# Scaling-up from High Throughput Screening to Continuous Process for the Synthesis of 1,6-Hexanediol from Renewable Feedstocks

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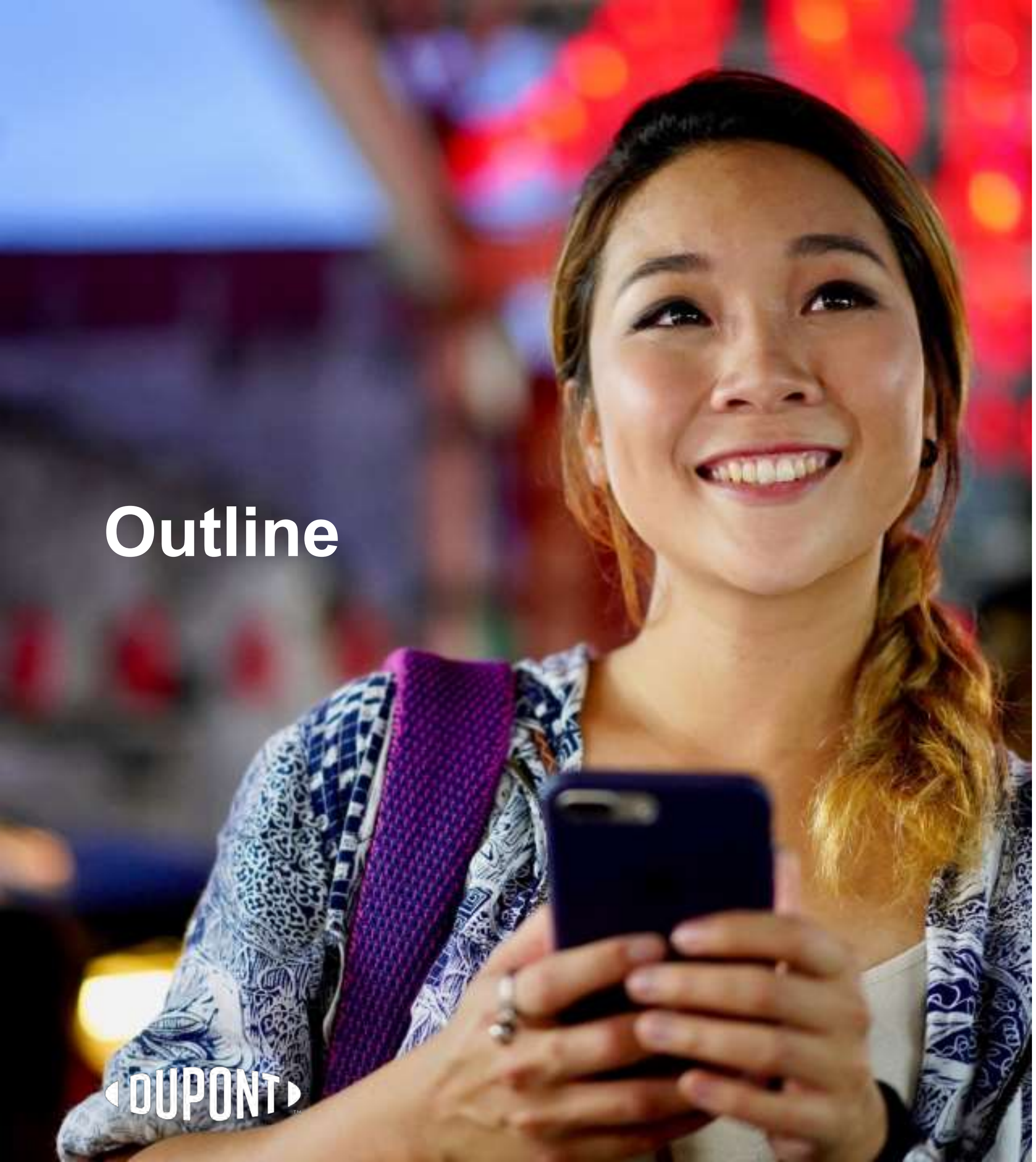
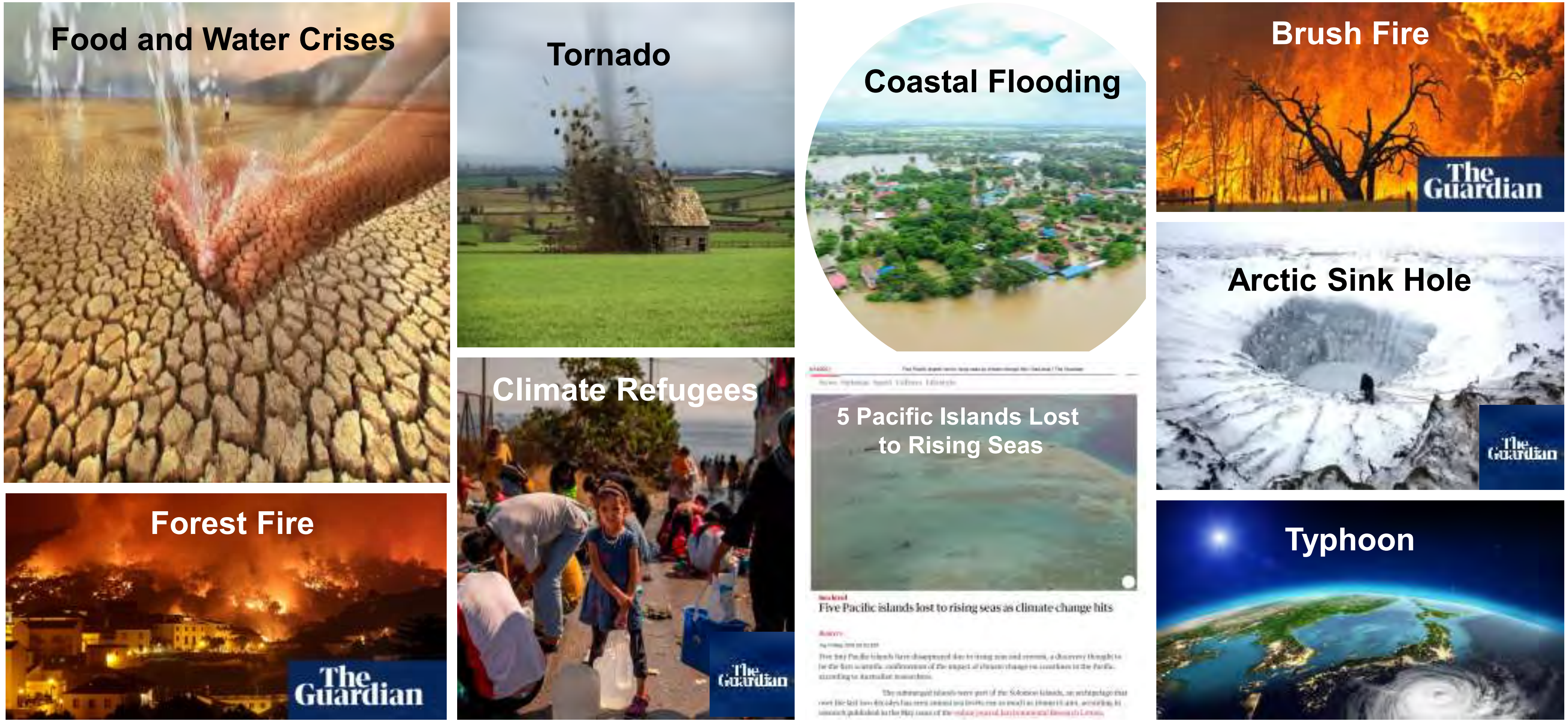
# Outline



