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PNNL-SA-116366

Challenges of Working with Complex Waste Streams

Catalysis, Separations, and product quality

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Energy and Environment Directorate and
the Institute for Integrated Catalysis

29 February 2016

Fundamental Science Needs to Address Waste to Energy Conversion Workshop

Value Proposition

Locally transform

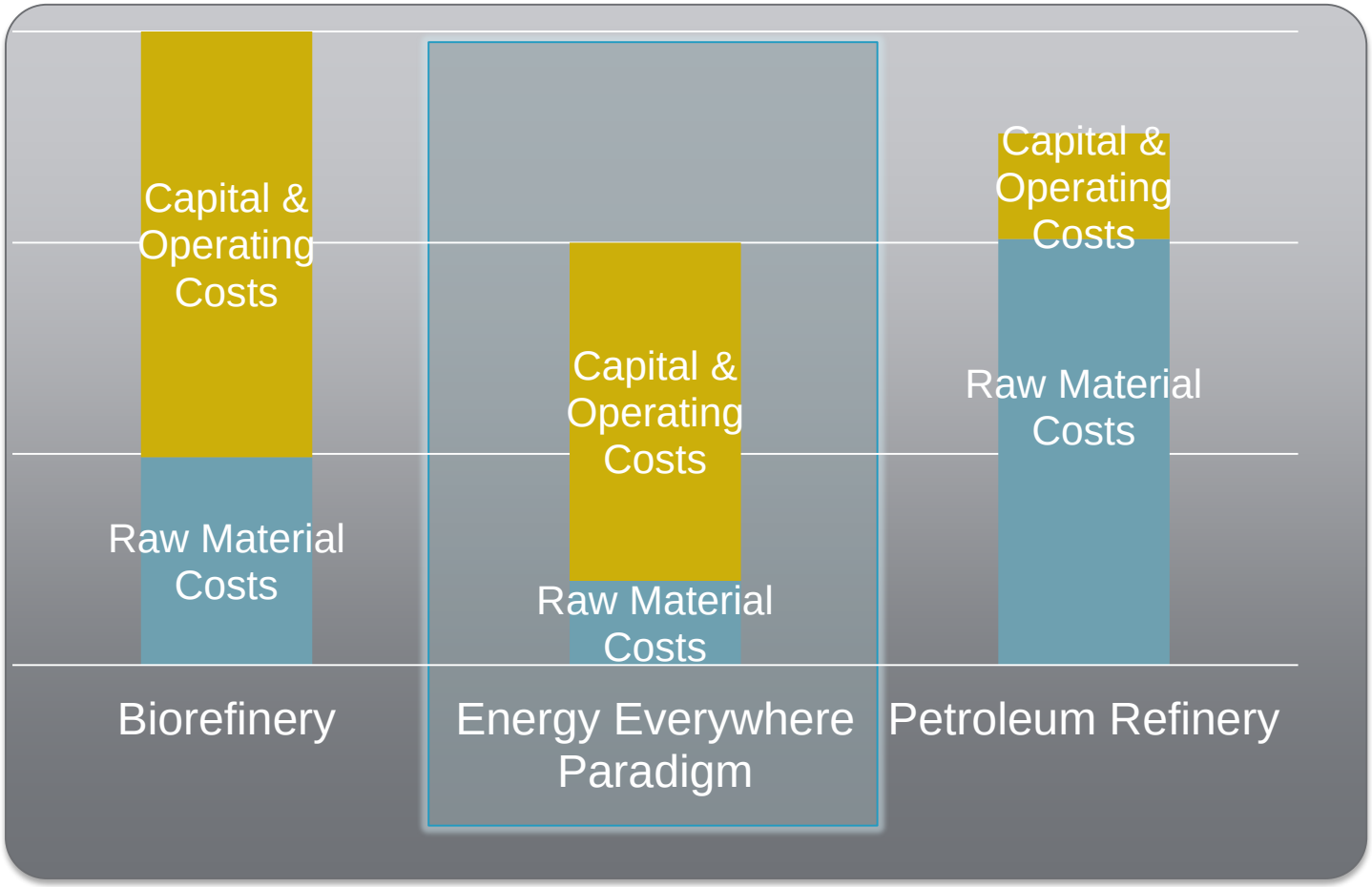
the nation's stranded, underutilized, and distributed waste into fuels and chemicals

replacing up to 40% of our crude oil used each year

Where there is waste, there is energy

Transformational technology to reduce operating and capital cost

Goal of Energy Everywhere Big Idea



Purpose of this workshop is to identify basic science that empowers needed transformational technologies

Premise 1: we can make high quality chemicals from waste

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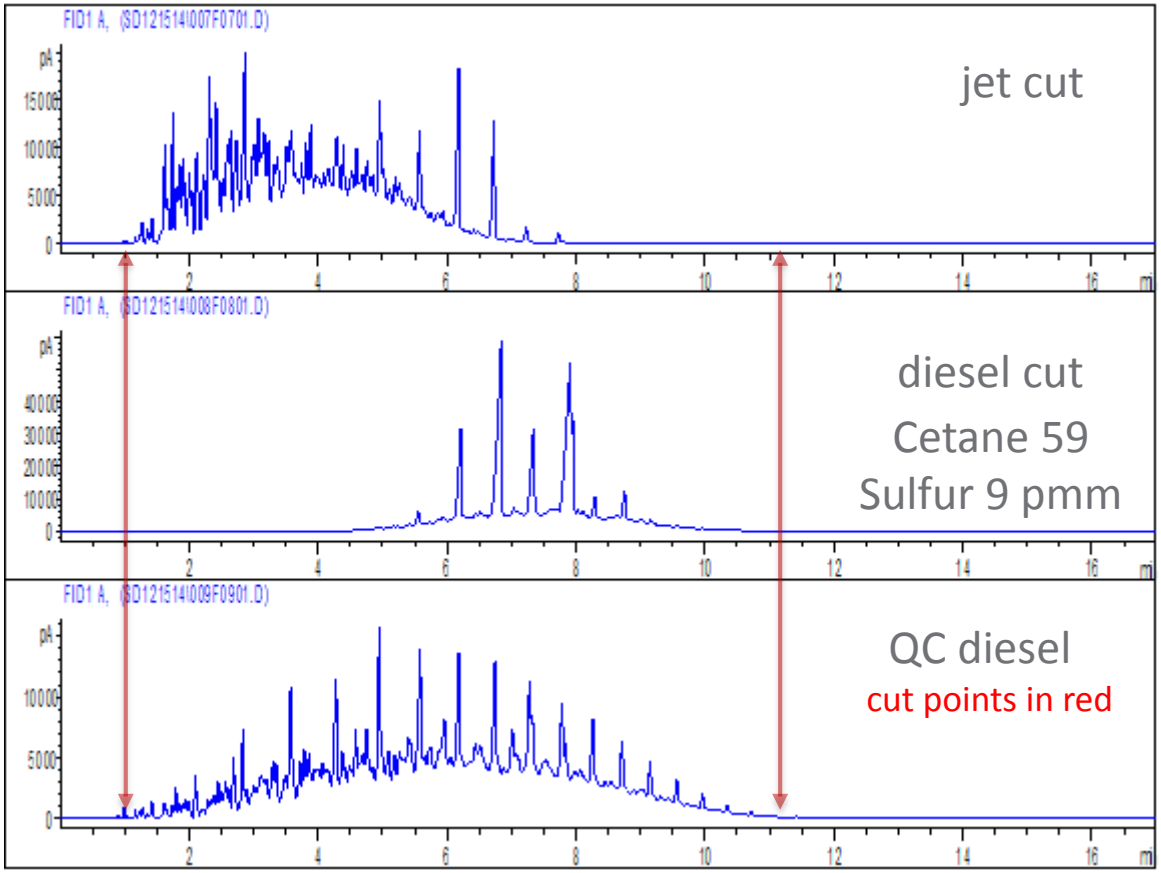
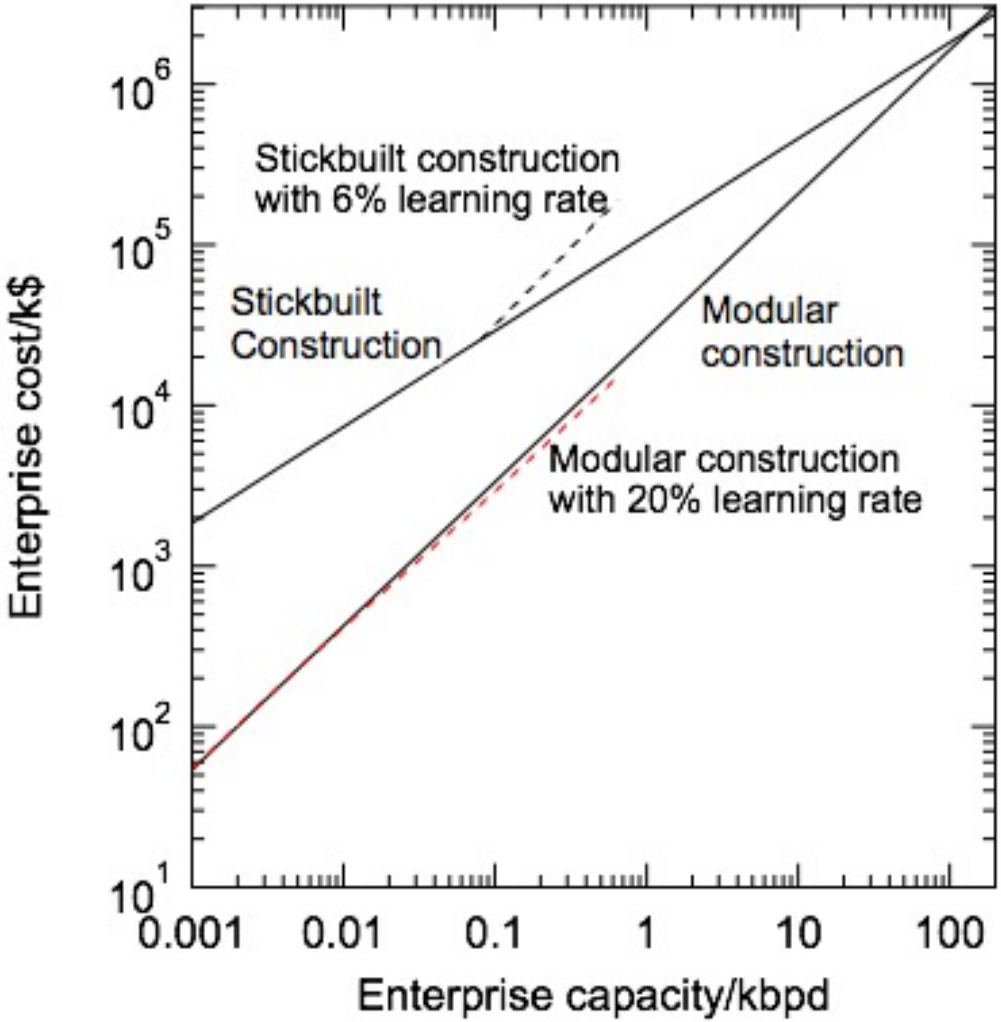
- Demonstrated production of high quality diesel fuel from many sources of wet waste*

