quo

- State-of-the-art steam reforming catalysts have by and large stayed “pellet-based” and so have the inherent deficiencies (of random packing) in terms of:
  - high pressure drop
  - limited heat transfer (sporadic catalyst-to-wall contact)
  - very low catalyst effectiveness (intrinsically diffusion limited)
  - catalyst attrition / breakage from thermal cycling
  - flow / temperature non-uniformity

- Various attempts for structured catalyst over the years, haven’t been successful due to few core challenges
ZoneFlow Reactor Technology
– an Innovative Breakthrough

- Advanced high-performance structured catalyst with step improvements on key performance parameters, compared to current pellet catalysts:
  - up to 2 times higher heat transfer (including internal radiative transfer)
  - up to 50% lower pressure drop
  - annular flexible casing design ensures wall proximity in cold and hot conditions and also creates “near-wall” flow
  - up to 10 times higher catalyst effectiveness
  - high strength metal substrate; no attrition from thermal cycling
  - uniformity of flow over (longer) operating life
  - uniquely befitting for Recuperative reforming also
Conventional SMR Catalyst vs. ZoneFlow™ (ZF)

- From random packing to uniform, engineered foil structure
- From irregular and scanty pellet-tubewall contact to uniform structure-to-wall contact in all conditions
- From strength-limited voidage and related flow resistance to robust high-voidage structure with near-wall turbulence

➢ ZF uniquely offers step-reduction in pressure drop combined with almost doubling of heat transfer coefficient

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Conventional SMR Catalyst vs. ZoneFlow™ (ZF)

- From diffusion-limited active sites’ access to high-GSA thin-fin structure with full surface access
  - High activity micro-layer catalyst with non-acidic and steam-stable substrate
    - Multifold increase in catalyst effectiveness; higher resistance to coking and upsets; longer operating life

- From limited crush strength to durable & flexible metal structure
  - No attrition or any breakage; stable pressure drop and flow uniformity over full life
ZF’s Development: Detailed CFD Modeling

- Empty tube
- Different ZF Casing Designs

Relative Heat Transfer Coefficient

- New SMRs
- Revamps

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ZF’s CFD Modeling and FE Analysis Results
ZF’s Commercial Demonstration

Installation

Operation

Extraction

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Demonstrated Results Compared to Pellet Tubes

- Up to 80° C lower TMT compared to adjacent tubes
- Up to 24% lower pressure drop
- No hot spots
- ZF structure intact in original form after >15,000 hrs operation and with 5 thermal cycles

- Lower S/C ratio operation was not available
ZFRT Pilot Plant

- At Université Catholique de Louvain (UCL), Belgium
- Fully equipped and instrumented pilot plant for extensive testing of ZF reactors under rigorous commercial conditions and beyond
- In collaboration with Prof. Gilbert Froment and Prof. Juray de Wilde
- Added micro-reactor lab for studying intrinsic reaction kinetics
- Operational 2Q 2018
ZFRT Pilot Plant Installation
ZF applications in (H₂)SMRs: Core-Merit Benefits

- ZF’s lower dP, higher HTC and higher catalyst effectiveness allow the following underlying advantages, especially for retrofits:
  - higher throughput without increasing pressure drop
  - higher SMR outlet temp without increasing maximum tube skin temperature (TSM)
  - higher heat flux and/or higher reforming severity without increasing bridge-wall temperature and thus related firing / flue gas
  - lower approach to equilibrium
- Exploitation of ZF’s annular structure supports “recuperating reforming”
ZF Solutions for Hydrogen SMRs

- **ZF-Single pass (ZF-SP)**
  - De-stressing and Retrofitting existing SMRs
  - Higher-flux, cost-effective and more reliable new SMRs

- **ZF-Convective pre-reforming (ZF-CPR)**
  - Unmatched in-situ retrofit for additional capacity in existing SMRs without major modifications
  - Efficient and cost-effective applications in new SMRs

- **ZF-Bayonet (ZF-B)**
  - Uniquely applicable for recuperative reforming in new SMRs, overcoming current challenges
ZF-SP for De-Stressing SMRs

- Stressed SMR Indicators / Attributes
  - Pressure drop (or its build up) limiting throughput
  - Loss of catalyst activity → hotter tubes limiting outlet temperature
  - Catalyst attrition / settling from thermal cycling
  - Carbon formation / hot spots
  - Impact on (remaining) tube life

- Constrained reforming capacity
- Replacing (pellet) catalyst in these SMRs with ZF-SP Reactors can overcome these deficiencies
## ZF-SP for De-Stressing of SMR

<table>
<thead>
<tr>
<th>SMR De-Stressing</th>
<th>SMR Design</th>
<th>Stressed Operation</th>
<th>ZF-SP replacing pellets</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Capacity, %</td>
<td>100</td>
<td>95</td>
<td>100</td>
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<tr>
<td>Capacity limitations</td>
<td>-</td>
<td>dP, TSM</td>
<td>removed</td>
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<tr>
<td>S/C Ratio</td>
<td>3.0</td>
<td>3.3</td>
<td>2.8</td>
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<tr>
<td>Outlet temp, C</td>
<td>860</td>
<td>843</td>
<td>868</td>
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<tr>
<td>Approach to Equilibrium EOR C</td>
<td>-10</td>
<td>-12</td>
<td>-7</td>
</tr>
<tr>
<td>CH4 slip, dry vol %</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Radiant Pressure drop, bar</td>
<td>2.8</td>
<td>2.8</td>
<td>2.3</td>
</tr>
<tr>
<td>Relative Radiant duty %</td>
<td>100</td>
<td>97</td>
<td>99</td>
</tr>
<tr>
<td>Avg heat flux, kW/m2</td>
<td>78</td>
<td>74</td>
<td>78</td>
</tr>
<tr>
<td>Bridgwall temp, C</td>
<td>1000</td>
<td>980</td>
<td>998</td>
</tr>
<tr>
<td>TSM (avg) C</td>
<td>935</td>
<td>935</td>
<td>926</td>
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</tbody>
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ZF-SP for De-bottlenecking or New SMR