- **Overview**
  - Effect of Climate Change
  - Sustainable Development
- **Biomass to Value Added Monomers**
  - Objectives
  - Approach
- **Renewable Monomers via Selective Hydrodeoxygenation**
  - Diols from Carbohydrate Feedstock
- **Catalyst Synthesis and Selection**
  - Catalyst Synthesis and Characterization
- **Catalyst Evaluation**
  - High Throughput Catalyst Synthesis & Screening
  - Scale up in Continuous Fixed Bed Reactors
- **Summary**

# Environmental Crisis and Sustainable Development




Naomi Klein

"Climate change isn't an 'issue' to add to the list of things to worry about ... it's a civilizational wake-up call ... telling us that we need an entirely new economic model"

Alexa Dembek

"We need to decouple carbon from growth"

# DuPont's Ten-year Path to a More Sustainable Future

## innovate **now**

### Delivering solutions for global challenges

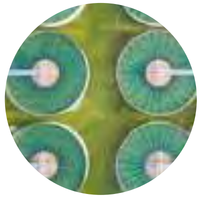
**Align 100% of the DuPont innovation portfolio** to meaningfully advance the UN SDGs and create value for our customers

### Enabling a circular economy

**Integrate circular economy principles** into our business models considering lifecycle impacts in the markets we serve

### Innovating safer by design

**Design 100% of our products and processes** using sustainability criteria including the principles of green chemistry



## protect **now**

### Acting on climate

**Reduce Green House Gas (GHGs) emissions 30% including sourcing 60% of electricity from** renewable energy

Deliver carbon neutral operations by 2050

### Leading water stewardship

**Implement holistic water strategies** across all facilities prioritizing manufacturing plants and communities in high-risk watersheds

**Enable millions of people access to clean water** through leadership in advancing water technology and enacting strategic partnerships

### Delivering world-class health & Safety

**Further our commitment to zero**: injuries, occupational illnesses, and incidents

## empower **now**

### Accelerating diversity, equity & inclusion

**Become one of the world's most inclusive companies**, with diversity well ahead of industry benchmarks

### Cultivating well-being & fulfillment

Create a workplace where employees report **high levels of well-being and fulfillment**

### Building thriving communities

**Improve over 100 million lives** through targeted social impact programs

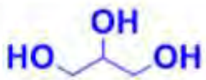
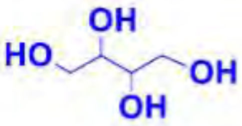
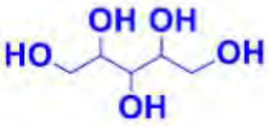
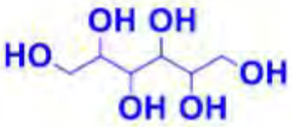
# Objectives

- **High value monomer production from bio-renewable resources**
  - Design and develop cost-advantaged, inherently safe, and sustainable processes based on renewably-sourced feedstocks for the production of fuels, chemicals, and advanced materials

- **Selective hydrodeoxygenation (HDO) of biomass-derived feedstocks**
  - Develop a cost-competitive process for the synthesis of 1,6-hexanediol from renewable feedstocks
  - Determine the activity, selectivity, and life of supported metal-metal oxide catalyst combinations using high throughput screening and continuous trickle bed reactors for the hydrodeoxygenation of 1,2,6-hexanetriol (1,2,6-HT) and tetrahydropyran-2-methanol (THP2M) to 1,6-hexanediol (1,6-HD)

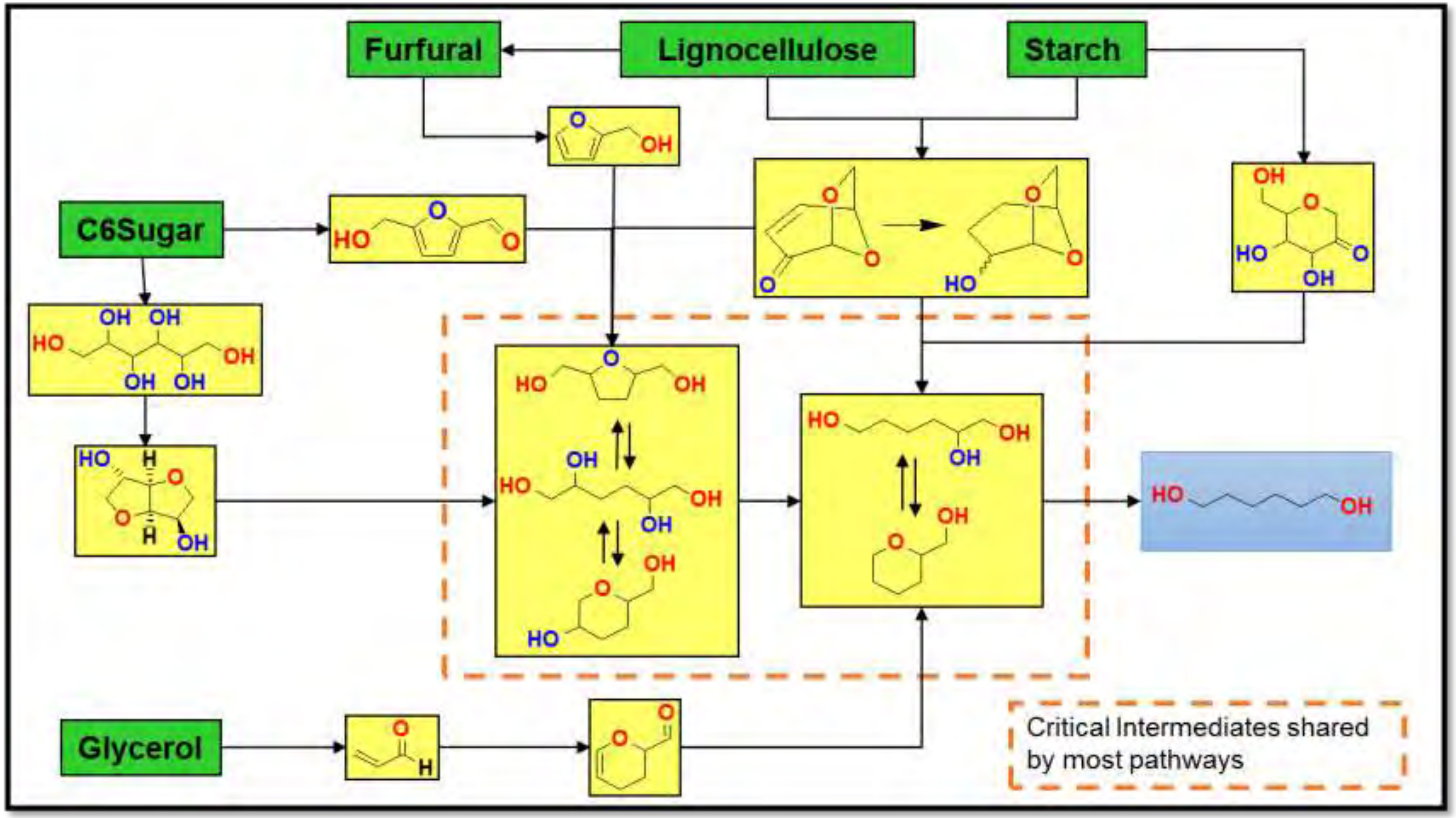
# Industrially Important Polyols from Biomass