Hydrotreated biocrude



Premise 2: small scale processing can be cost competitive

- Fabrication learning curve
  - 18% (3x faster than stick-built)
- Scale economies (power law) can be near unity (0.9 rather than 0.6)
- What science is needed for modularization?
- What science is needed for technologies that work at small scale?



Implications for the technology

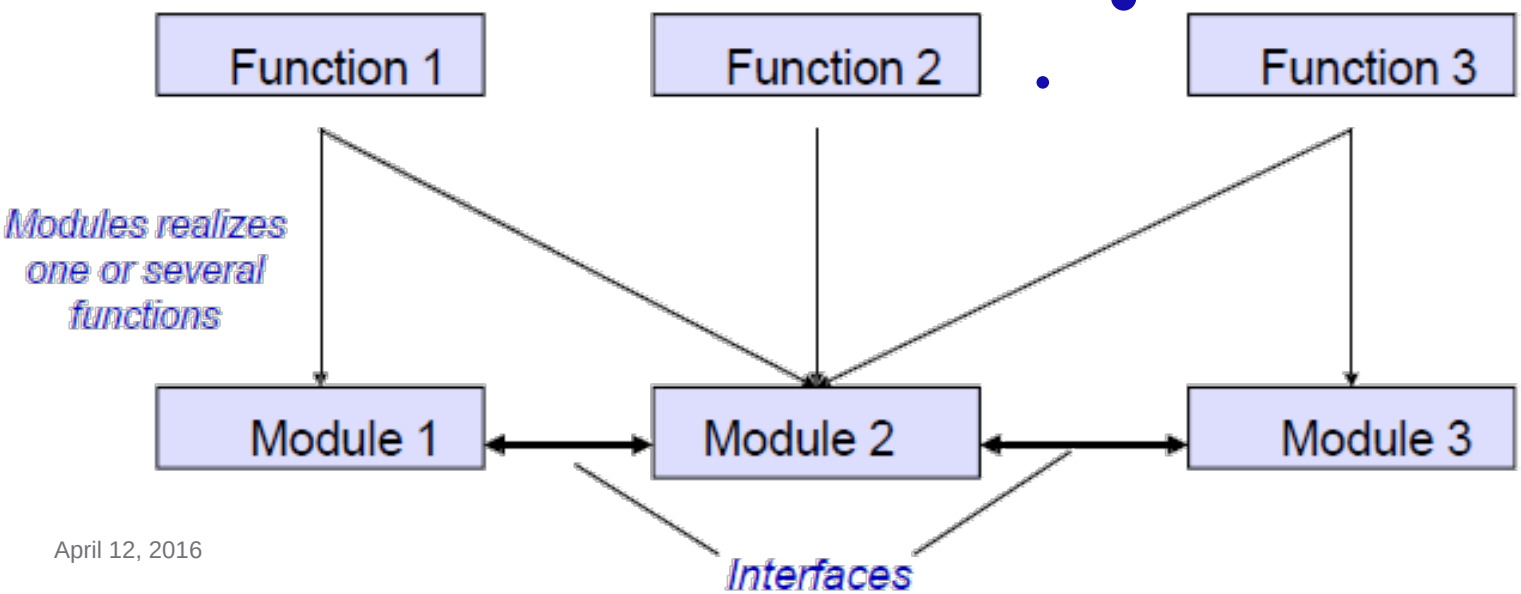
Resource dispersion necessitates:

- Low exergy operation (temperatures and pressures near ambient) because there are no economic sinks or sources for enthalpy
- Operation without access to process utilities except electricity (notably, high pressure H_2)
- Compact, robust units (opportunities for process intensification)
- Telemetry and feed-forward control (minimize need for 24/7 skilled operators)

Modular design

- Definition: Share components that can be separated and recombined
- Common platform
  - Mix and match components
  - Plug and play
  - Reconfigurable

What does this mean to science?
e.g., kinetic coupling of reactors



Science needs

- Catalysts – stable and active
  "low temperature" / condensed phase
- Separations – lower energy
- Analytical – understand reactions

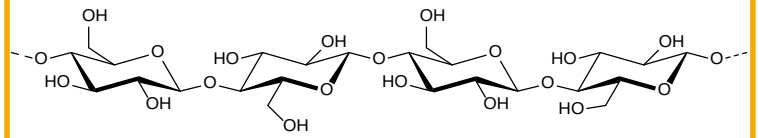
Physics of multiflow systems and chemistry of complex mixtures

Liquefaction

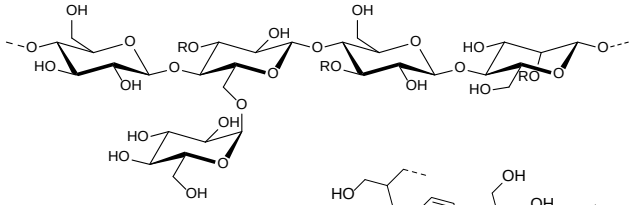
- Thermal conversion of carbon stream (waste) into an intermediate oil
- Upgrade oil into useful chemicals

Thermal conversion to an intermediate oil

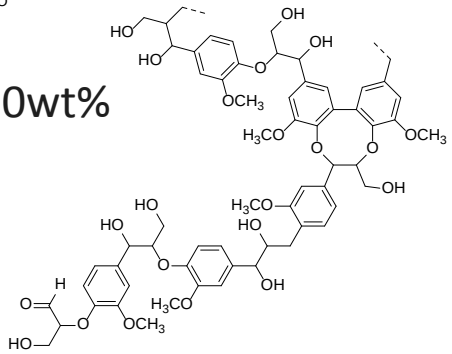
Cellulose = 0 - 45 wt%



Hemicellulose = 0 - 30 wt%



Lignin = 0 - 30wt%

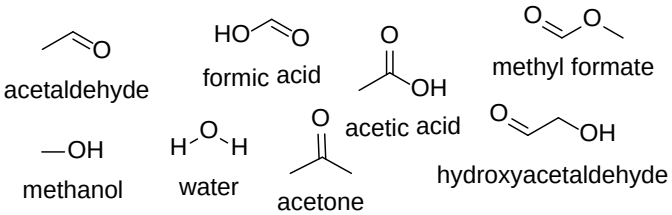


Inorganic = 0.1 - 20 wt%

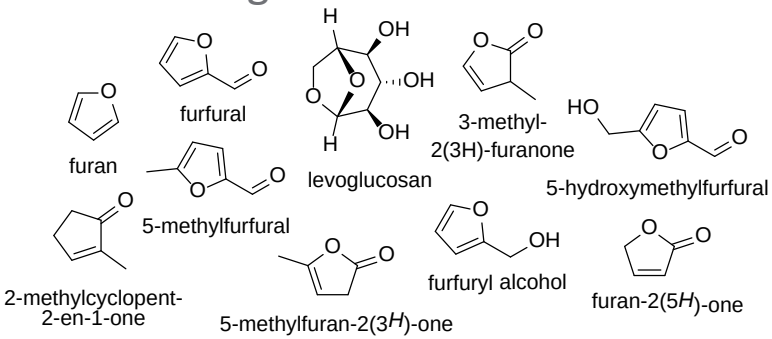
K, Na, Ca, P, Mg, Mn, Si, etc.

