POCA 2
Implementation of NeSSI for LAMIMS MicroReactivity Testing
High Speed Characterization and Testing of Materials

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UOP LLC
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UOP LLC Who We Are

- World’s Largest & Oldest Refining and Petrochemical Technology Licensing Organization
- Leading supplier of catalysts to the processing industry
- World’s largest supplier of molecular sieve adsorbents
- Roughly 90 years of innovative solutions for the hydrocarbon processing industry
- Global company with 12 manufacturing sites
What We Do

- Develop technology that provides solutions to problems
- License, design, engineer, and service process technology
- Manufacture and provide catalysts, molecular sieves, adsorbents, and specialized equipment
- Transfer technology to customers who achieve high yield of high quality products
UOP Sites Around the World

All Manufacturing Sites are ISO 9002 Registered
Universal Oil Products formed

Sold to major oil companies

Placed in trust to American Chemical Society

Relaunched as a public company

Acquired by Signal Corporation

Signal merges with Allied Corporation

UOP merges with Union Carbide’s EP&P and CAPS Groups

UOP acquires Unocal’s process technology licensing business

UOP ownership changes to DOW/Honeywell
World’s Largest Technology Licensing Organization

- 30,000+ patents, 90% licensable
- 70 licensed processes
- 70 catalysts
- Molecular sieves adsorbents
- 30 Engineered products
  - Packaged process units and systems
  - Proprietary equipment
  - Control systems and instrumentation
- Engineering, technical and training services
Catalyst and Adsorbent Supports
- Metal oxides, including alumina, silica, titania, zirconia, and clays
- Numerous techniques, including oil dropping, bead forming, extrusion and spray drying
  - Shapes include powders, spheres, and extrudates

Catalytic Component Additions (Catalysts)
- Core competency in noble metals, especially salts of platinum and palladium
- Comparable strength in base metals, especially oxides and nitrates of tungsten, cobalt, nickel, and molybdenum
- Understanding and use of of catalytic modifiers, attenuators, and extenders

Catalyst Processing
- Noble and base metal loading (solutions, spray, co-mull, IX)
- Drying and activation by oxidation
- Reduction capacity for noble metal products
UOP Engineering Competencies

- Process design development
- Process Synthesis
- Cost estimating (capital, operating)
- Ability to integrate process and mechanical systems
  - Reactors/regenerators and internals
- Reaction systems
  - Select most appropriate system for task
- Solids circulation
- Specialized unit operations
  - Low dp heaters/exchangers, high pressure heaters
- Thermodynamics and process modeling
UOP Research & Development Resources

- More than 185 pilot plants, > 60 operating each day
- More than 20,000 pilot plant-days per year
- Combinatorial chemistry capabilities
- 300 million data points generated per day
- 350,000 laboratory analyses performed per year
- Modeling Capabilities include: physical, computational fluid dynamics, kinetic and process simulations (dynamic and steady-state)
- Average Annual R&D Spending: 8-10% of Sales
# Key Research and Development Competencies

## Catalyst / Adsorbents
- Noble, base metal and super acid catalysts
- Molecular sieves, metal oxides, pillared clays
- Binding, forming, oil dropping, extrusion, wash coating
- Molecular modeling
- **Surface science and characterization**

## Reactors
- Fixed and radial flow
- Temp controlled reactor (TCR)
- Fluidized, transport, slurry, trickle, and ebullated bed
- Bubble column reactor
- Hybrid reaction / distillation
- Hybrid reaction / adsorption
- Batch / continuous modeling

## Separations
- Adsorptive separations
- Polymeric membranes
- Pressure swing adsorption
- Temperature swing adsorption
- Solvent extraction
- Distillation trays / tubes

## Commercialization
- Exploratory R & D
- Pilot plant facilities
- Kinetics measurement and analysis
- Risk management
- Scale-up engineering
- Novel hardware design
- Catalyst and adsorbent manufacture
Advanced Characterization

**Structural**
- Powder X-ray Diffraction
  - High temp
- Specialty X-Ray Diffraction
  - Microbeam analysis
- Metallurgy
- Microscopy
  - SEM
  - Low Vacuum SEM
  - TEM
  - STEM
  - AFM
  - Optical
- NMR solids & liquids

**Reactivity Adsorption Mechanism**
- High Temperature Calorimetry
- Diffusion
- Microreactors
- Specialty Microreactors
  - TEOM
  - TSR
  - SSITKA
  - TAP
  - Isotopic Labeling

**Active Sites**
- XPS
- X-ray Adsorption
  - XANES
  - EXAFS
  - In-situ XANES/EXAFS
- Gas Adsorption
  - TPR
  - NH3 TPD
  - TMP NMR
- IR and RAMAN
- Specialty X-ray Fluorescence

Where we are planning to apply NeSSI
Combinatorial Chemistry

■ **Vision:** Utilize combinatorial tools and methods to reduce cycle time for new product invention and commercialization.