- Achieve >5% more equivalent capacity
- Higher average heat flux (without exceeding tube design temperature)
- Improved temperature uniformity
- Extended tube life and improved reliability
- Extended EOR
- Optimized operation and enhanced reliability
# ZF-SP for Debottlenecking

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference</th>
<th>ZF-Radiant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Capacity, %</td>
<td>100</td>
<td>105</td>
</tr>
<tr>
<td>Capacity limitations</td>
<td>dP, TSM</td>
<td>removed</td>
</tr>
<tr>
<td>S/C Ratio</td>
<td>3.0</td>
<td>2.8</td>
</tr>
<tr>
<td>Outlet temp, C</td>
<td>865</td>
<td>870</td>
</tr>
<tr>
<td>Approach to Equilibrium, C</td>
<td>-10</td>
<td>-7</td>
</tr>
<tr>
<td>CH4 slip, vol %</td>
<td>5.5</td>
<td>5.7</td>
</tr>
<tr>
<td>Radiant Pressure drop, bar</td>
<td>2.8</td>
<td>2.5</td>
</tr>
<tr>
<td>Relative Radiant duty, %</td>
<td>100</td>
<td>104</td>
</tr>
<tr>
<td>Avg heat flux, kW/m²</td>
<td>75</td>
<td>78</td>
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<tr>
<td>Bridgwall temp, C</td>
<td>1008</td>
<td>1004</td>
</tr>
<tr>
<td>TSM</td>
<td>940</td>
<td>938</td>
</tr>
</tbody>
</table>
In-situ efficient use of higher grade convective heat using existing process coils

Adiabatic pre-reforming (APR)

ZoneFlow™
Convective pre-reforming (CPR)
ZF Convective Pre-reforming (ZF-CPR)

- Non-adiabatic convective pre-reforming using ZF-CPR inserts
- Tailored structured packing for very low dP, high GSA and (low temp reforming) activity
- **In-situ horizontal loading** in the mixed feed superheat coils
- Avoids major modifications and also the related downtime
- Optimization of pressure drop in combination with ZF-SP in SMR radiant tubes

- For revamps, 8-12% additional reforming without increasing SMR firing duty
- For New SMRs, 10-15% smaller SMR and proportionately also the steam system.
## ZF-CPR for SMR Capacity Upgrade

<table>
<thead>
<tr>
<th></th>
<th>Existing</th>
<th>ZF + CPR</th>
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</thead>
<tbody>
<tr>
<td><strong>Relative Capacity,</strong> %</td>
<td>100</td>
<td>115</td>
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<tr>
<td><strong>S/C Ratio</strong></td>
<td>3.0</td>
<td>2.8</td>
</tr>
<tr>
<td><strong>SMR inlet temp,</strong> C</td>
<td>550</td>
<td>550 / 575 *</td>
</tr>
<tr>
<td><strong>SMR outlet temp,</strong> C</td>
<td>870</td>
<td>870 / 878 *</td>
</tr>
<tr>
<td><strong>Approach to Equilibrium</strong></td>
<td>EOR C</td>
<td>-10</td>
</tr>
<tr>
<td><strong>CH4 slip,</strong> dry vol %</td>
<td>4.8</td>
<td>5.4 / 5.0</td>
</tr>
<tr>
<td><strong>Radiant Pressure drop,</strong> bar</td>
<td>2.5</td>
<td>2.3</td>
</tr>
<tr>
<td><strong>Avg heat flux</strong> kW/m2</td>
<td>80</td>
<td>80 - 82</td>
</tr>
<tr>
<td><strong>Relative Radiant duty</strong> %</td>
<td>100</td>
<td>100 / 103</td>
</tr>
<tr>
<td><strong>Bridgewall temp,</strong> C</td>
<td>1020</td>
<td>1009 / 1018</td>
</tr>
<tr>
<td><strong>TSM</strong> C</td>
<td>950</td>
<td>938 / 948</td>
</tr>
</tbody>
</table>

* Exploiting of existing plant design margins
ZF-Bayonet Configurations

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ZF-Bayonet Modeling and Simulation Results

Graphs showing molar flow rate (mol/h) and temperature (°C) along the position (m) for various gases and components.
Drivers and Benefits of ZF-Bayonet

- Direct exploitation of ZF’s inherent annular design
- Overcomes innate limitations of the “pellet” catalyst against crushing from differential expansion / thermal cycling
- SMR size reduction up to 20% based on high grade heat recovery for reforming
- Allows “Zero export steam” hydrogen plants for:
  - remote, stand-alone or “distributed” hydrogen plants not having a steam host
  - cases where export steam has low or no credit compared to fuel
- Allows lowering of carbon-footprint from reduced firing per unit H2
- Compact / modularized SMR units
- Applicable in various SMR configurations and designs
Conclusions

- Hydrogen demand growth projections are strongly encouraging
- Steam reformer is the heart of an H2 plant; its performance and tube life are governed by catalyst
- Current pellet catalysts have inherent deficiencies, thus limiting the extent of possible improvements.
- ZoneFlow Reactor Technologies (ZFRT) has developed an innovative structured catalyst
- Exceptional and advanced solutions for revamping as well as new hydrogen SMRs, offering OPEX and CAPEX benefits.
- Successful demonstrations and pilot plant for testing under commercial / client-specific conditions
Thank You!

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