A Low-Cost High-Yield Process for the Direct Production of High Energy Density Liquid Fuel from Biomass

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2013 BETO Project Peer Review

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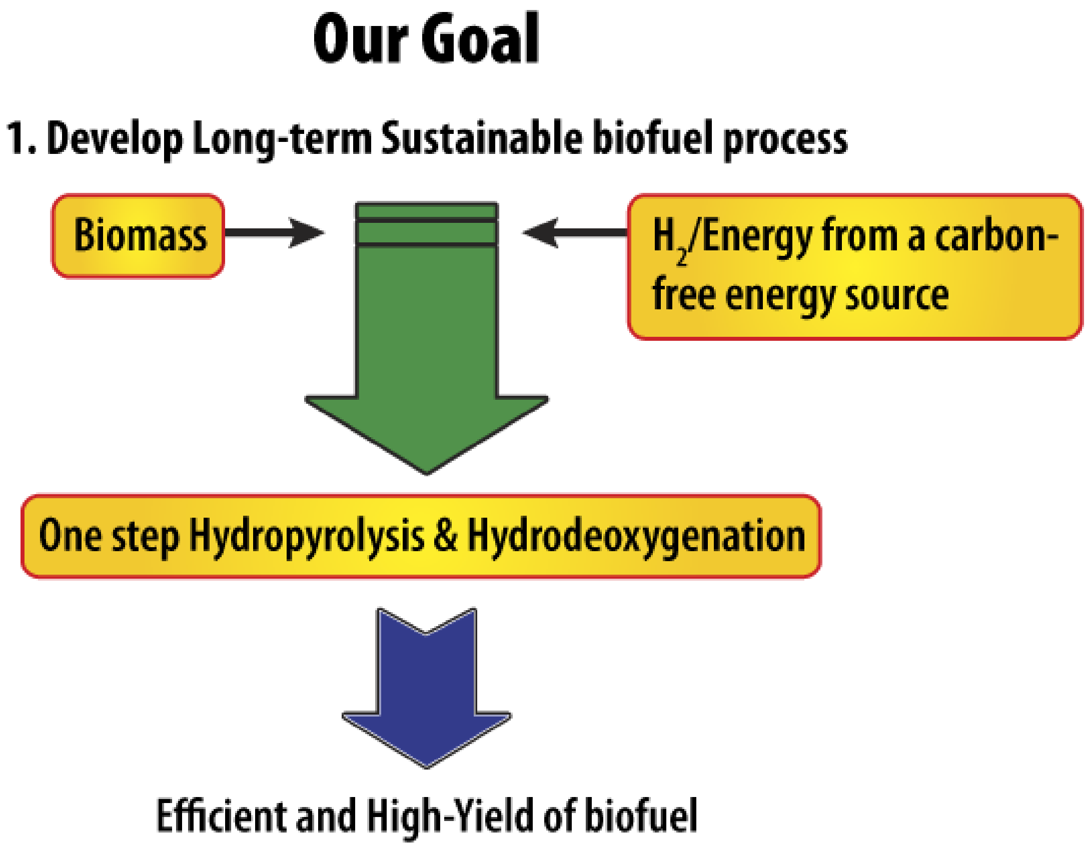
Goal Statement



Our Goal

1. Develop Long-term Sustainable biofuel process

Biomass

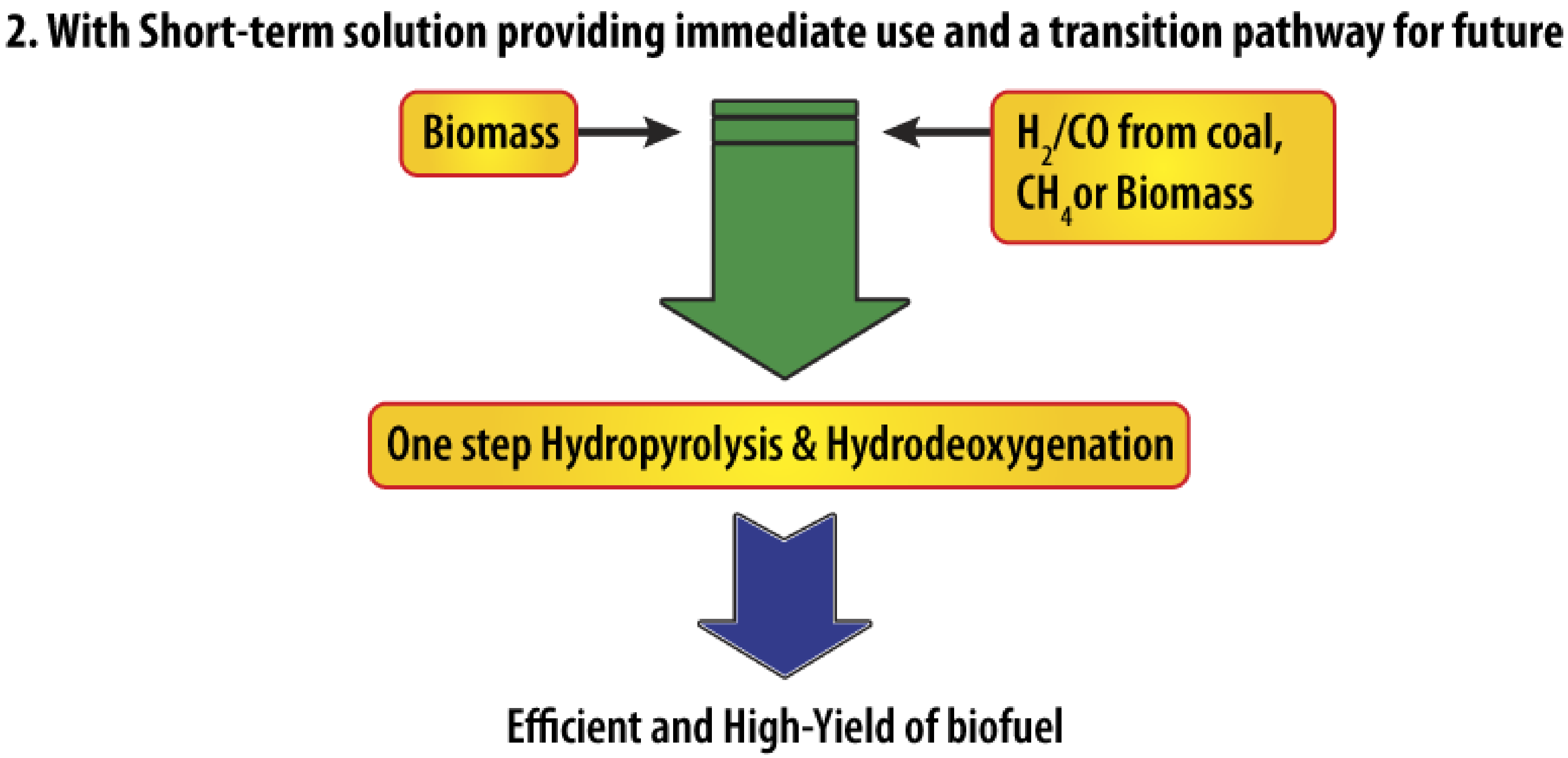
H_2/Energy from a carbon-free energy source