**Opportunity:** Conversion of inexpensive oxygen-rich biomass into industrially useful functionalized building blocks

| Biomass | | | Diol | Application |
|---|---|---|---|---|
| **Glycerol**<br>waste by-product of biodiesel production |   | → |  <br>**1,3-Propanediol** | Sorona™ (DuPont)<br>Corterra™ (Shell) |
| **Erythritol**<br>Biofermentation of cornsugar/starch |   | → |  <br>**THF** | Lycra™<br>Industrial Solvent |
| **Xylitol**<br>Acid digestion/pyrolysis hemi-cellulose<br>eg: corn cobs |   | → |  <br>**1,5-Pentanediol** | Thermoplastic Polyurethanes<br>Polyesters |
| **Sorbitol**<br>hydrogenation of glucose from corn/beet/cane sugar |   | → |  <br>**1,6-Hexanediol** | Polyurethanes<br>Polyesters<br>Potential Nylon-6,6 precursor |

Fluctuations in oil prices and increase in greenhouse gas emission have prompted the quest for alternative cost-competitive pathways for the synthesis of chemicals, materials, and fuel from renewable feedstocks

# Conversion of Biomass to Renewable 1,6-HD




Reaction network delineating key intermediates for converting various biomass to renewable 1,6-hexanediol (1,6-HD)

# Process Development, Design, and Scale-up

## *Lab, Pilot, and Commercial Scale Reactors*

| Lab Scale Reactor | Pilot Scale Reactor | Commercial Scale Reactor |
|---|---|---|
| Design for basic data | Design to confirm commercial reactor concept | Design reaction condition for optimal performance |
| Scale up or scale down of commercial reactor | Scale down of commercial scale reactor, as close as possible | Safe, low footprint, minimal upstream and downstream processing |
| Maintain isothermal condition | May require more than one scale | Model required to evaluate optimal conditions |
| Model required for interpretation of data | Iterate between lab and pilot to refine design and operating conditions | Iterate with lab and pilot scale reactors to refine design and operating conditions |

# Batch vs Continuous Processes

| Batch Process | Continuous Process |
|---|---|
| Can be easily adapted to different processes/chemistries (tolling) | Higher throughput |
| Well-suited for small scale operation (specialty chemicals) | Benefit of scale |
| Suitable for complex recipes (e.g. pharma, biotech) | Higher uptime |
| Well mixed system | Lower inventory of feed/product in reactor |
| Near isothermal condition | Easy coupling with continuous upstream and downstream processes |
| Higher mass and heat transfer | Higher yield/selectivity |
| Easy scale-up and scale-down | Better safety, control and operability, lower environmental footprint |
| Easy to operate | Lower capital investment |

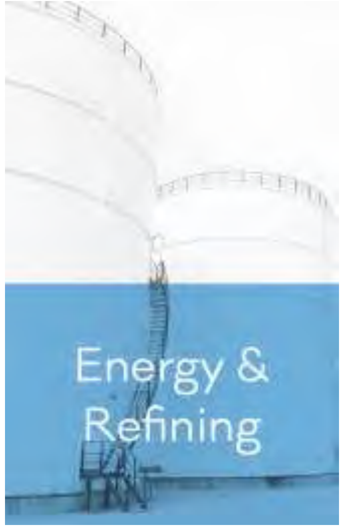
# hte

## *The High Throughput Experimentation Company*

- Turn-key ready test systems
- Contract research

for catalyst R&D

Client owns IP on catalyst and process







Fields of competencies

# Overview of hte Toolbox

## *Development from Batch to Continuous Flow Reactors*

| Batch | fixed bed | | fluidized bed |
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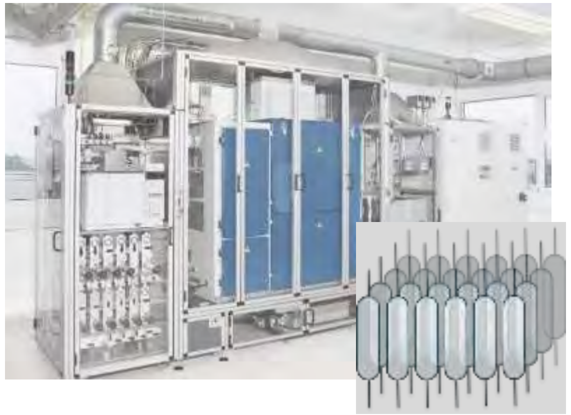
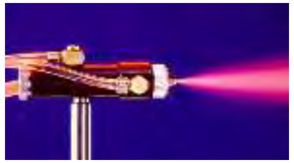
|  |  |  |  |
| Batch / semi-batch reactors (x8 fold) | Gas phase & trickle-bed reactors (x16 – x48 fold) powder and extrudate | Bench-scale system (x1 - x8 fold) extrudate | Micro Down-Flow Unit (MDU) |
| • Catalyst testing<br>• Feed testing<br>• POCs | • Catalyst testing<br>• Feed screening<br>• ~1-50 ml of catalyst | • Process optimization<br>• Upscaling<br>• ~100 – 300 ml of catalyst | • Fluidized bed catalyst testing |

# Catalyst Synthesis Tool Box


**Comprehensive Catalyst Synthesis**

- Tier 1, powder synthesis – incipient wetness impregnation, co-precipitation
- Tier 2, upscaling – shell impregnation
- Tier 3, lead optimization (loading, support)



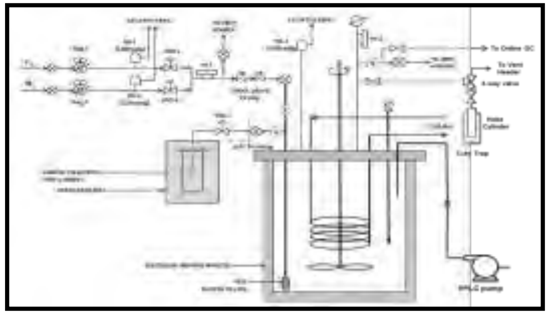
Multi-tier catalyst synthesis strategy used to find promising catalyst formulations and subsequent catalyst upscaling and lead optimization (synthesis, support, and loading)

# Catalyst Testing Tool Box

**Multitier Catalyst Assessment**

- Tier 1 batch proof of concept
- Tier 2, yields, SEL
- Tier 3 kin. data, scale up, STY
- Internal and external capabilities

HTE Trickle Bed Unit

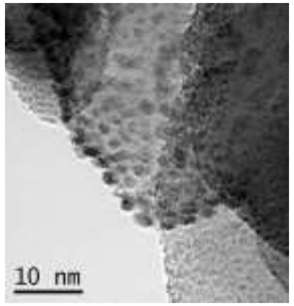



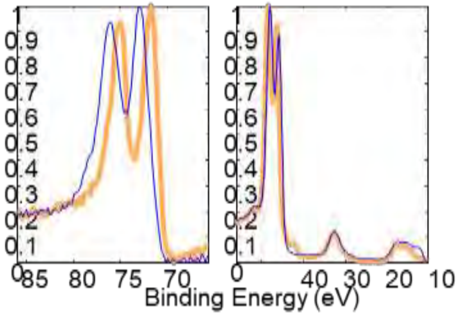
Bench scale Trickle Bed Unit

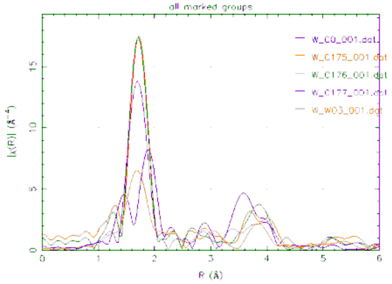
Multitier catalyst screening strategy was used, internally and externally, to determine lead catalyst candidates and subsequent process development and catalyst optimization