Conditions: 500 °C, very short residence
Quench vaports

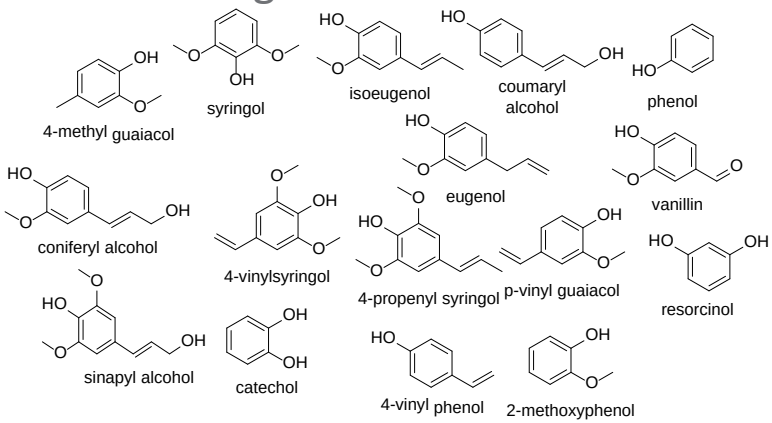
Light oxygenates



Sugar derivatives



Lignin derivatives



Upgrade oil into useful chemicals

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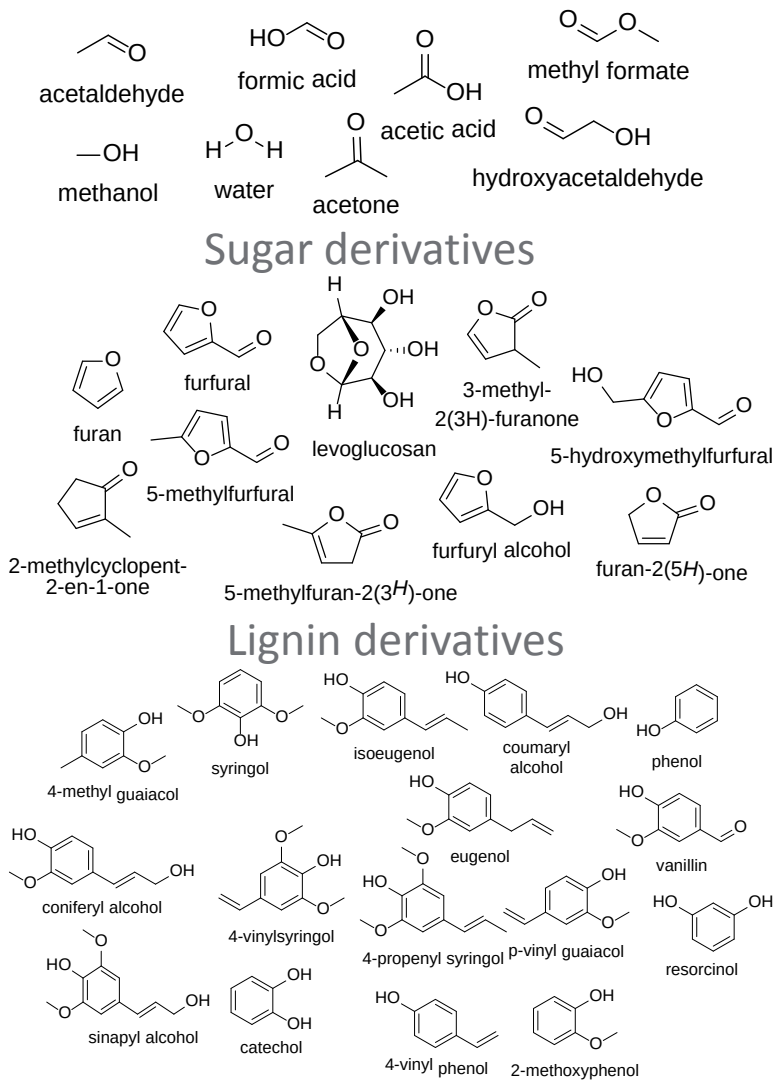
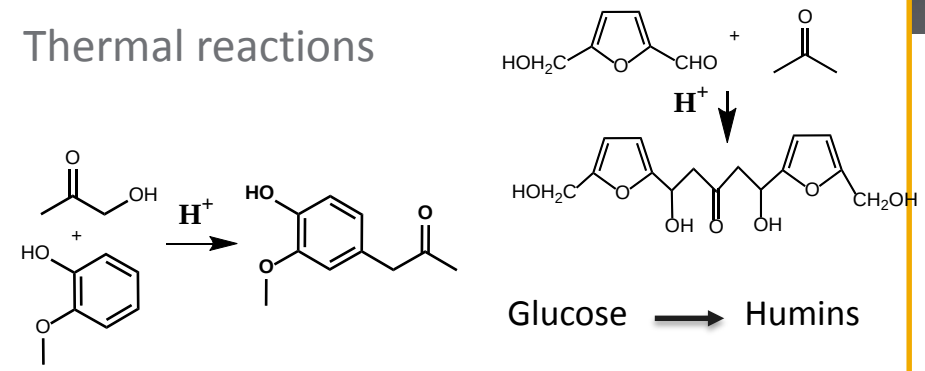
Light oxygenates

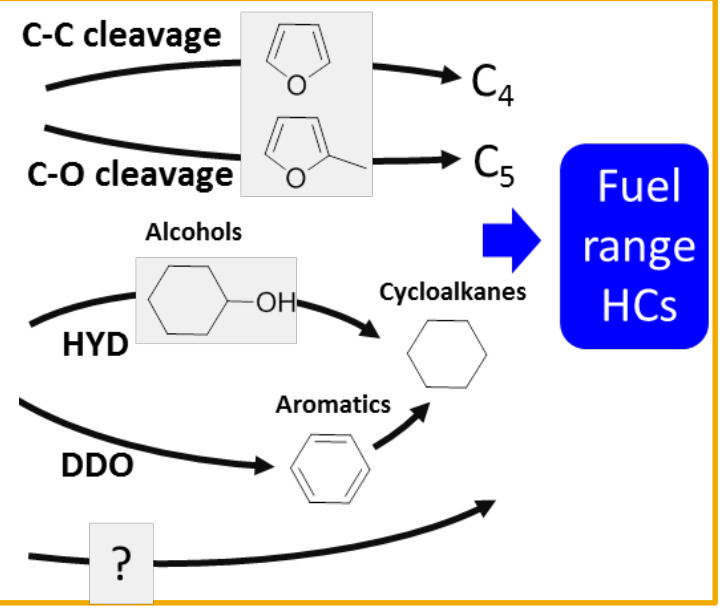


Thermal reactions



Char and polymeric "gums"

Catalytic reactions



AIChE J ***2013,*** *59,* 888 *Patent US7671246*
ACS Catal ***2013.*** *3,* 1047

Address technology disconnects

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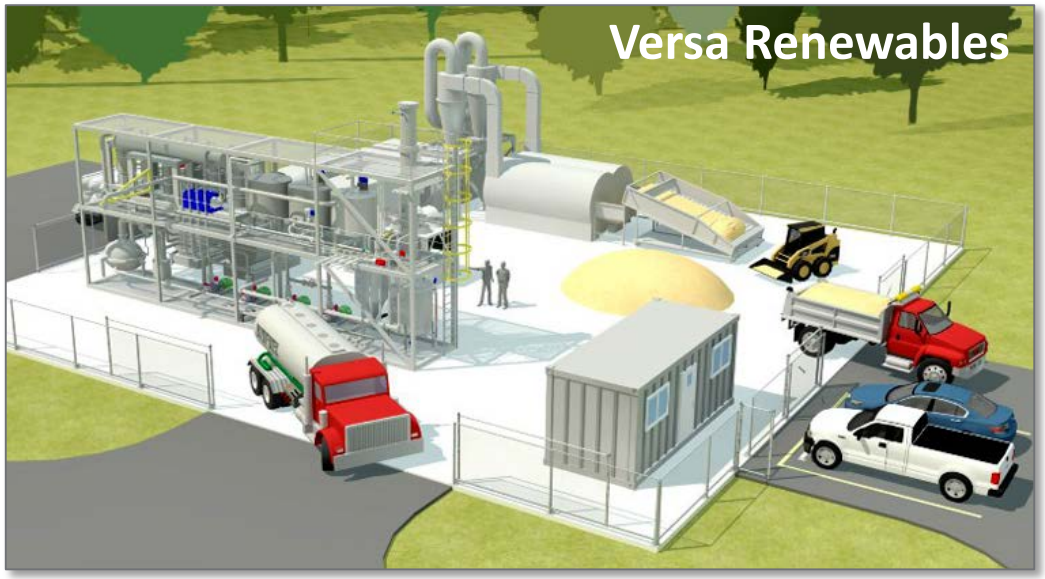
- Design elements
  - Sized smaller to use stranded carbon
  - Modular design to reduce capital
  - Products of higher value: chemical or finished fuel