One step Hydropyrolysis & Hydrodeoxygenation

Efficient and High-Yield of biofuel

- **Develop a low-cost process for high yield of liquid fuel from biomass**
- **Sustainable and Synergistic use of Solar H_2 with Biomass (long-term goal)**

Goal Statement



2. With Short-term solution providing immediate use and a transition pathway for future

Biomass

H_2/CO from coal, CH_4 or Biomass

One step Hydropyrolysis & Hydrodeoxygenation

Efficient and High-Yield of biofuel

- Utilize H_2 from non-renewable resources as a transition pathway for future (short-term goal)

Quad Chart Overview

Timeline

- Project start date: June 1st 2008
- Project end date: May 31st, 2013
- Percent complete: 100%

Barriers

- Barriers addressed
  - Tt-E: Pyrolysis of Biomass
  - Tt-G: Fuels Catalyst Development

Partners

- None

Budget

Total Project Funding: $1.6 M total

- $1 M DOE
- $ 0.672 M cost-share

Funding received in FY09:

- $ 775K DOE
- $ 541K Cost Share

Funding received in FY10:

- $ 225K DOE
- $ 131K Cost Share

ARRA Funding: $0

Duration of the project – 5 Years

Average Annual Funding

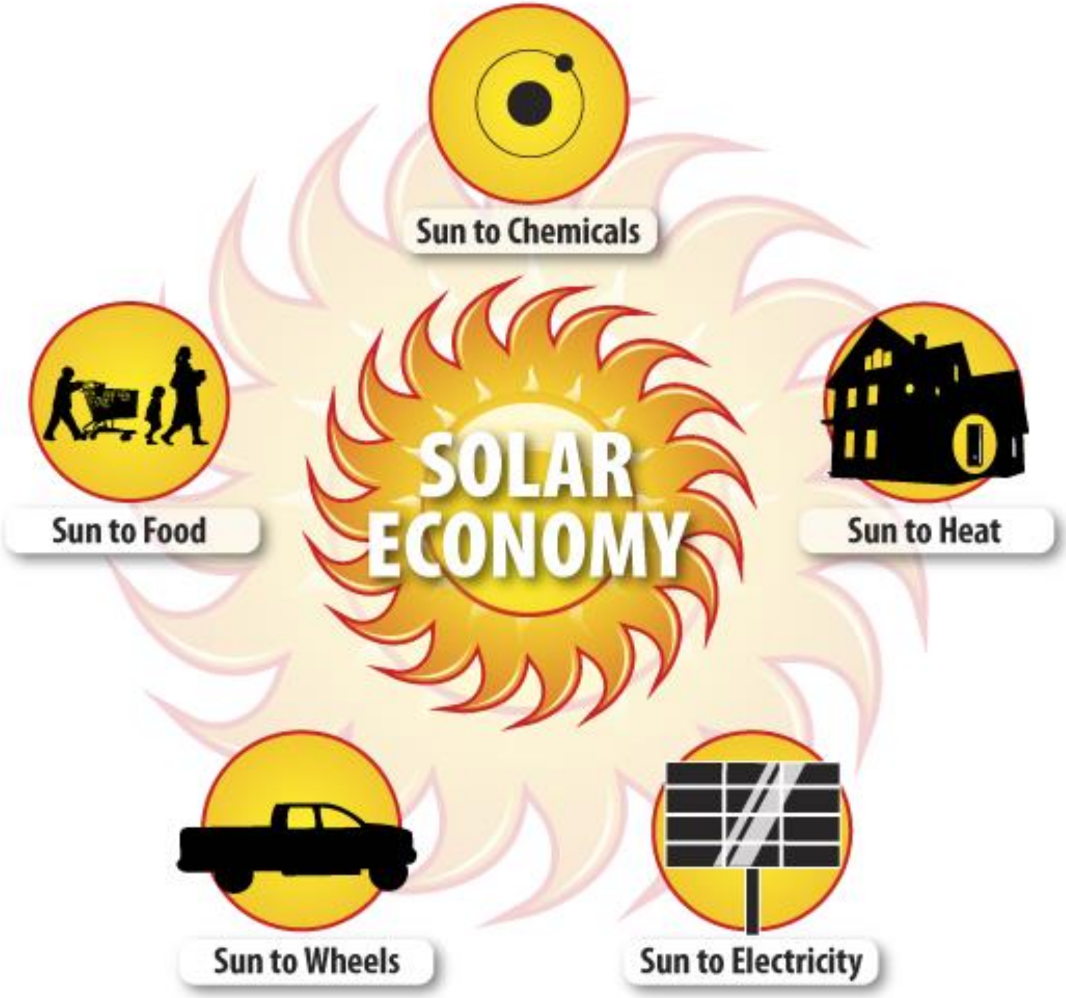
- $ 200K DOE
- $ 134.4K Cost Share

Annual Spending

- FY09 - $339,701 DOE/$197,756 C/S
- FY10 - $284,756 DOE/$275,347 C/S
- FY11 - $174,329 DOE/$30,430 C/S
- FY12 - $131,798 DOE/$56,229 C/S