# Analytical Tool Box

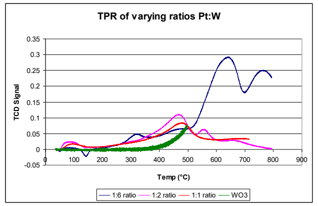
**Catalyst characterization**
- BET, PVD, PSD
- TG, Chemisorption, TPD
- Density, Strength
- XRD, XRF, XAS
- ESCA
- TEM, SEM, EDS
- EA, ICP-OES/MS



**Offline GC for product characterization**
- Method development
- Optimization of given method (e.g. run length 2 h → 1 h)

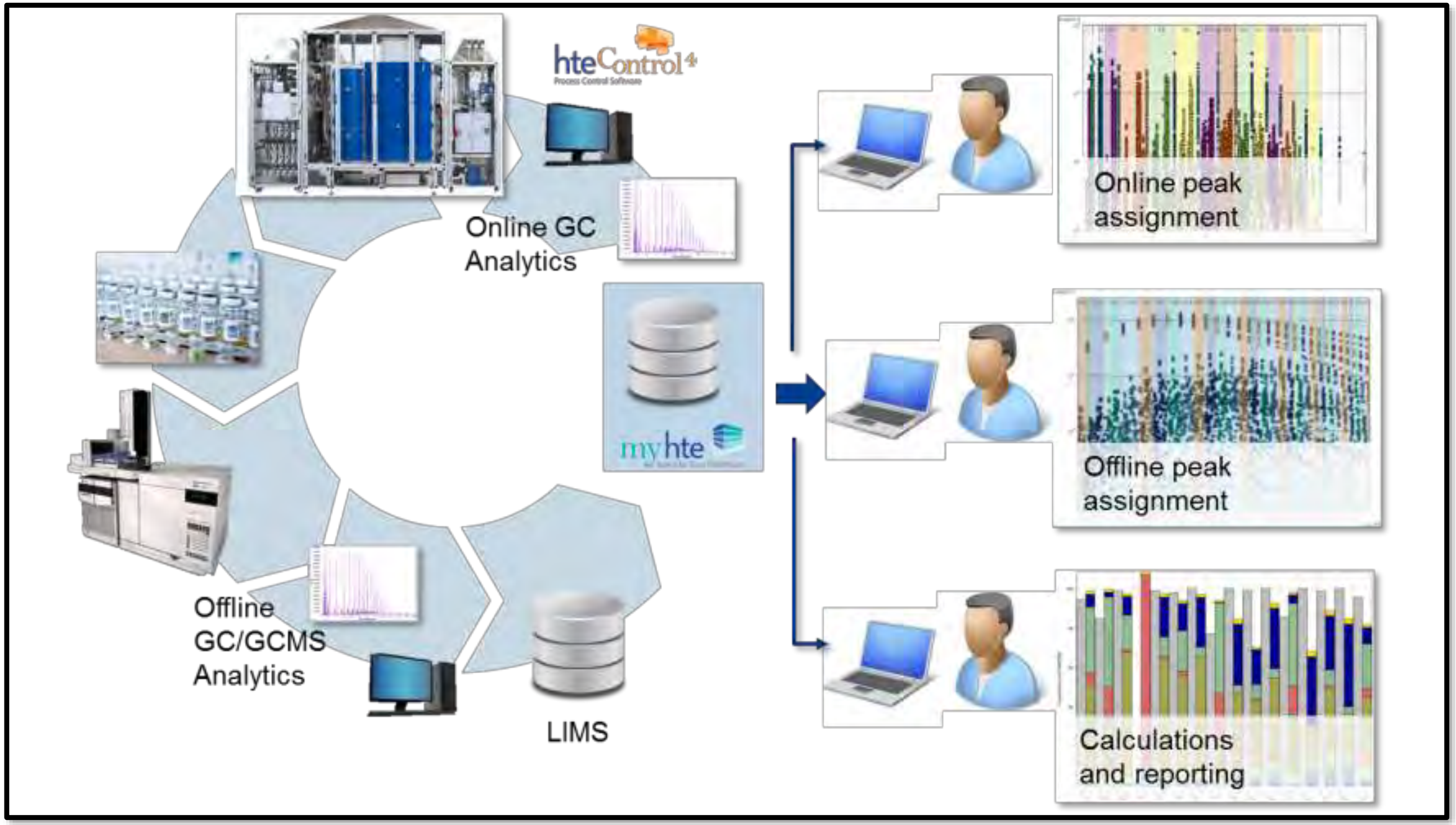



**Compound identification – GC-MS & Injection**
- Varying substrates & solvents
- Approx. 180 compounds identified – known & unknown

**Peak separation and quantification**
- Proper peak separation and high sample throughput
- Two Agilent GC 7890 Dual Channel 2xFID in operation

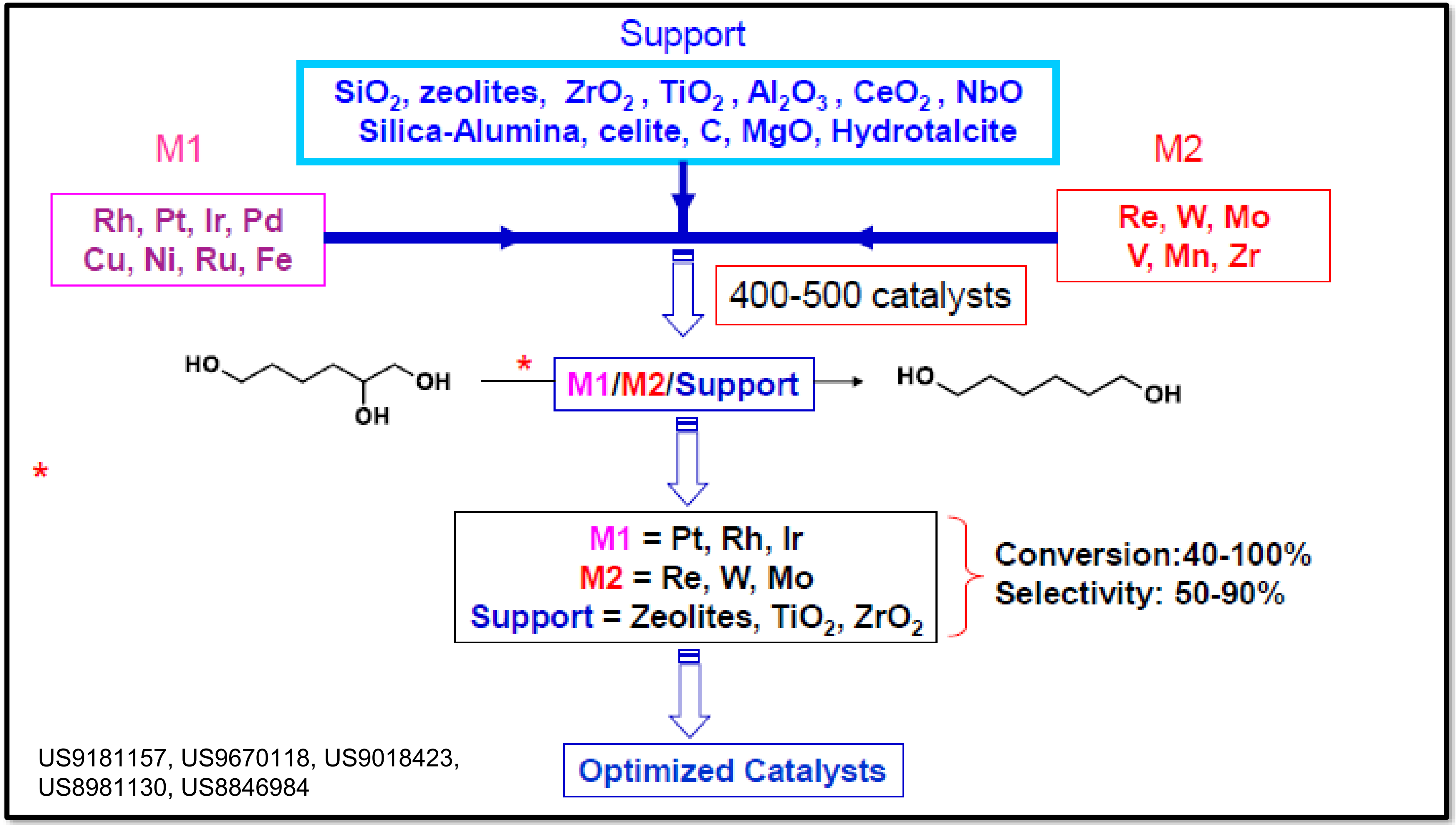
Detailed characterization of catalyst, feedstocks, and gaseous and liquid products by various analytical tools to optimize catalysts and quantify product distribution as a function of catalyst and feedstock