■ **Implication:** Invent and implement combinatorial tools and methods that effectively link combi scale to pilot and commercial scales
  – Sample preparation is representative
  – Screening tests are predictive

- **Combi** → **Micro** → **Pilot** → **Demo** → **Commercial**
- **Scalable Predictive**
Combinatorial Vision

Discovery Research
(1000s of ideas)

Focus Research
(100s of ideas)

Catalyst Preparation
Catalyst Testing
Modeling
Informatics

Successful Commercial Operation
(1 prototype)

Process Development
(2-5 leads)

Combi is a Step in the Technology Delivery Process
Enablers of Combinatorial Characterization

- Efficient ways of materials synthesis
- Parallel preparation of experimental catalysts
- Availability and development of high-speed characterization tools
- Parallel and high throughput testing of catalytic properties
- Data analysis techniques - informatics
- Accelerated processes of discovery and technology delivery
Combinatorial Capabilities

- Modular
- Interchangeable
- Stand-alone
- Flexible

Diagram:
- Material Synthesis
  - Characterization
  - Data Analysis
- Catalyst Preparation
  - Heat Treatment Unit
  - Reactor Assay
LAMIMS

(Laser activated membrane introduction mass spectrometry)

- Micro reactivity Test
- Closed environment (realistic catalyst exposure history)
- No moving parts
- Very broad temperature application
- Full QMS product analysis
- Real world catalysts
- State-of-art catalyst as standard (universal ranking)
The LAMIMS Screening System

- LAMIMS reactant delivery system
- A 25 watt CO₂ barcode writing laser
- LAMIMS reactor
- Quadrupole mass spectrometer (QMS)
LAMIMS Reactor

- Carbon paper is overlaid upon the membrane
  - Heat dissipater protecting polymer membrane
- Catalyst array is deposited upon the carbon paper
- Entire reactor is heated to base temperature
- Laser tuning of catalyst spot temperature
- QMS analysis of product distribution
Methylcyclohexane (MCH) dehydrogenation

\[ \text{MCH} \rightleftharpoons \text{toluene} + 3 \text{H}_2 \]

MCH Conversion to toluene is a measure of metal reactivity
Data from Reactor System
Forty five Pt (0.2%) catalysts.

Toluene Production
The vision...
Lab Automation using NeSSI

- Honeywell sensors
- Parker Hannifin Intraflow substrate and components
- GO pressure regulators
- Parker valves and actuators
- Brooks mass flow controllers

- Used Ethernet and DeviceNet networks and commercially available Gen I products
- LabView software on PC for configuration, control, data and diagnostics
- Proved the need for low power small size actuators and valves
- Exceptional diagnostic, control, and data collection capabilities
- Remote monitoring and control via standard internet tools
- Fast and easy configuration using LabView
System Overview

Overall

Detailed
# Automated System Components

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Component Description</th>
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</thead>
<tbody>
<tr>
<td>3</td>
<td>Device Net Flow controllers</td>
</tr>
<tr>
<td>3</td>
<td>Back Pressure Regulators</td>
</tr>
<tr>
<td>2</td>
<td>4 port two position valves</td>
</tr>
<tr>
<td>1</td>
<td>3 port two position valve</td>
</tr>
<tr>
<td>6</td>
<td>24VDC bellows sealed valves</td>
</tr>
<tr>
<td>6</td>
<td>Honeywell Pressure Indicators</td>
</tr>
<tr>
<td>3</td>
<td>Pressure reducing regulators</td>
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</tbody>
</table>
LAMIMS Gas Handling System

Construction and Demonstration Accelerated with NeSSI

Mass Spectrometer installed
Laser installed
NESSI gas manifold installed
Automation software completed
Safety review completed

<table>
<thead>
<tr>
<th>Resources</th>
<th>W/NeSSI</th>
<th>Typical</th>
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<tbody>
<tr>
<td>Elapsed time</td>
<td>4 months</td>
<td>6 months</td>
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<tr>
<td>Personnel time</td>
<td>2 months</td>
<td>4 months</td>
</tr>
<tr>
<td>Manifold cost</td>
<td>+10%</td>
<td>baseline</td>
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</tbody>
</table>
Installation Went Very Well

List of Minor Issues

The check valves were ordered with a 1psi cracking pressure. However, the check valves were delivered with a much higher cracking pressure. This was corrected the following day by ordering new springs for the check valves.

- All the block valves and the mass flow controller for the nitrogen line were specified to be normally opened. They all were delivered normally closed. A “simple” nitrogen line (needle valve and block valve) added to correct this safety issue.

- All the connections to the Neslab four-way valve (KV-4001) and to the vent four-way valve (KV-4005) were incorrectly installed. We had to take apart most of the NeSSI system to correct this.

- Original design to put all electronics modules (labview field point modules, power supply, etc.) inside an enclosure. The NeSSI system arrived without such an enclosure, and all the electronics parts were exposed to the outside, including the 110V cables.

- The Brooks mass flow controllers failed to communicate (DeviceNet communication) correctly with the automation software. Falaah resolved this issue with Brooks.

- “Overall the NeSSI system performs well.”
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