Project Overview

The Solar Economy Vision



Project Overview

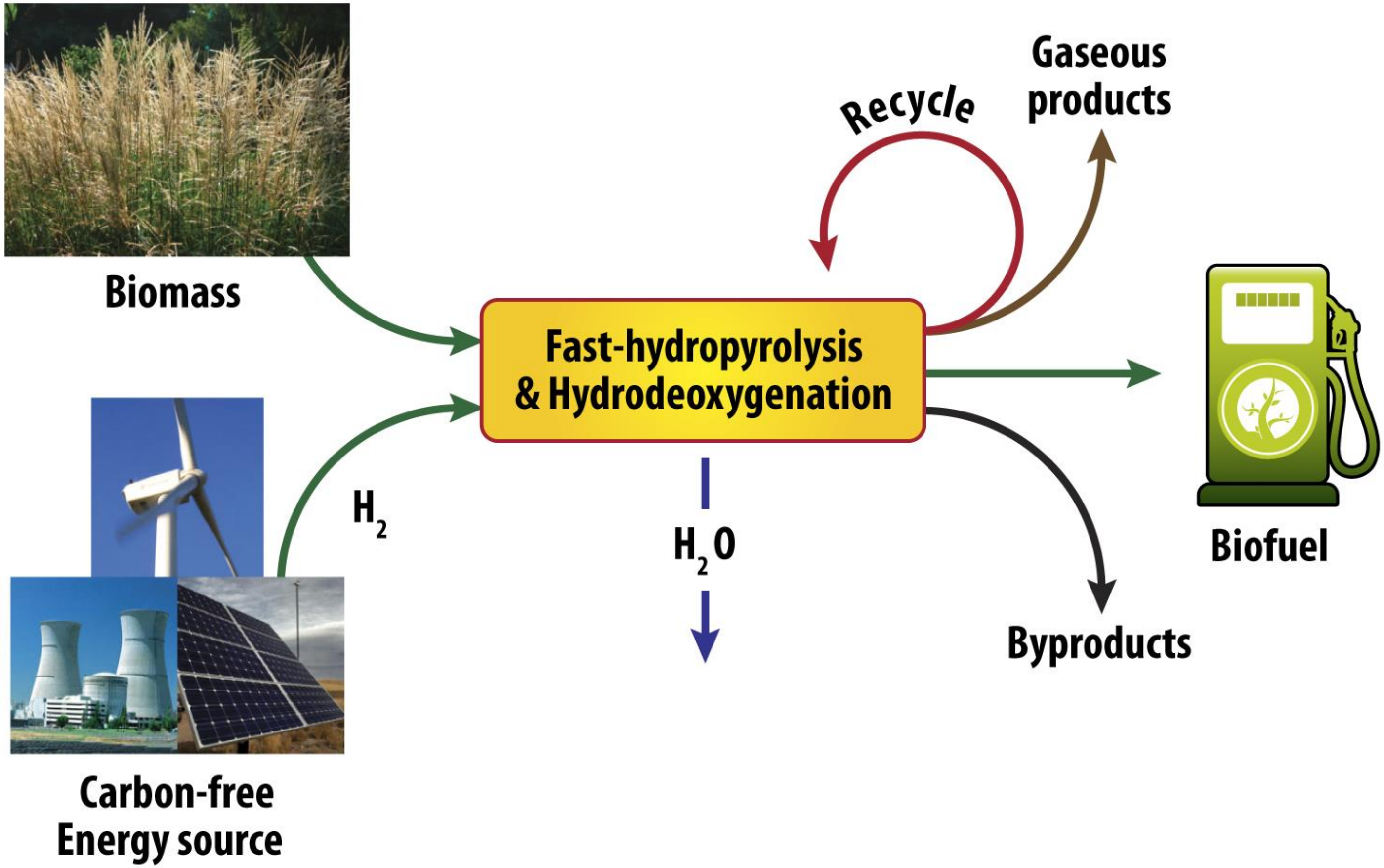
Impact of Process Inefficiency

Biomass	Energy content (MJ/kg)	Energy content (kJ/mol C)	Carbon loss due to conservation of energy (%)	Process Efficiency (%)	Total Carbon loss (%)
Gasoline	43.5	604			
Switchgrass	17.2	485	24.5	75	43.4
Poplar	19.6	455	32.8	75	49.6
Sugar	14.1	423	42.8	97	44.5

Carbon recovery of ~50% is realistic

Project Overview

Fast-Hydropyrolysis: The H_2Bioil Process



Agrawal and Singh, *AIChE J,* 2009

Technical Approach

- Utilize energy systems-based modeling approach to identify set of efficient biomass-to-fuels processes which in turn guides experimental research program
- Generate proof-of-concept results experimentally using versatile, lab-scale, continuous-flow reactor systems
  - Process development and optimization
  - Catalyst discovery
- Utilize model compounds initially to simulate both biomass and biomass-derived oils to reduce chemical complexity