# Data Collection and Integration Tool Box




Integrated software workflow for collecting, evaluating and reporting all operational, gas and liquid samples as well as, kinetic data in a comprehensive database

# Catalyst Synthesis




Plethora of reducible metal and oxophilic metal oxide combinations were prepared and tested in high-throughput catalyst screening reactors for catalyst evaluation

# Catalyst Upscaling

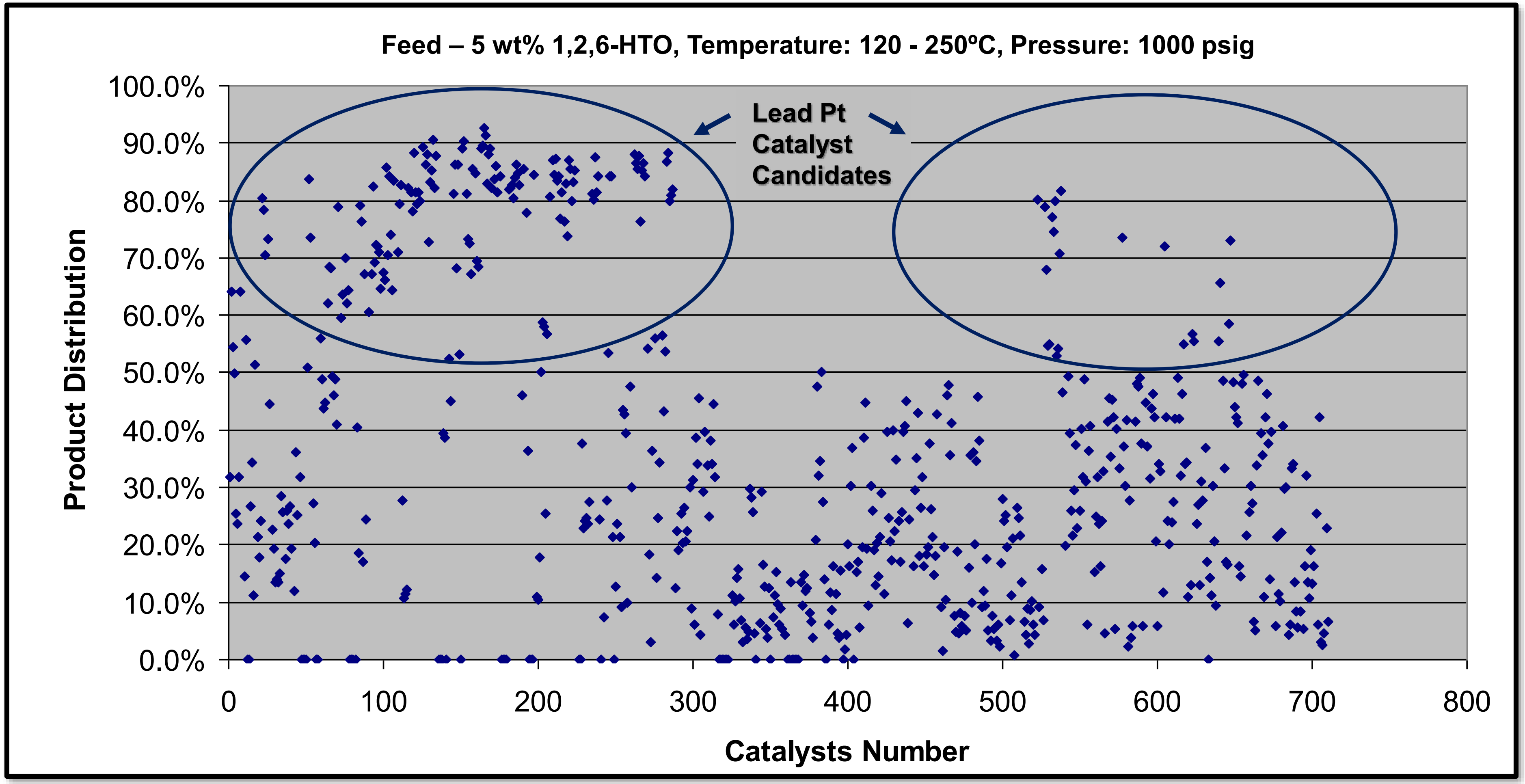
## *From Powder to Extrudate*

Shell Impregnation

Full characterization of the synthesized catalysts by different techniques:
BET, PVD, PSD, TG, Density, Strength, XRD, XRF, EA, ICP-OES/MS
Shell thickness optimization and investigation of metal loading vs catalytic activity

Shell thickness measurement using microscopic techniques

# Catalyst Screening




Identified catalyst compositions and synthesis techniques to achieve single pass >70 mol% 1,6-HD.

# Trickle Bed Reactor Test Units

Catalyst embedding

16-fold high-throughput trickle-bed reactor unit

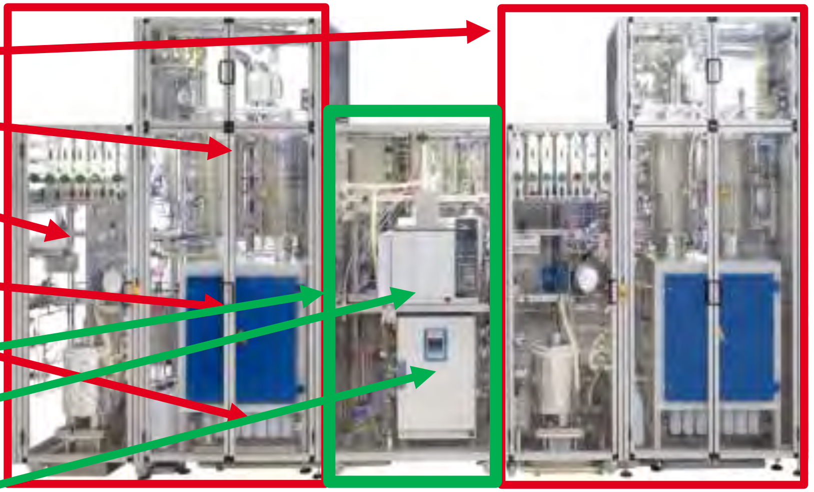
- Cover all trickle bed applications
- Simulating industrial operating conditions
  - Up to 450°C (higher on-demand)
  - 4x4 heating blocks or 16 individual heaters
  - Up to 260 barg
  - Up- or downflow, once-through, reactors in series, ínterstage dosing/sampling, adiabatic T-profile
- Reactor: ID 5 – 8 mm, up to 200 mm isothermal zone
- Catalyst: up to 10 ml, powder, commercial shapes
- One or two liquid feed supplies
- Full mass balance of gas and liquid products
- Automated 24/7 operation