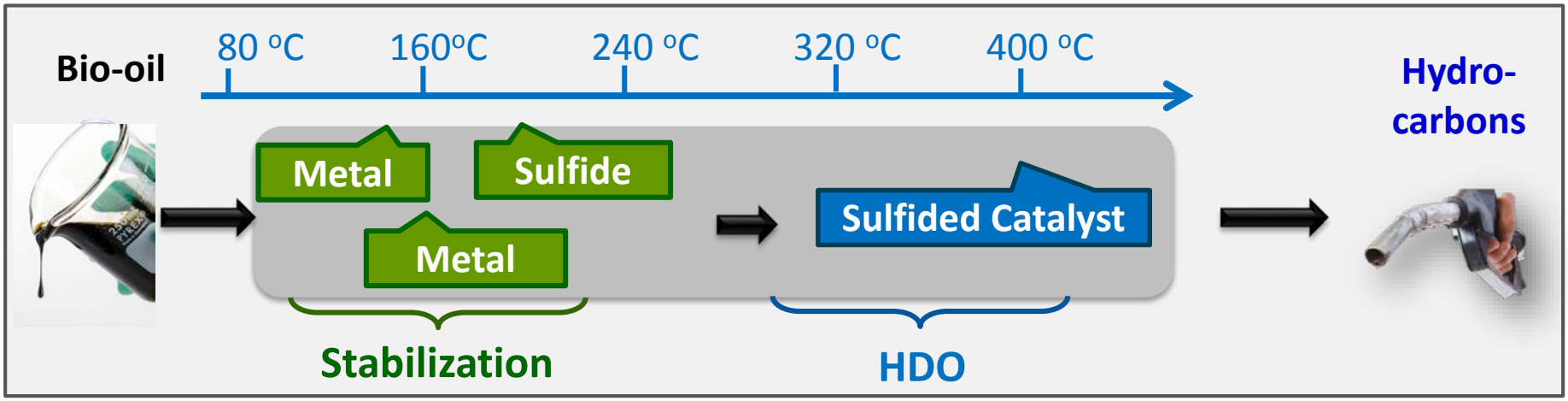


Designed for 2-20 barrel of oil equivalent per day

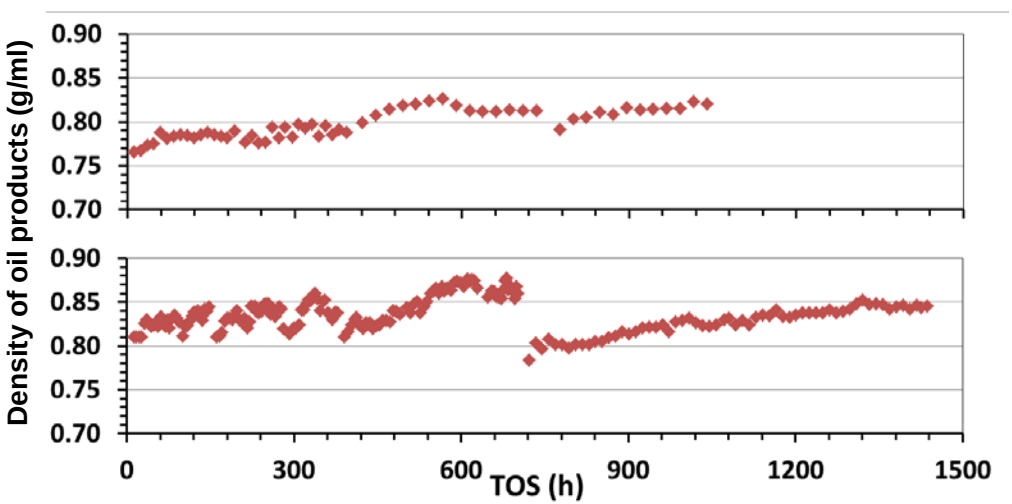
☑ replace fluidized bed (more efficient) with an auger (cheaper), simpler design, and sized to local feedstock

☒ Upgrade is an hydrotreater — doesn't scale down, yet alternatives suffer high yield loss

Brief overview of upgrading chemistry



Ru/TiO_2 followed by CoMoS/C, T: 250 - 410°C, pressure: 15 MPa H_2, space velocity: 0.1-0.4



Long term stability
High rates
Selectivity

Identify key challenges where our science foundation is insufficient

Reactor systems must be robust

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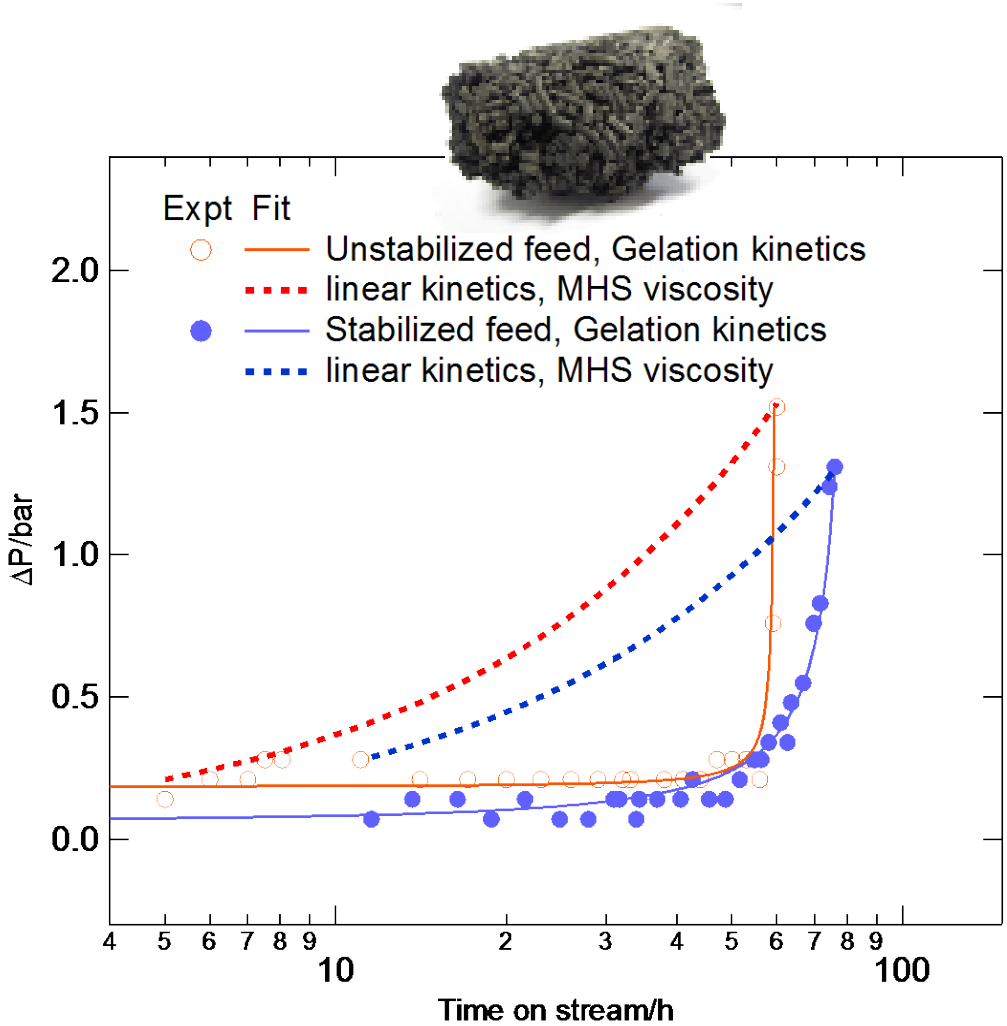
- Major challenge
  - System robustness

In condensed phase speciation at surfaces impact catalysis

Problem: polyvalent centers that nucleate growth (sugars)

Sugars must be removed at relatively low temperatures

General Need: more active catalysts



Catalysis that are faster yet more stable

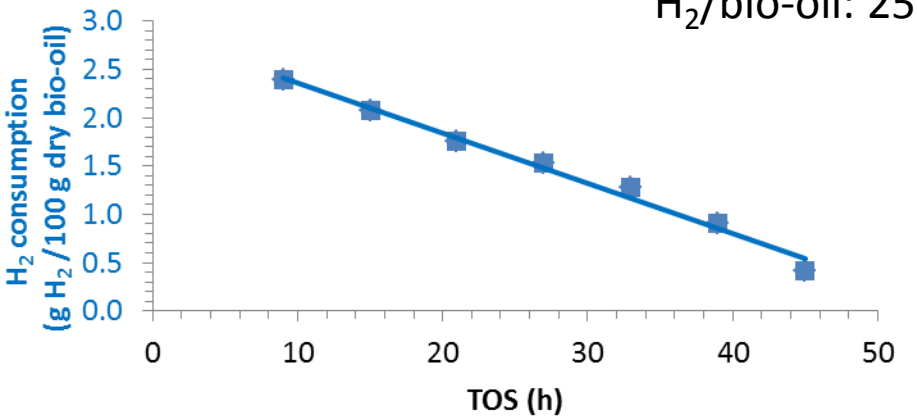
- Major challenge
  - Catalyst poisoning