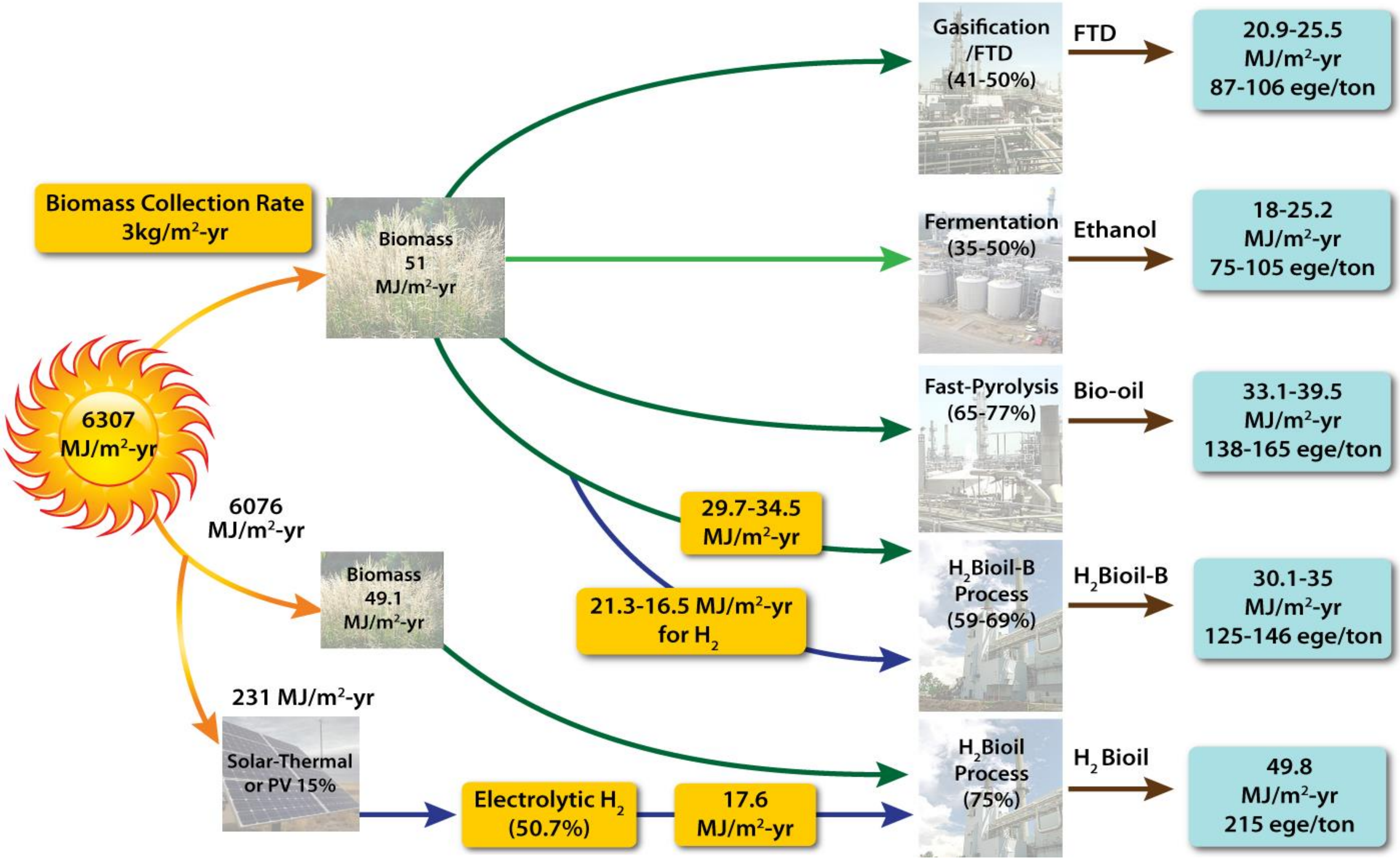
Management Approach

- Quantitative milestones were derived to track technical progress at all levels of research
  - Identification of processes which maximize carbon utilization and sun-to-fuel efficiency
  - Lab-scale research equipment technology development
    - Reliable and safe operation
    - Reactor performance (high heating rates and low residence times)
  - Catalyst and biomass-to-fuel chemistry discovery
    - Develop catalysts for model compounds and biomass
    - Quantitative analysis of products

Management Approach

- Periodic safety and design reviews of key pieces of equipment
  - Safety concerns surrounding H_2 usage
  - Ensuring that equipment is versatile enough for future research
- Go/ no-Go decision points
  - Determine beneficial effects (if any) of increased H_2 pressure on fast-hydropyrolysis.
  - Determine benefits of upgrading hydropyrolysis oil directly in vapor-phase
  - Systems engineering and process modeling to guide experimental efforts

Technical Accomplishments/ Progress/Results



Singh, Delgass, Ribeiro and Agrawal, *Environ. Sci. Tech., 2010*

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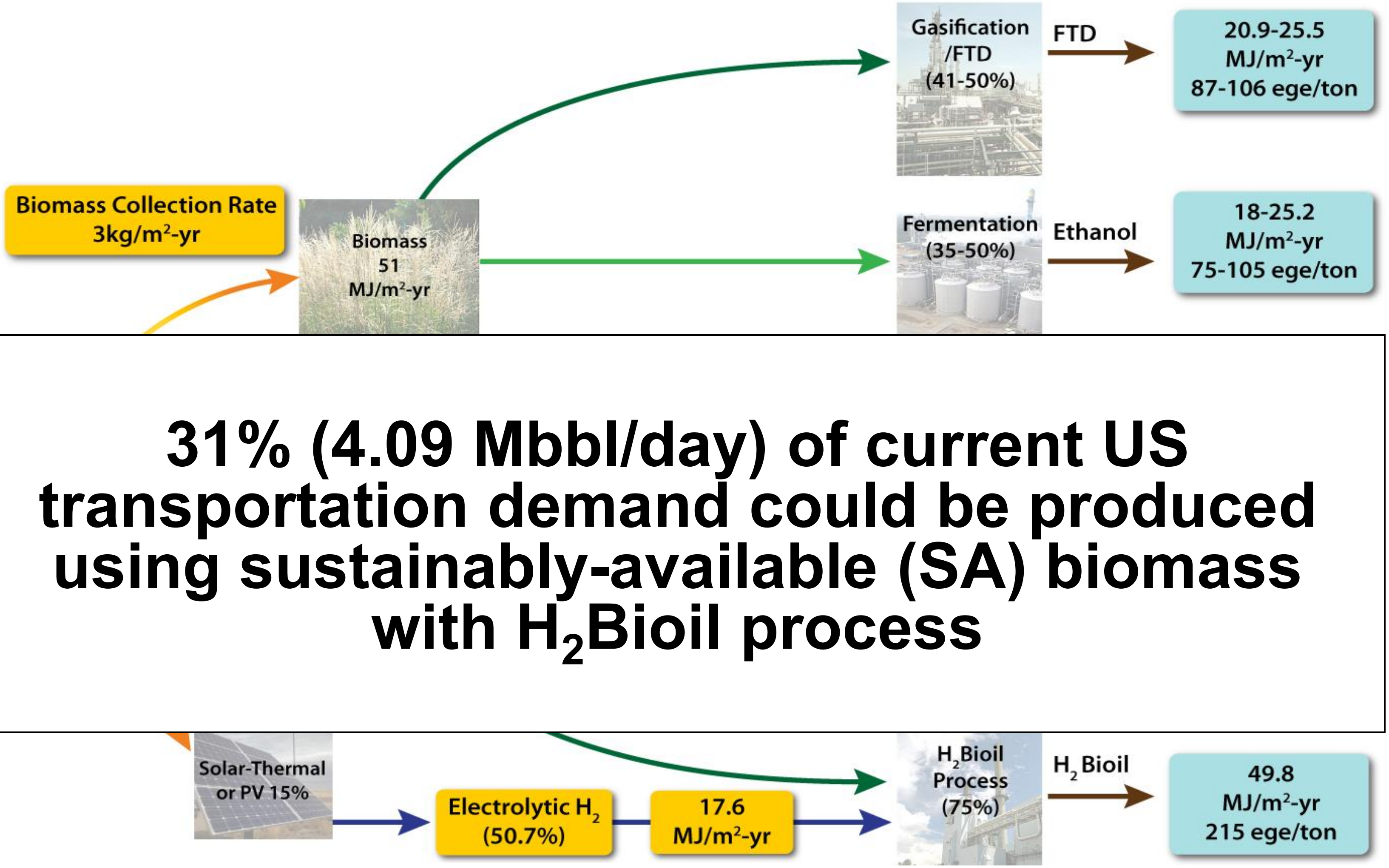


Biomass Collection Rate 3kg/m²-yr

Biomass 51 MJ/m²-yr

Gasification /FTD (41-50%)

FTD

20.9-25.5 MJ/m²-yr 87-106 ege/ton

Fermentation (35-50%)

Ethanol

18-25.2 MJ/m²-yr 75-105 ege/ton

Solar-Thermal or PV 15%

Electrolytic H_2 (50.7%)

17.6 MJ/m²-yr

H_2Bioil Process (75%)

H_2Bioil

49.8 MJ/m²-yr 215 ege/ton

31% (4.09 Mbbl/day) of current US transportation demand could be produced using sustainably-available (SA) biomass with H_2Bioil process