Independent Modules

- 2 reactors (parallel/series)
- Gas/liquid supply
- Downstream Separator
- Liquid sampling

Analytics

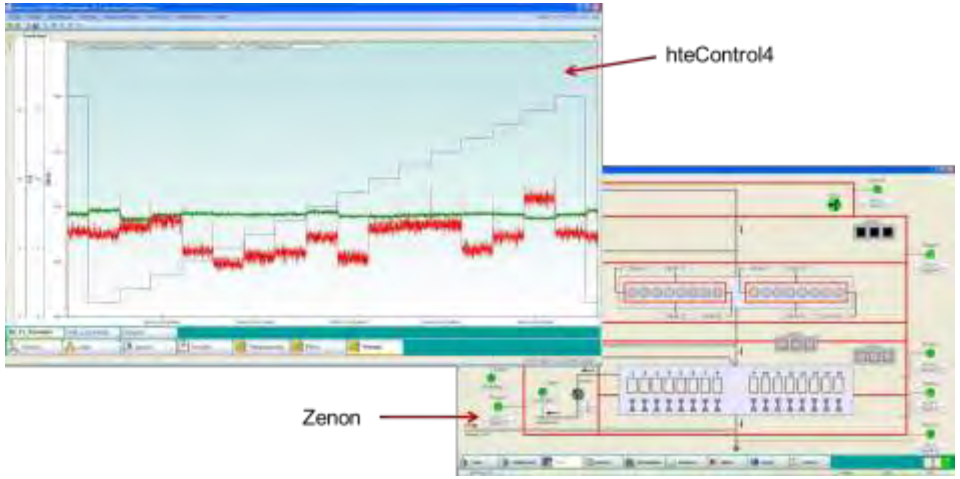
- Online GC
- Heating/Valves, FI – Gas flow



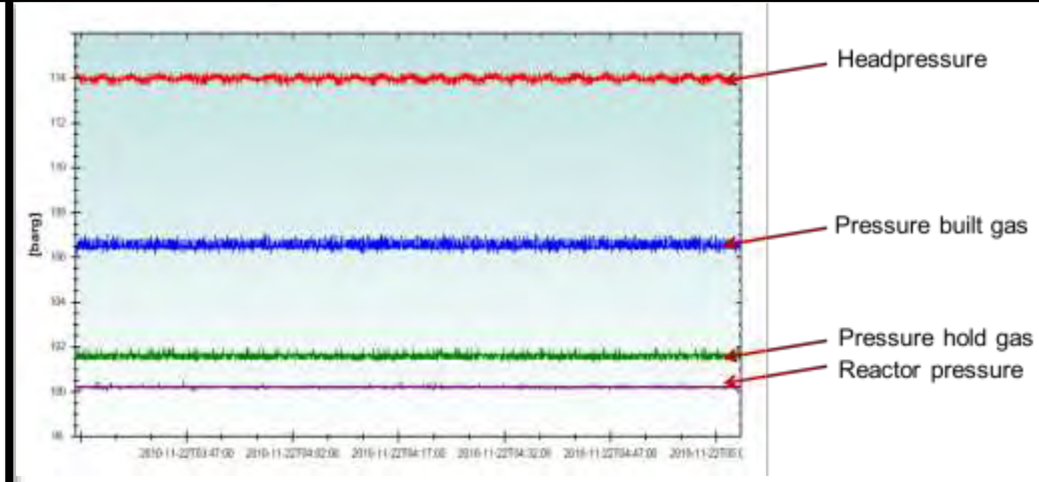
8-fold bench-scale trickle-bed reactor unit

- Cover all trickle bed applications
- Simulating industrial operation conditions
  - Up to 450°C (higher on-demand), individual heaters
  - Up to 170 barg (higher on-demand)
  - Up-/downflow, once-through, reactors in series, ínterstage dosing/sampling, adiabatic T-profiles
- Reactor: ID 12 – 24 mm, up to 300 mm isothermal zone
- Catalyst: up to 80 ml, commercial shapes
- Individual operation with separate feed and operating variables per module (4 modules with 2 reactors each)
- Full mass balance of gas and liquid products
- Automated 24/7 operation