Non-sulfided catalysts (Ru/TiO_2) have activity to reduce sugars at T < 160 °C

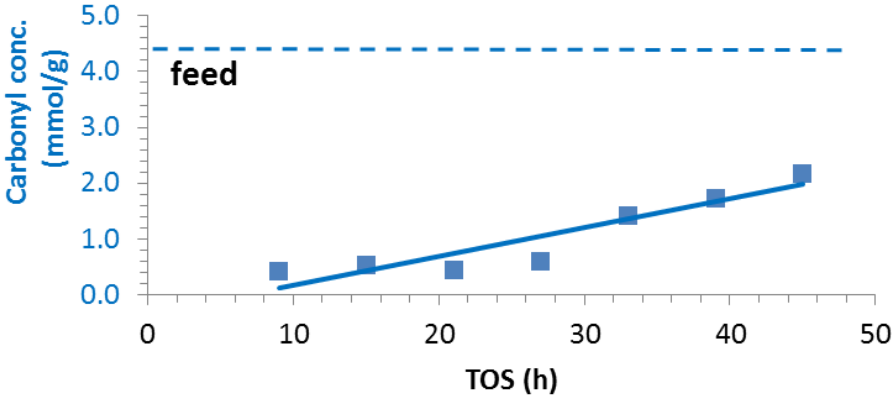
S deactivation (60 ppm)

General Need: understand deactivation pathways and develop new stabilizing functions

Aging test: **Ru/TiO_2**, 160 ˚C, 0.4 LHSV, 1500 psig, H_2/bio-oil: 2500 L/L



H_2 consumption decreases



Decrease in ability to reduce carbonyls

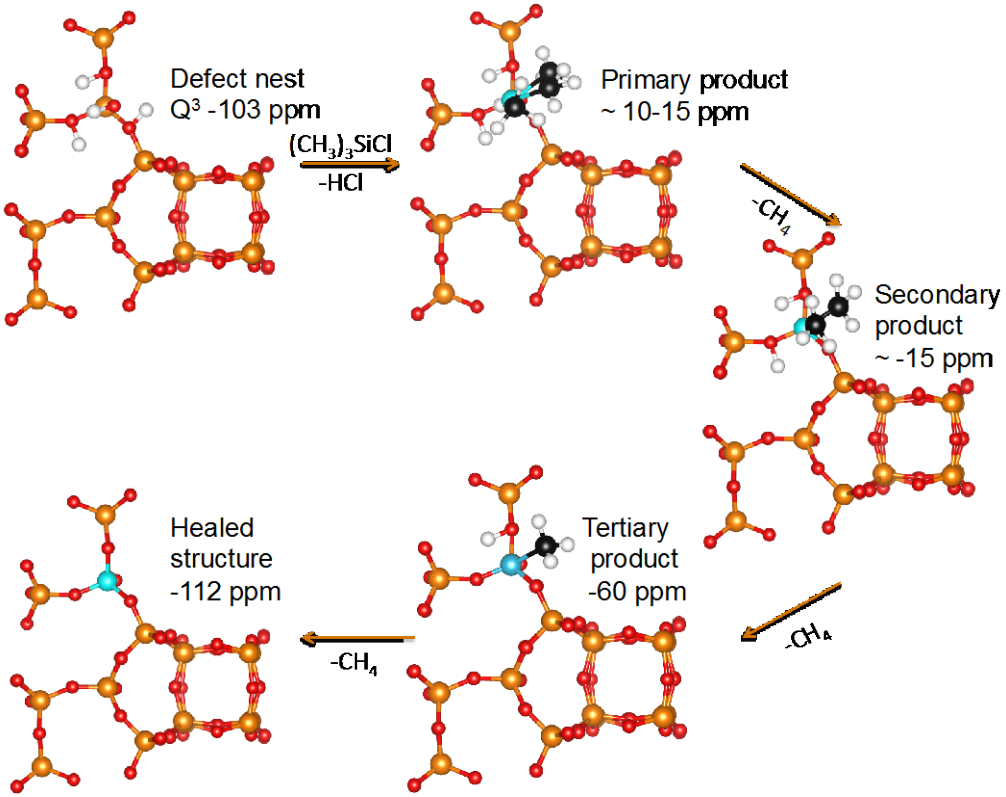
Stable zeolytic materials

- Major challenge
  - Carbon-carbon bond manipulations

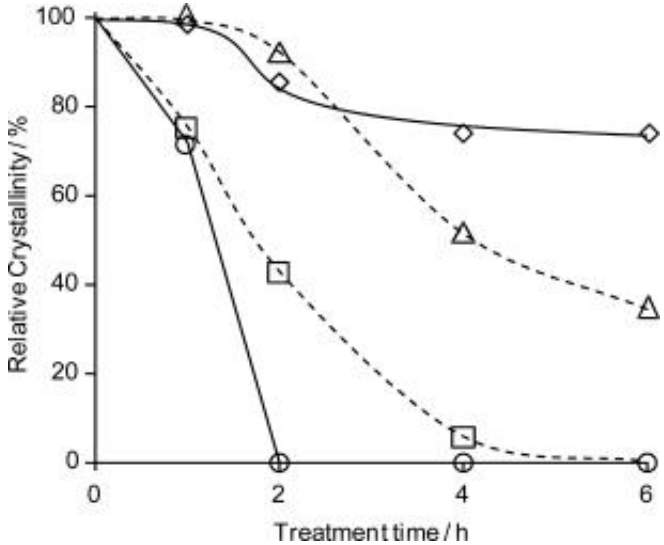
Need for alkylation (small molecules) points to zeolitic materials

Hydrothermal instability is a challenge

General Need: new ways to stabilize supports toward hot water

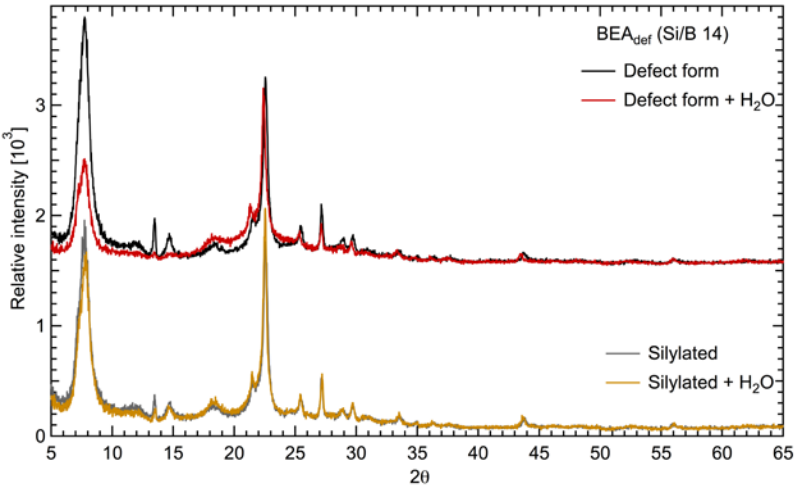


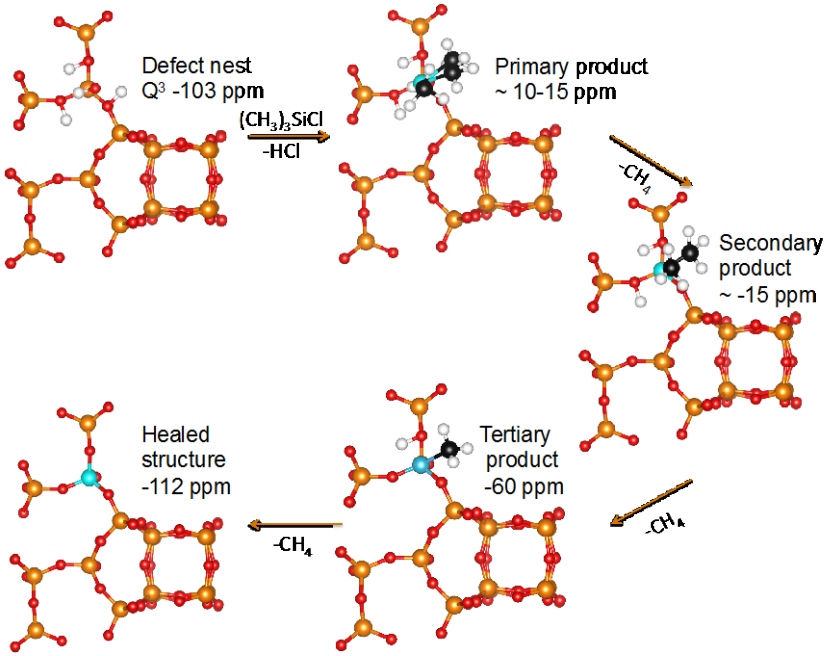
Improving the hydrothermal stability of Zeolites by sylation of defect sites



Relative crystallinity of zeolite Y (Si/Al 40) treated at 150 °C (O) and 200 °C (□) and Y (Si/Al 14) at 150 °C (◆) and 200 °C (Δ).[2]