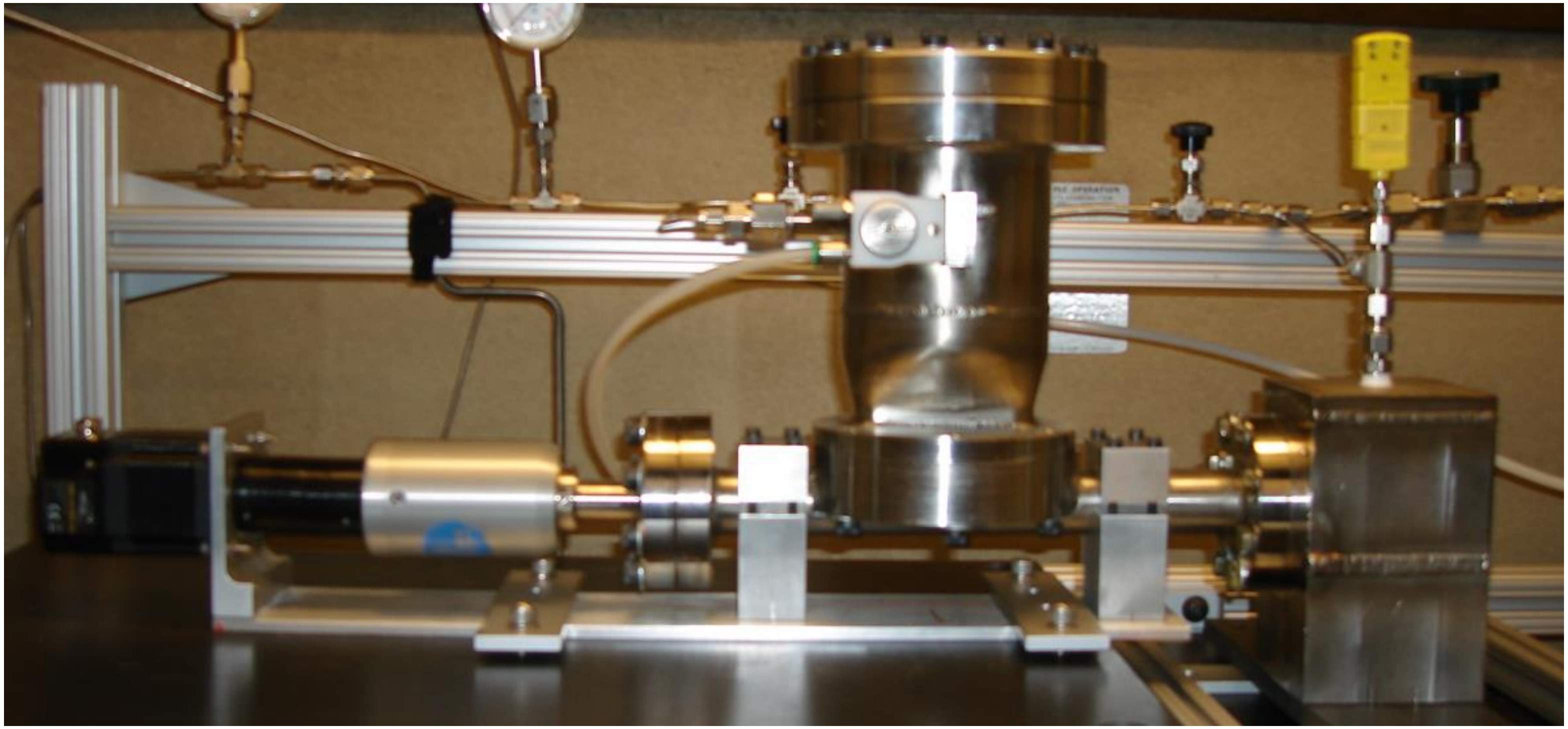
Singh, Delgass, Ribeiro and Agrawal, *Environ. Sci. Tech., 2010*

Technical Accomplishments/ Progress/Results

- Construction Activities (Task A)
  - Lab-scale, high-pressure, screw feeder (M.4.19.1)
  - Continuous, high-pressure, fast-hydropyrolysis reactor (**FHP**) (M.4.19.2)
  - Stand-alone ,fixed-bed, model-compounds reactor system (**FBR**) for catalyst discovery and development (M.4.20.1)

High-Pressure Screw Feeder

Two, high-pressure screw feeders have been built and tested which are capable of feeding 0.1-40 g min^{-1} solids at pressures up to 67 bar (meets A.ML.1)



Continuous-Flow High-Pressure Fast-Hydropyrolysis (FHP) Reactors

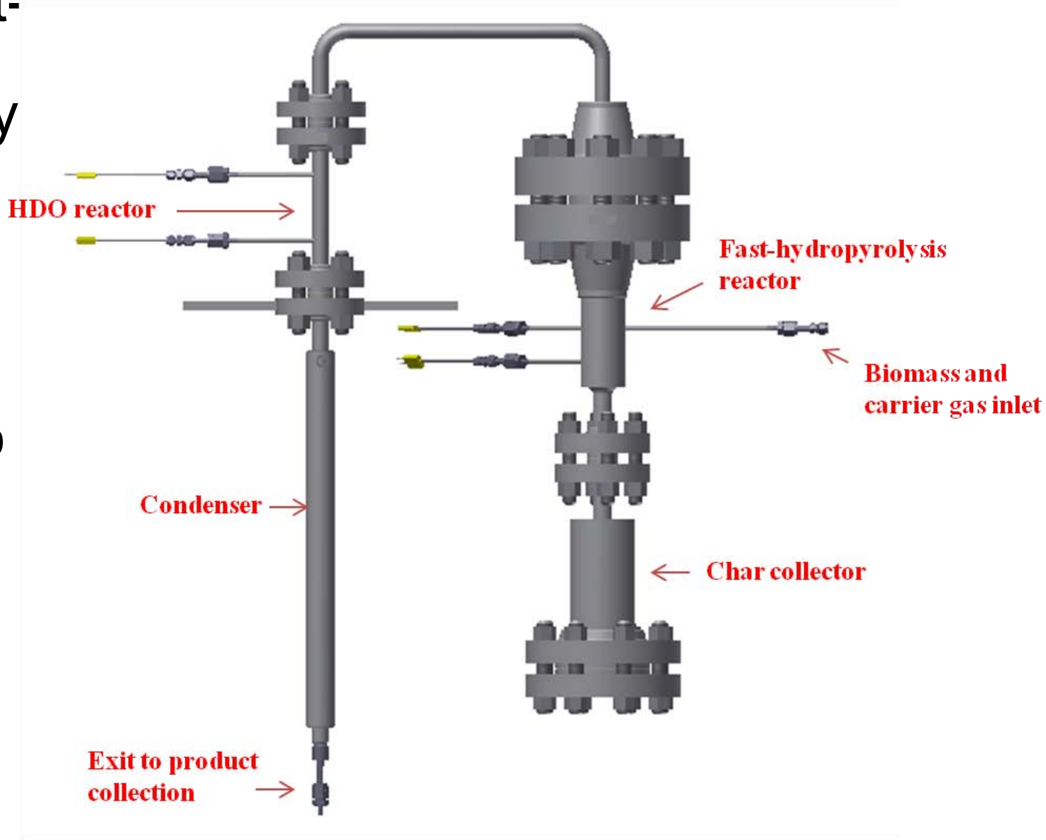
We have screened several prototype reactor configurations at pressures up to 50 bar in He using cellulose as a model biomass feedstock