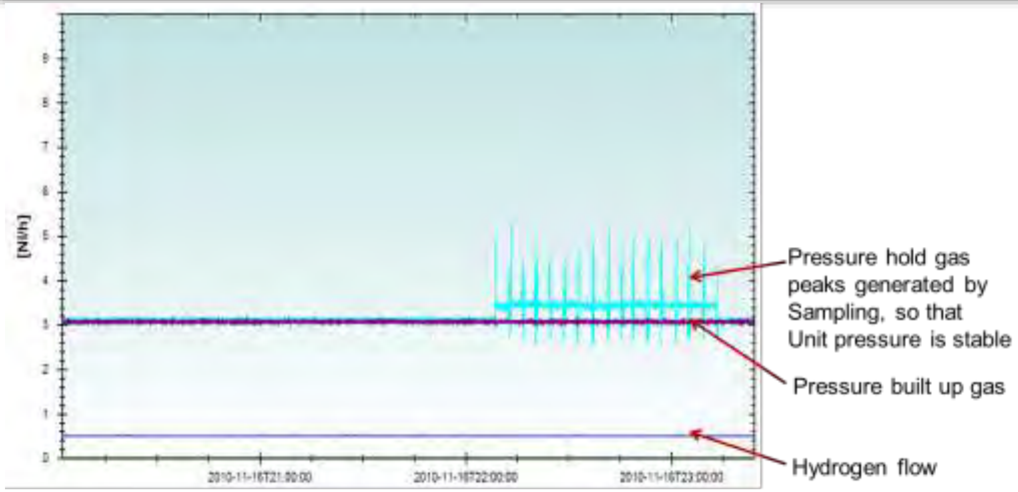
# Reactor Validation



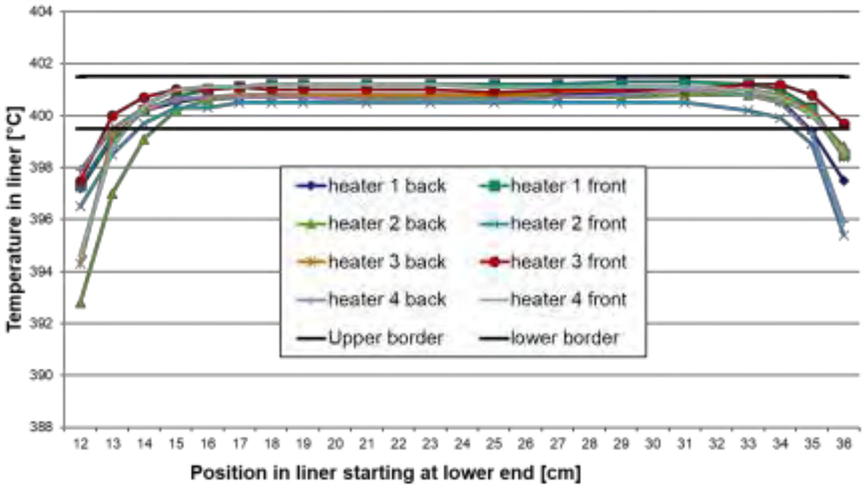

**Process control softwares hteControl4 and Zenon**




**Pressure stability at 100barg**

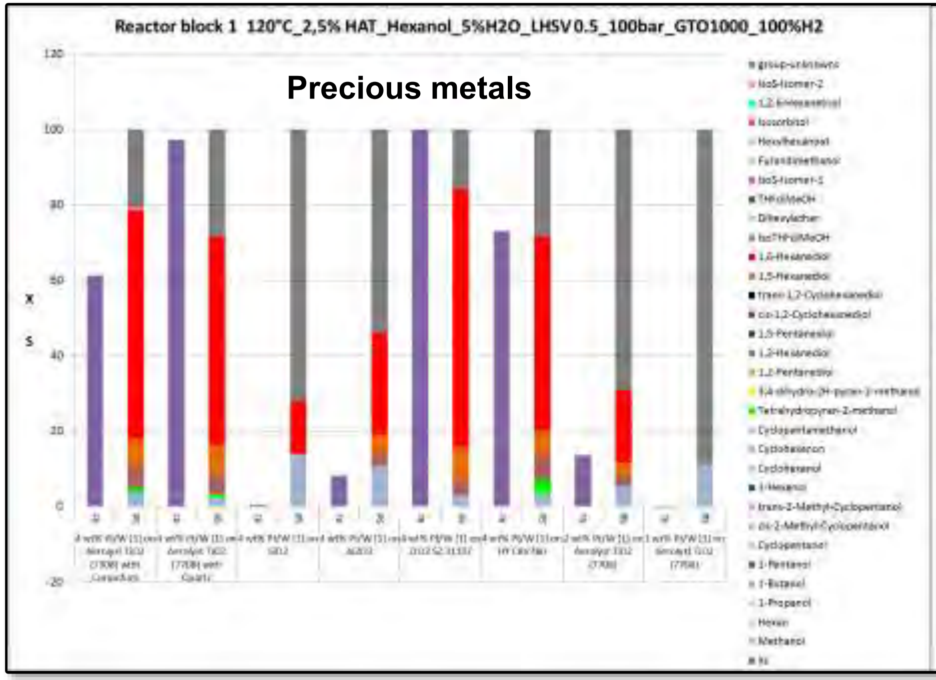


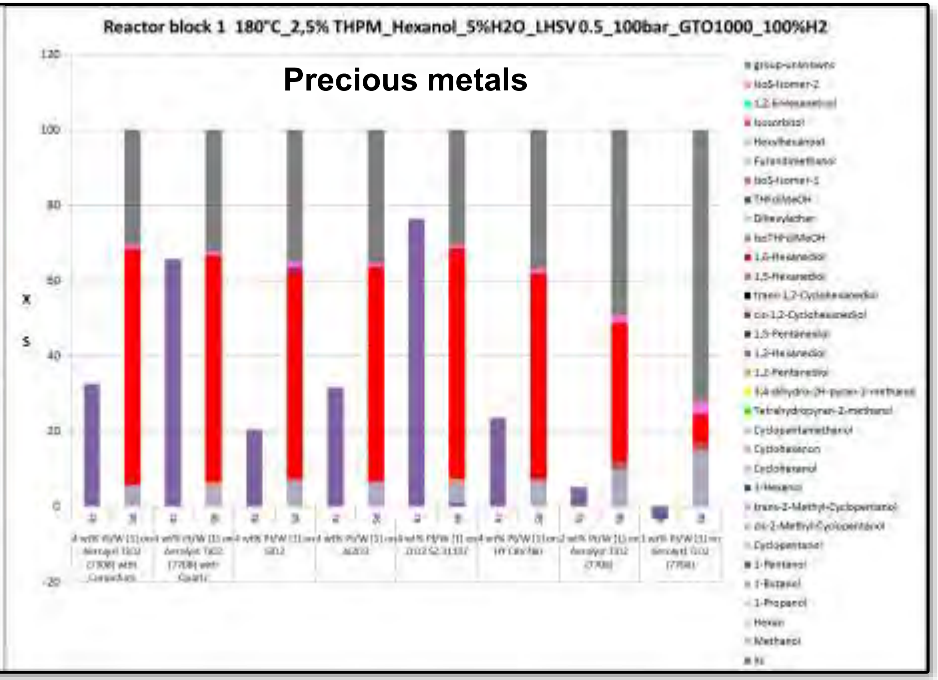

**Flow stability at 100barg**




**Isothermal temperature profile for catalyst bed zone (± 1 °C)**

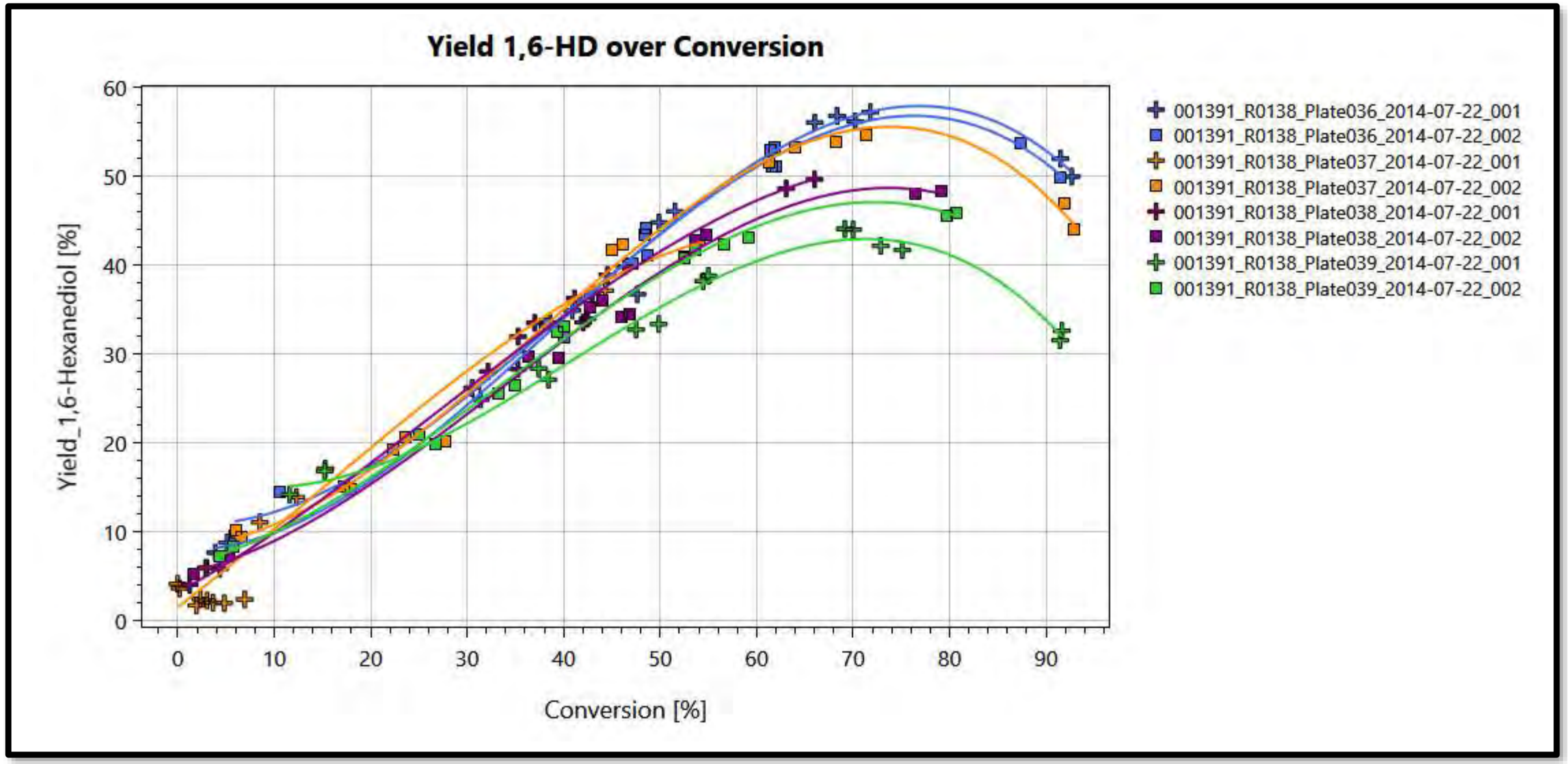
# High Throughput Screening




- Tested approximately 500 catalysts, 16 catalysts at a time, catalyst loading 1.5 ml
- Compared **base and precious metal catalysts**
- Screened **different substrates** (1,2,6-HAT, THP2M, THFDM, and others) to **1,6-Hexanediol**
- Screened **different solvent and/or solvent blends** (Water, Hexanol, Dioxane)
- Screened catalysts at **different temperatures** in parallel
- Continuous operation of up to **1 to 3 month(s) time on stream**
- Analytical identification of important unknowns by GC-MS

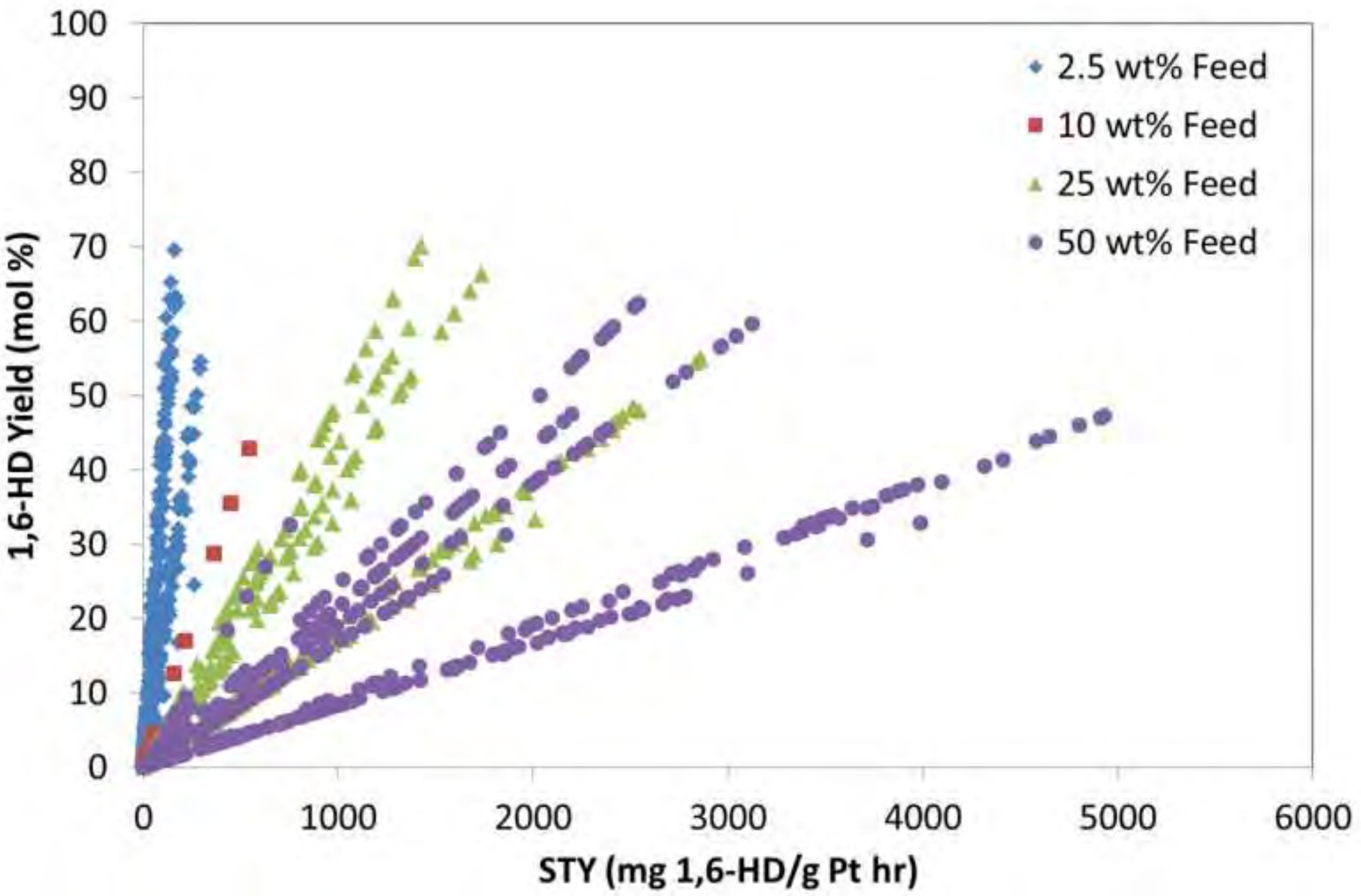
# Bench-scale Process Optimization




- Catalyst upscaling and **lead catalyst optimization**
- Individual **process optimization** of lead catalysts, catalyst loading 20 ml
  - Different Pressure and temperature range
  - Upflow vs. downflow reactor configuration
  - Per-pass conversion and recycle operation
- **Feedstock screening** for increased diversity