- Zeolites are critical class of catalysts
- Stability in steam is impressive, stability in hot liquid water is poor.
- Stabilization through post treatment of defect sites via silation reactions





Silation of defect sites

Kinetic data needed for scaling

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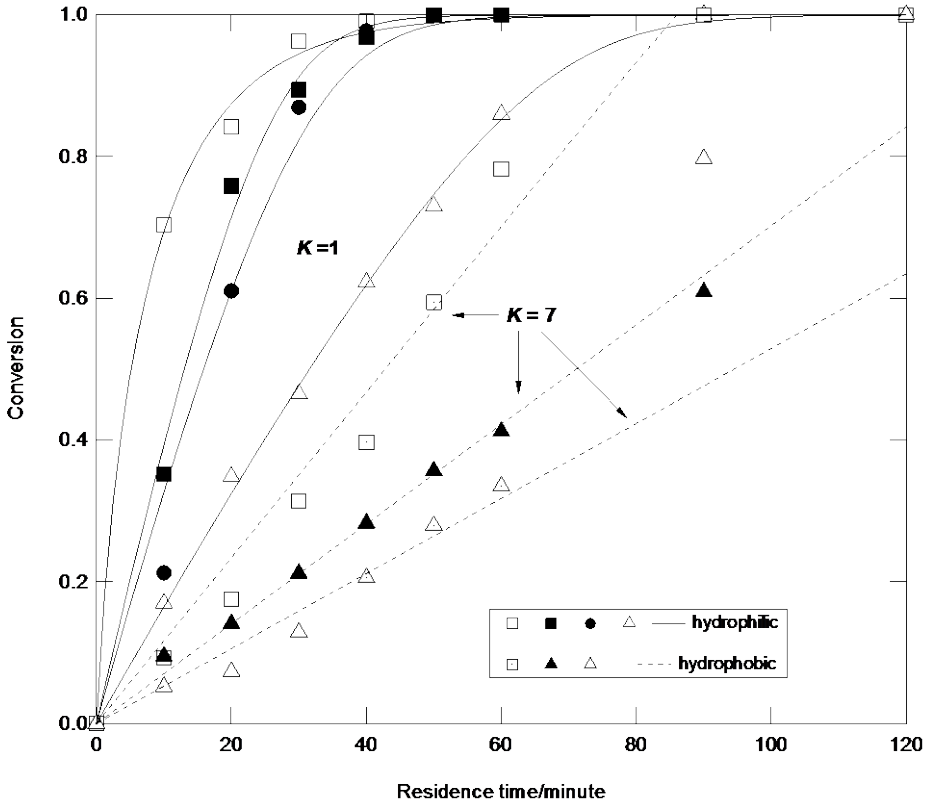
- Major challenge
  - Paucity of intrinsic kinetics measured in real system

    Complex reactions with hundreds of species

    Very little high quality kinetic measurements –

    Yet this is essential for coupling modular units

    General need: new methods to understand complex reaction space



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Hydrogen demand

Understanding impact of adding oxygenates to a petroleum refinery

Petroleum hydrodesulfurization				Petroleum hydrocracking			Pyrolysis oil
Naptha HDS	Kerosene HDS	ATM resid HDS	Gas oil HDS	Mild HCK	Single STG HCK	Resid HCK	HDO
45	555	460	422	358	1150	660	~3400

H_2 chemical consumption, scf/bbl fd (standard cubic feet/barrel feed)

- H_2 in a petroleum refinery is to remove S or hydrocracking
- The need to remove O increases H_2 demand

Opportunity for new systems

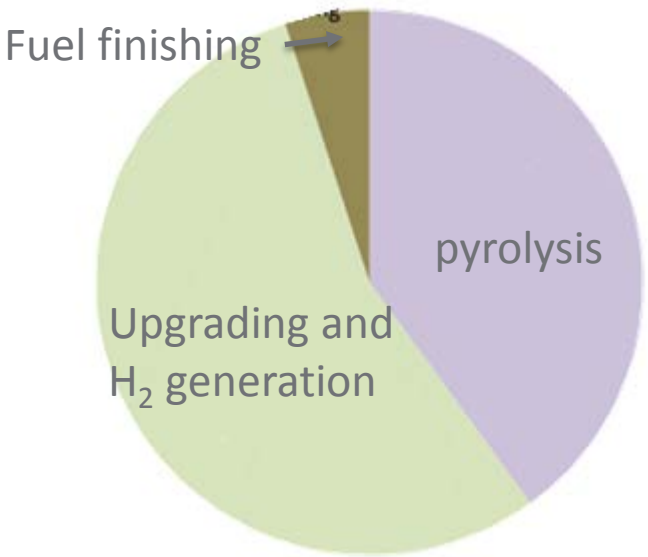
- Major challenge
  - High oxygen content

Upgrading and H_2 generation are the primary CAPEX, OPEX, and energy sinks

Alternatives are also expensive, add complexity, and reduce yield

General need: New technologies for major cost drivers

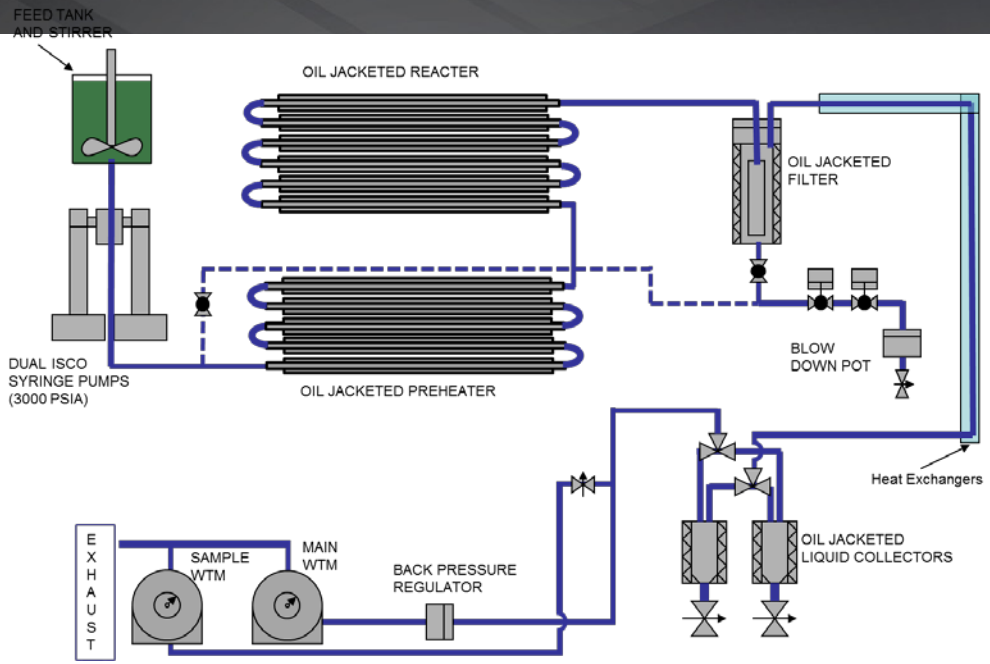
CAPEX distribution (pyrolysis oil):



Biorefinery – pyrolysis of wood

CAPEX = 55%
OPEX = 81%
Primary energy sink

Opportunities for new technology



Design elements

- Convert high water carbon sources into biocrude oil
- Simple, pipe reactor system
- Demonstrated food processing waste, waste water sludge, mixed algae streams

Concept consistent with the big idea

HTL biocrude upgrading

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Upgrading the biocrude

- The clean up step
  - Biocrude filtered and acid washed
- Hydrotreating (24 cc bed)
  - 1500 psi and 400°C
  - Alfa Aesar $CoMo/Al_2O_3$ sulfided
  - LHSV: 0.25 cm^3/ cm^3-cat/h
  - WHSV tested: 0.34 g/g-cat/h
  - H_2 Flow = 125 scc/min
- Duration 103 and 210 h

Biocrude from *Tetraselmis* and waste water sludge are high in lipids and make high quality diesel fuel

No understanding of reaction chemistry

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- Major challenge—
  - No understanding of reaction mechanism

Complex reactions with hundreds of species

Condensed phase—chemistry differs from pyrolysis

General need: Computation and basic mechanistic studies in condensed phase

Quality biocrude oil

Waste water sludge

Biocrude	
Density [g/cm^3, 40°C]	1.00
Viscosity [cSt, 40°C]	571
HHV [MJ/kg, calc]	37.8
TAN [mg_{KOH}/g_{oil}]	65
Oxygen [wt%, dry basis]	8.1%
Nitrogen [wt%, dry basis]	4.3%
Moisture [wt%, KF]	13.0%
Ash [wt%]	0.33%