- **Fluidized-bed (design study only)**
  - Requirement of high gas flows for fluidization could not be safely met within our laboratory constraints
- **Free-fall**
  - Reactor height needed for sufficient biomass conversion could not be met within our laboratory constraints
- **Ablative**
  - Issues of fouling of heated surface with char
- **Cyclone**
  - Compact design
  - Reliable operation without clogging

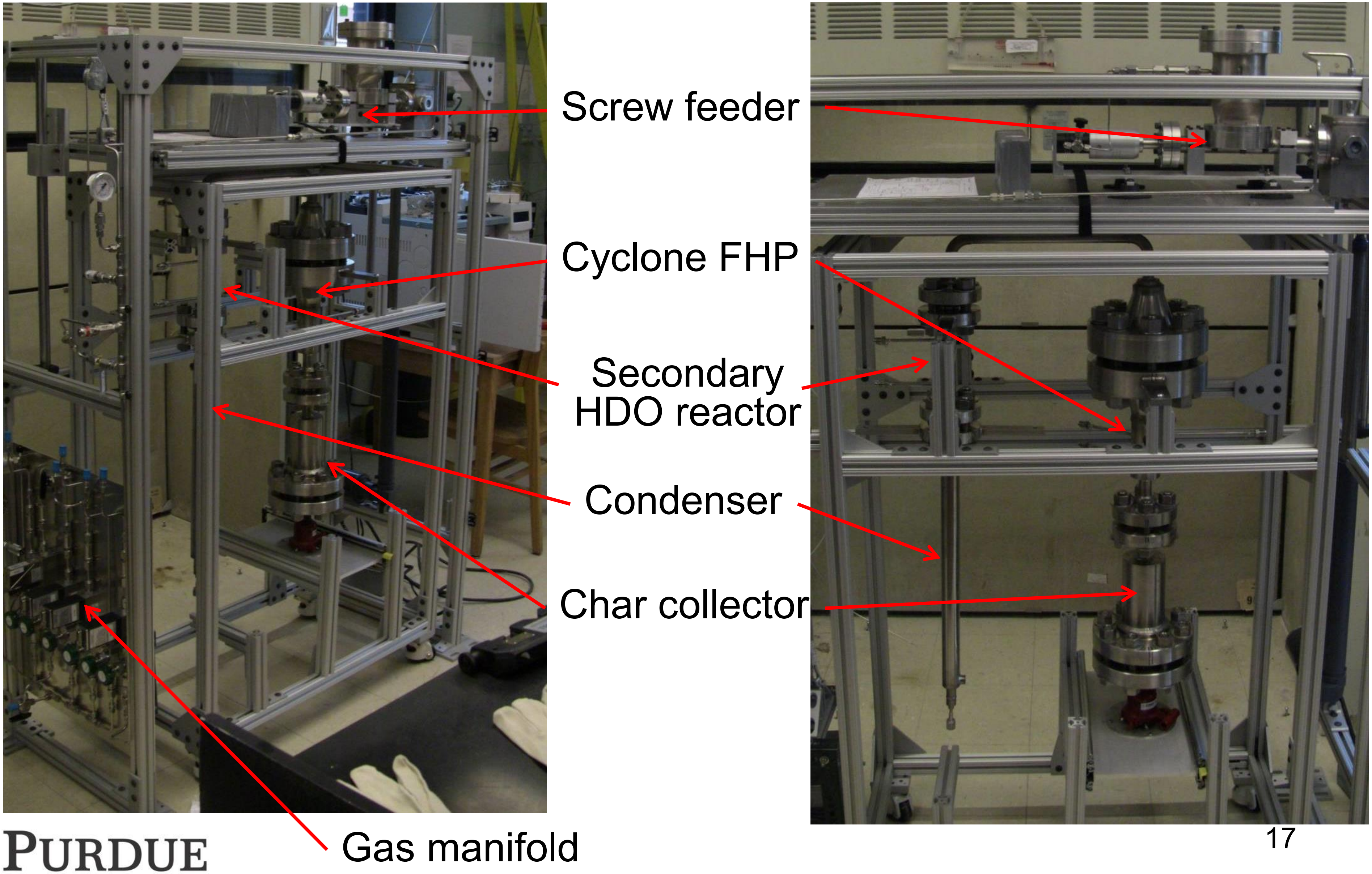
Continuous-Flow FHP Reactor

2nd generation cyclone-type fast-hydropyrolysis (FHP) reactor which was designed to be safely operated at up to 100 bar H_2, 650°C

- Features
  - High inlet gas velocities to avoid clogging of biomass
  - Compact, low vapor residence times
  - On-stream vapor-phase fixed-bed reactor
  - Process monitoring and control using custom built LabVIEW software