- 30 feed formulations (7 substrates, 3 solvents)
- 2 – 3 month time on stream (1000 – 2000 h TOS)

# Optimization of Pt/W Catalysts

## *STY as a Function of Metal Loading and Feed Composition*



# Summary

- Developed platform technology for selective hydrodeoxygenation of biomass
- Built biomass conversion catalysis and catalyst screening competency
- Identified proprietary classes of lead catalyst candidates enabling key functionalities in good yields (up to 85%) and selectivity
- Developed Supported Precious Metal Catalysts:
  - $Pt/W/TiO_2$, $Pt/WO_3$, Rh/Re/HY, $Pt/Fe/TiO_2$
- Demonstrated the lead catalyst selection from batch screening of catalysts to continuous fixed bed reactor technology for the hydrodeoxygenation of critical renewable chemical precursors to 1,6-hexanediol
- Established sophisticated catalyst characterization tools; in conjunction with kinetic data, gaining detailed insight towards reaction mechanism and catalyst's structure activity relationships

# Change Takes Time

I am certain that one day we will be successful in changing hearts and minds. Perhaps the change will be slow. Perhaps it will come one day at a time and one person at a time. But one day, we'll find that whole nations have changed, and our world has embraced a new paradigm and we will have a blueprint for safe and sustainable products and processes, by design, for our future generations.