Half the H_2 demand

Reduce temperature

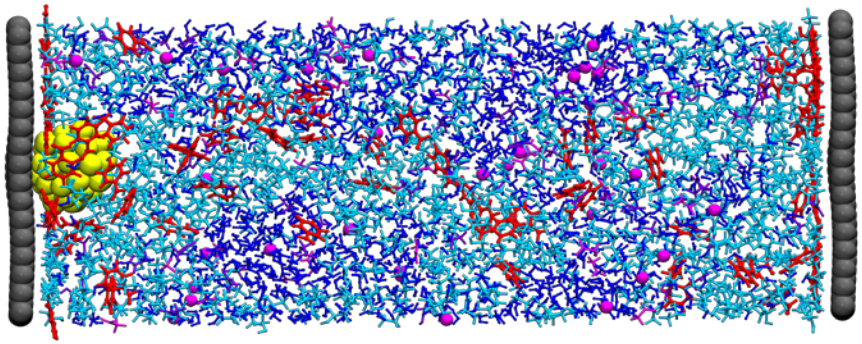
Science underpinnings of condensed phase

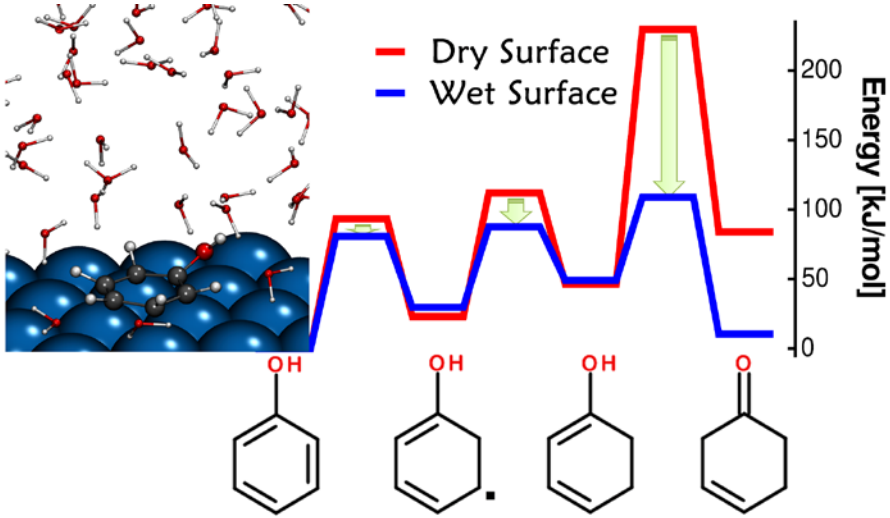
- Major challenge—
  - little mechanistic understanding of condensed phase

Boundary layer were structure, composition and dynamics are radically different than the bulk liquid

General need: science in condensed media

MD Simulation Snapshot at 298K.





Commercial operation today

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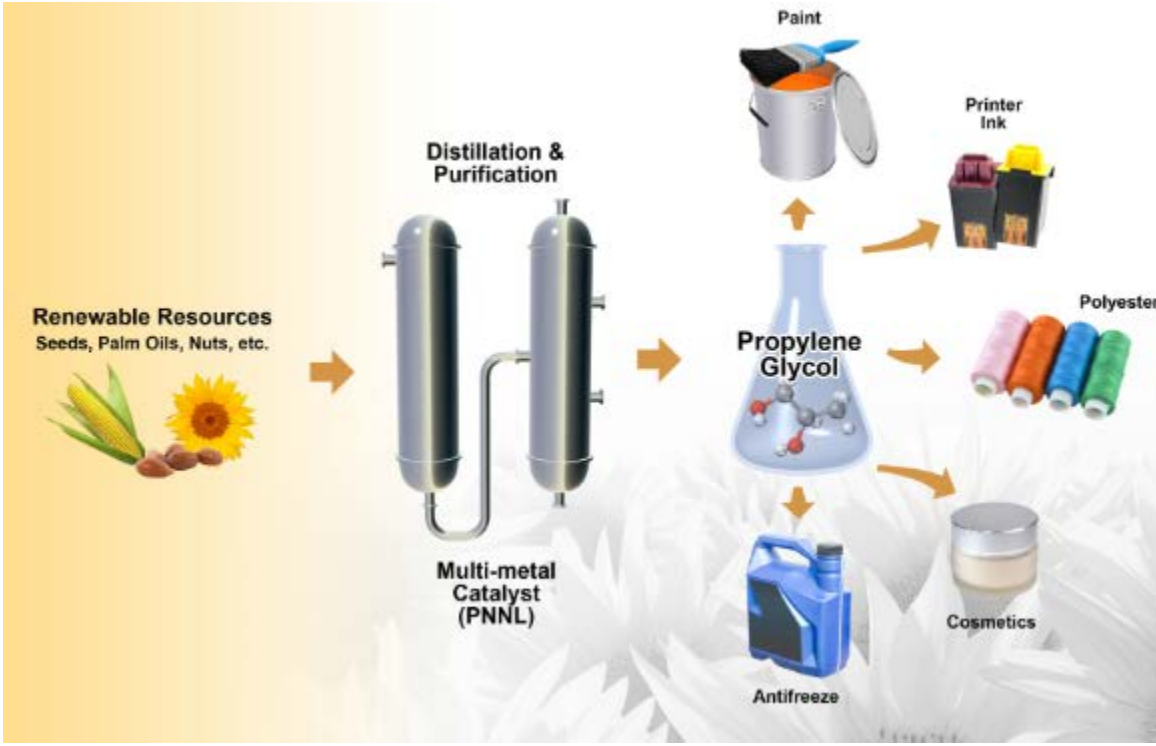
- Major challenge—
  - Catalyst-substrate interactions

Trace byproduct co-elutes

Have little understanding of substrate-support and substrate-metal interactions

General need: analytics, improved understanding of substrate-support/catalyst interactions



Steel mill waste gas (CO) to jet fuel

- Major challenge
  - Selective dehydrations

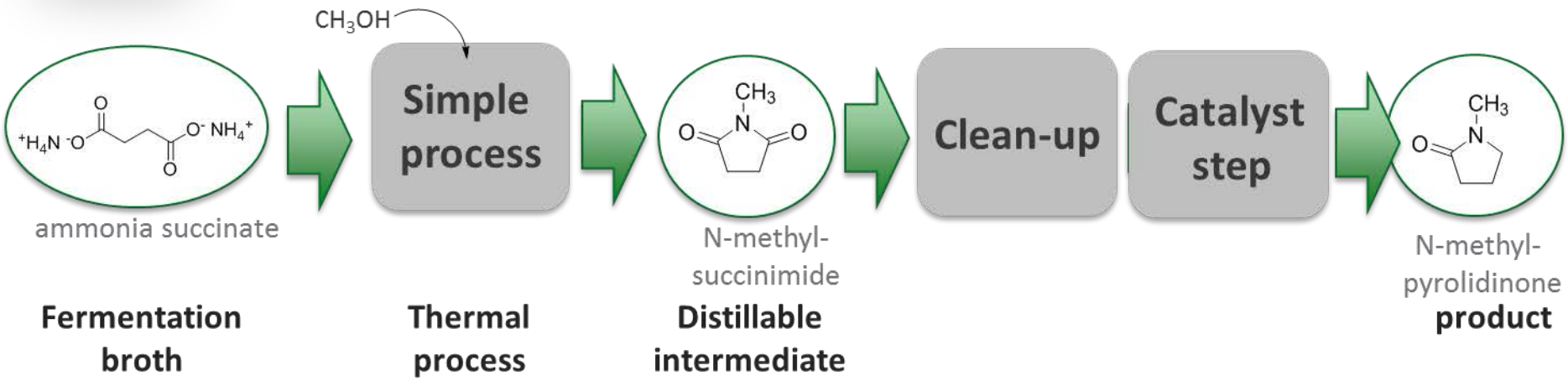
    Dehydrations allows removal of O without loss C or addition of H_2

    Selective dehydrations of polyols is challenging

General Need: guidance on support-hydroxyl interactions that can lead to control of polyfunctional groups

Consider separations and conversions together

1. Develop simple systems that can process complex waste
   - Determine the lowest cost point for “clean up”



Energy Everywhere considerations

1. Develop simple systems that can process complex waste
   - Determine the lowest cost point for “clean up”
   - Understand nature of inhibitors and poisons

2. Understand squeeze points for small scale
   - What systems are less expensive at small scale?
   - Understand nature of inhibitors and poisons
   - Need to have low energy/cost separations

3. Pay attention to analytical data
   - Trace impurities can be Achilles heel
   - e.g., example of full ADM’s propylene glycol plant

Energy Everywhere needs

4. Feedstock analysis on the fly
   - Sorting, conversion vs. recycling?

5. Conversion process technologies that downscale well
   - electrochemistry
   - photochemistry including microwaves; tribochemistry (reactive grinding)

6. Separations that don't require distillations
   - Membrane systems; reactive separations, other technologies?

7. Telemetric sensing and control (algorithms, plant models for feed-forward control)
   - basic mechanistic science needed

Mechanical or electrochemical instead of thermal separations?

- Spinning bed distillation?
- Membrane separation (osmosis)?
- Active transport?