Continuous-Flow FHP Reactor



Screw feeder

Cyclone FHP

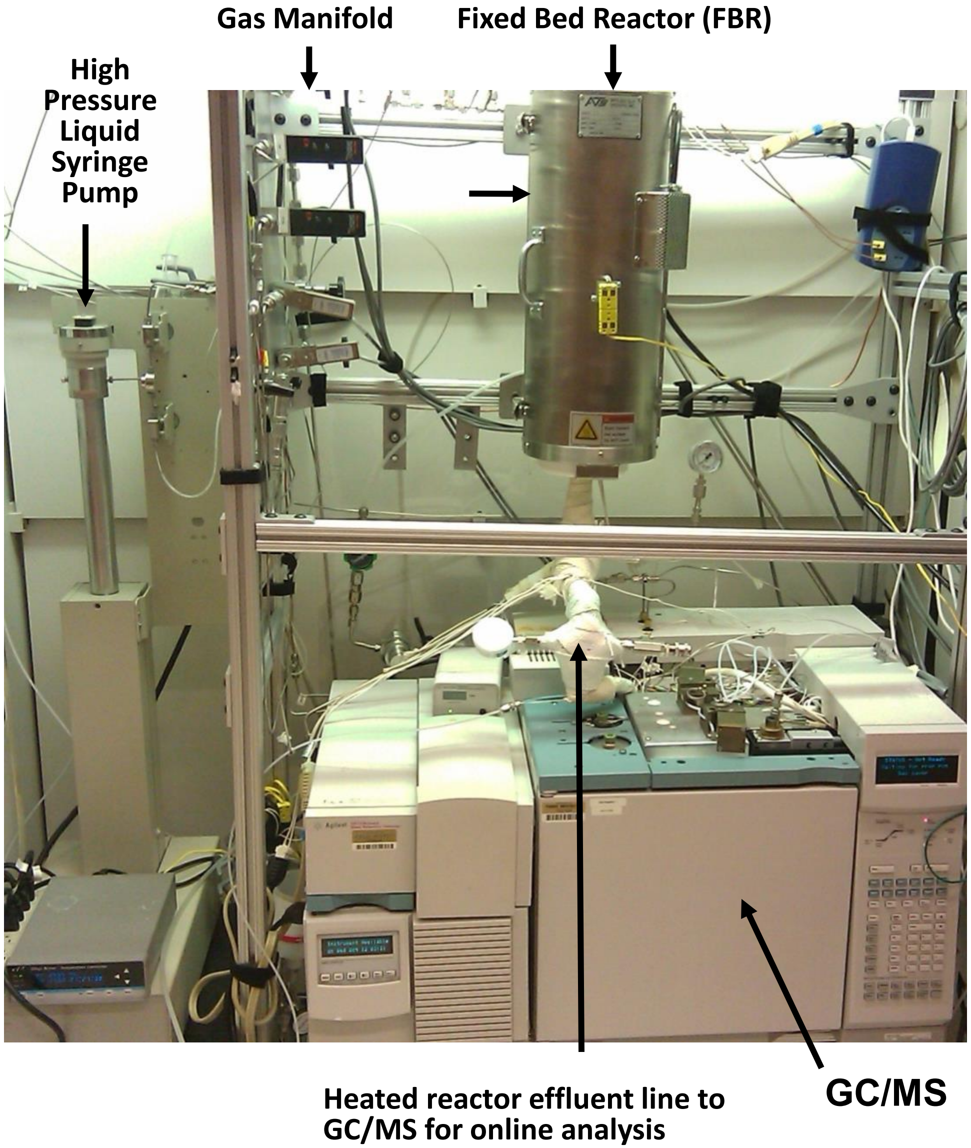
Secondary HDO reactor

Condenser

Char collector

Gas manifold

Stand-Alone Fixed-Bed Reactor (FBR) for HDO Studies



- We have built a stand-alone fixed-bed reactor which is capable of operating at pressures up to 100 bar and >500 °C
  - Liquid reactant feed and vaporization system
  - Gas manifold (MFC) for H_2, CO, CH_4, and air
  - Online product analysis by GC/MS
- Ability to study various model compounds representative of cellulose and lignin derived oils

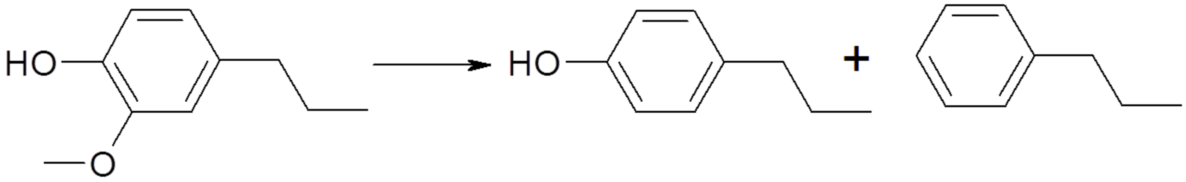
Technical Accomplishments/ Progress/Results

- Task B: Model Compounds Study (M 4.20.1)
  - Conventional pyrolysis and hydropyrolysis in a single stage with model biomass compounds
  - Catalyst testing and development using model compounds

Lignin Model Compound: Dihydroeugenol

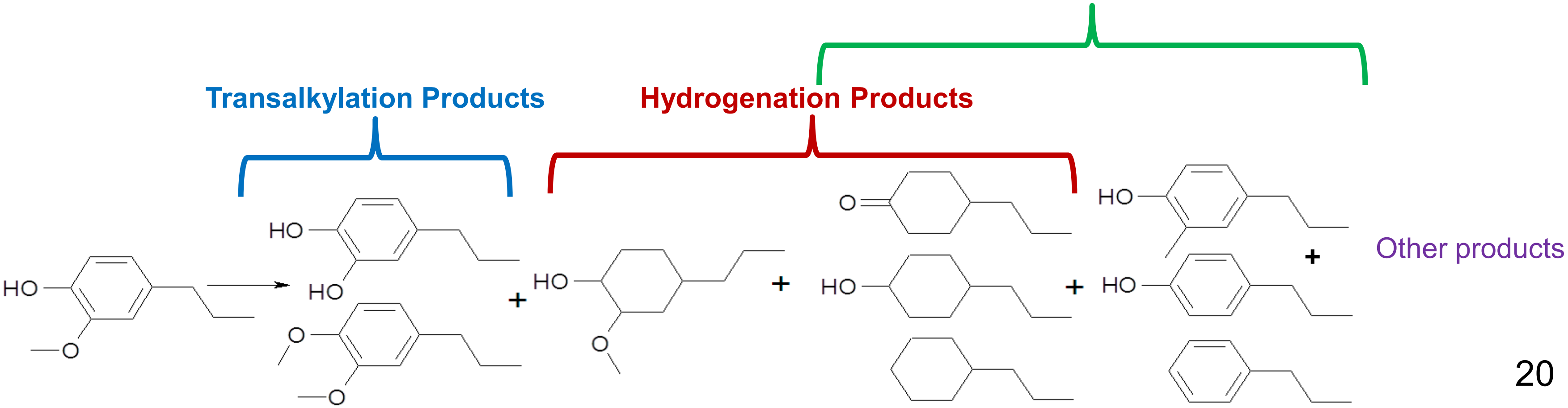
GOAL: Selective cleavage of oxygen from ring, without hydrogenation

(optimize selectivity to propylbenzene)

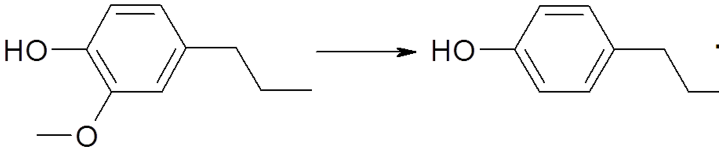


2-methoxy-4-propyl phenol (ie Dihydroeugenol)

- Dihydroeugenol contains a variety of functional groups ideal for studying catalyst reactivity towards lignin-derived Compounds
- Catalysts: 2%Pt/ZrO_2 & 2%Ru/ZrO_2
- Conditions: 300°C, 0-23 bar hydrogen partial pressure, 0-01-1.2 bar Dihydroeugenol partial pressure, WHSV range of 0.1-10 g hr $^{-1}$ g cat $^{-1}$