Implications for the technology

Resource dispersion necessitates:

- Low exergy operation (temperatures and pressures near ambient) because there are no economic sinks or sources for enthalpy
- Operation without access to process utilities except electricity (notably, high pressure H_2)
- Compact, robust units (opportunities for process intensification)
- Telemetry and feed-forward control (minimize need for 24/7 skilled operators)

To move forward throwing technologies over the fence will not suffice

Integrate disciplines and science foci

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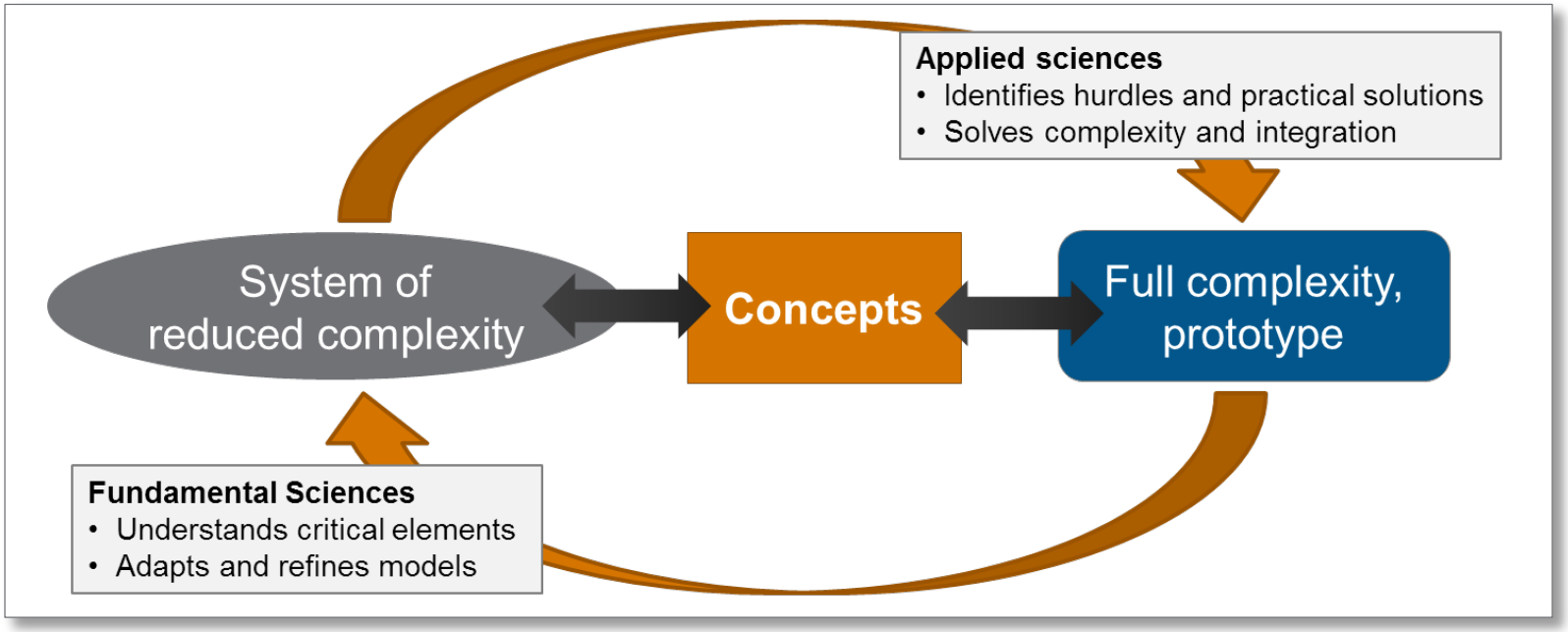
- A call to focus on some common problems in catalysis and conversion technologies
  - Variety of methods for multiple length/time scales



DISCOVERY *in Action*

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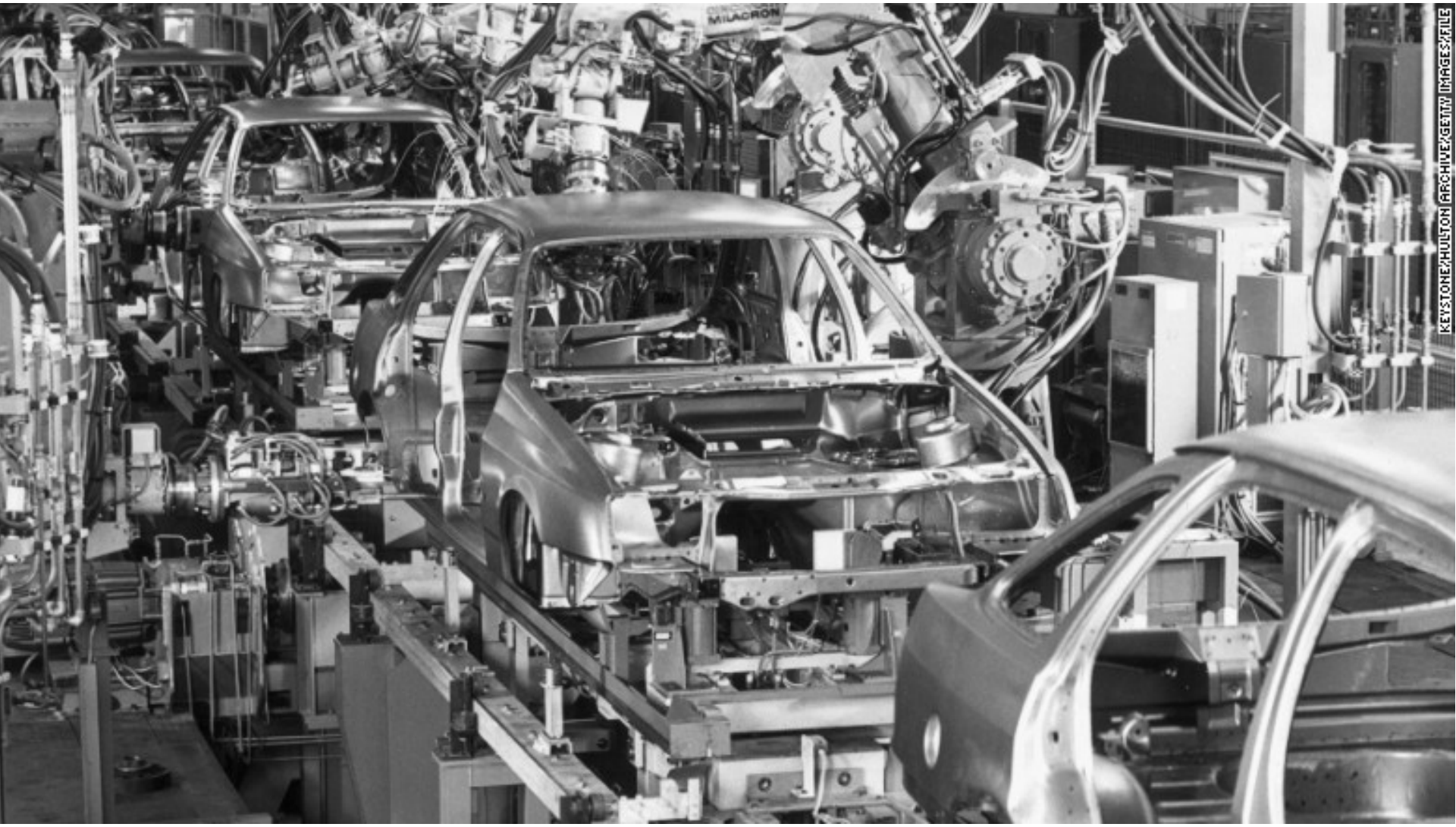
COURTESY FORD


MILACRON
KEYSTONE/HULTON ARCHIVE/GETTY IMAGES/FILE

Standardization of Modular Carbon Conversion for Mass Production

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Standardize the Safety Analysis, Design Basis, Fabrication & Acceptance, and Operational Readiness

National Accelerator - Carbon Conversion Mass Modularization

Design & Safety Basis

- Hazards Analysis
- Design Basis
- Safety Basis

Fabrication & Acceptance

- Fabrication
- Acceptance testing

Operational Readiness

- Configuration Management
- Controls & Diagnostics
- Maintenance & Calibration
- Operator Training & Qualifications

Comparitive fuel properties to a 98% isoparaffin made at PNNL from ethanol

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PNNL-LanzaTech

- Ethanol to Gasoline (61666-113-D1H)[1]
  - RON = 85
  - MON = 81
  - Final Octane (R+M)/2 = 83 (Regular unleaded is 87; Premium unleaded is 91)
- Ethanol to Jet (61666-107-ETJ-FIN)[2]
  - Density = 0.782 (0.775-0.840 for Jet A/JP-8/Jet A-1)
  - Flash Point = 56°C (ASTM D1655 requires > 38°C)
  - Freeze Point = < -70°C (ASTM D1655 requires < -40°C)
- Ethanol to Diesel (61666-77-H7)[3]
  - Cetane = 53.6 (Diesel fuels are typically in the 40-55 range)
  - Cloud Point = -60.1°C (ASTM D 975 is regional, but an extreme case is < -28°C for MN. European standard EN 590 specifies < -34°C for Class 4 arctic diesel)
  - Pour Point = -66.0°C

[1]RON and MON determined via NIR method
[2]Ethanol to Jet data generated by AFRL
[3]Cetane determined by closed cup derived cetane method

Part 1: Catalyst challenges

1. Support stability
2. Deactivation (S)
3. Deactivation (protein)