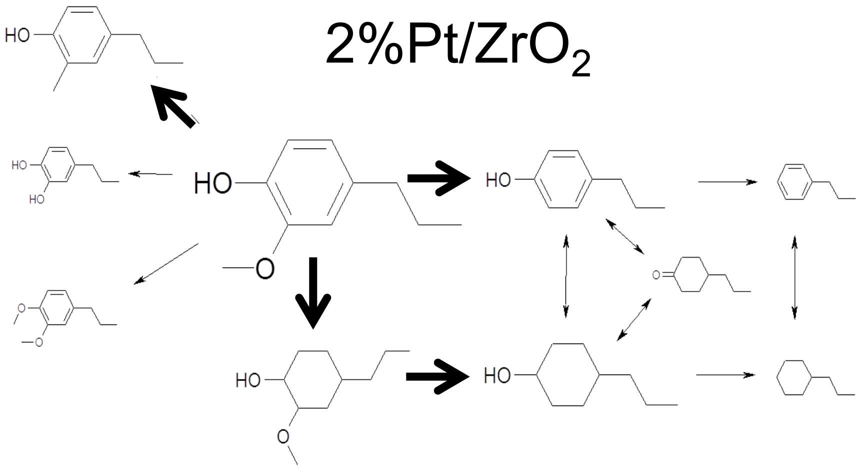
HDO Studies using Stand-alone FBR on Lignin Model Compound

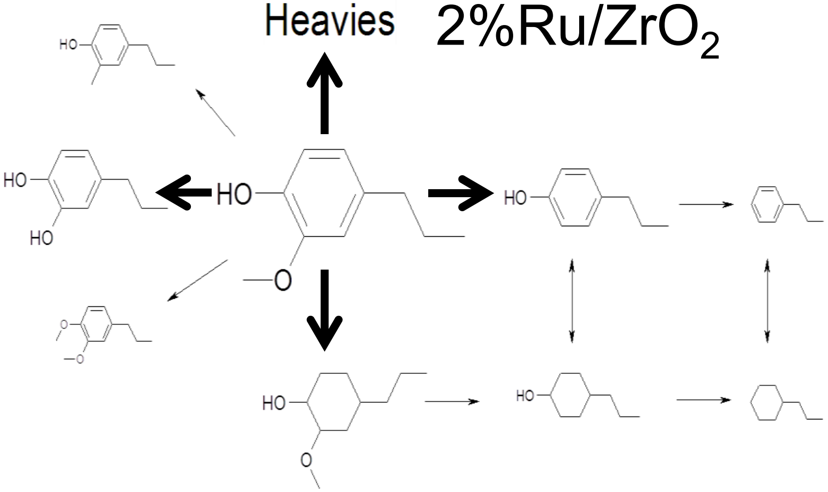


- Promising Catalysts:
    - 2%Ru/ZrO_2
    - 2%Pt/ZrO_2
- Catalysts exhibited methoxy cleavage activity to 4-propyl-phenol at 300-500 °C
    - Significant increase in rate with H_2 pressure and temperature
- <u>HDO activity on the 2%Ru/ZrO_2 catalyst meet our oxygen reduction milestone, B.ML.1</u>
    - 35 wt% reduction in oxygen content from molecule containing least 20 wt% oxygen.

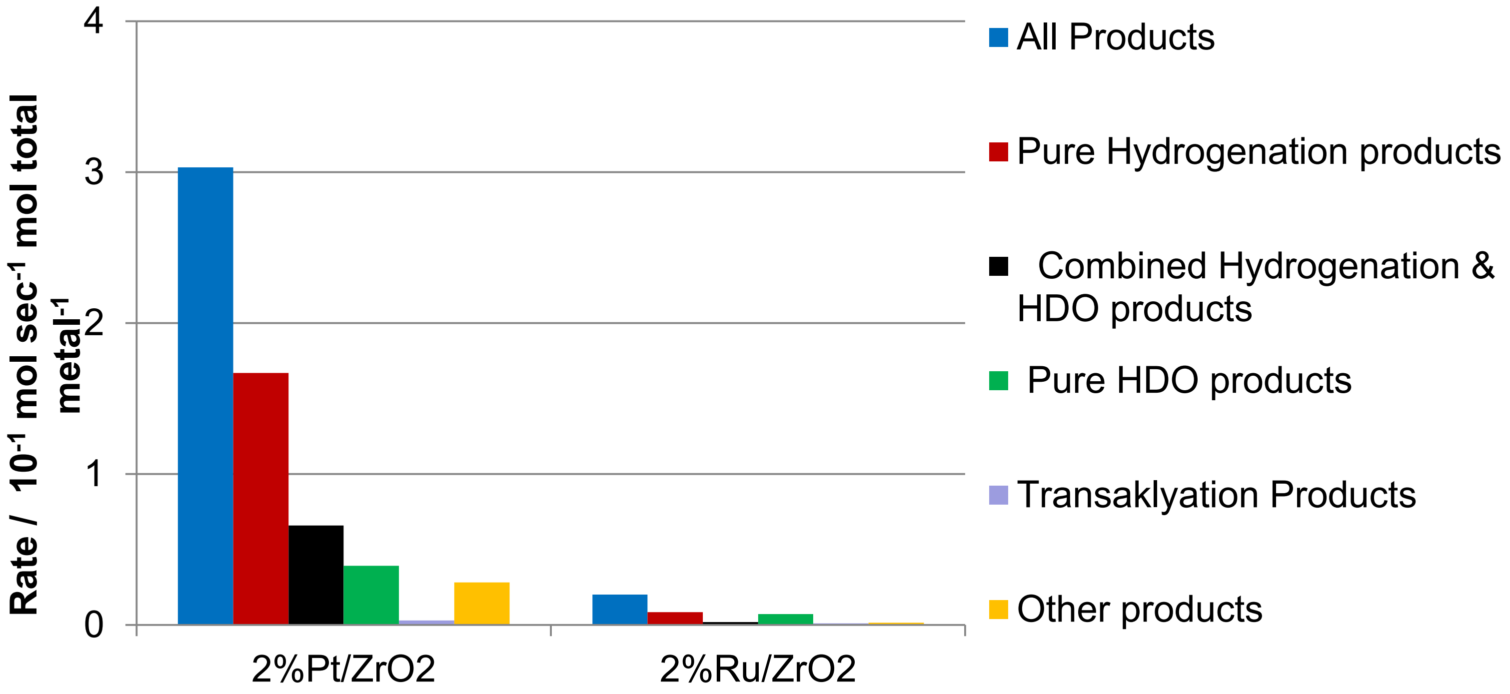
Lignin Model Compound Dihydroeugnol Reaction Pathways

- HDO pathway
  - Series reaction : methoxy group removal, followed by phenol group removal
  - Deoxygenation of methoxy group
    - Lose of methyl to form biphenyl species, which deoxygenated
    - Direct cleavage of methoxy group
      - See both methane and methanol as minor products
- Transalkylation
  - Lose of methyl group from methoxy
  - Methyl group attaches to ring and to phenol group to form dimethoxy species
- Hydrogenation
  - Hydrogenation occurs later for Ru than for Pt





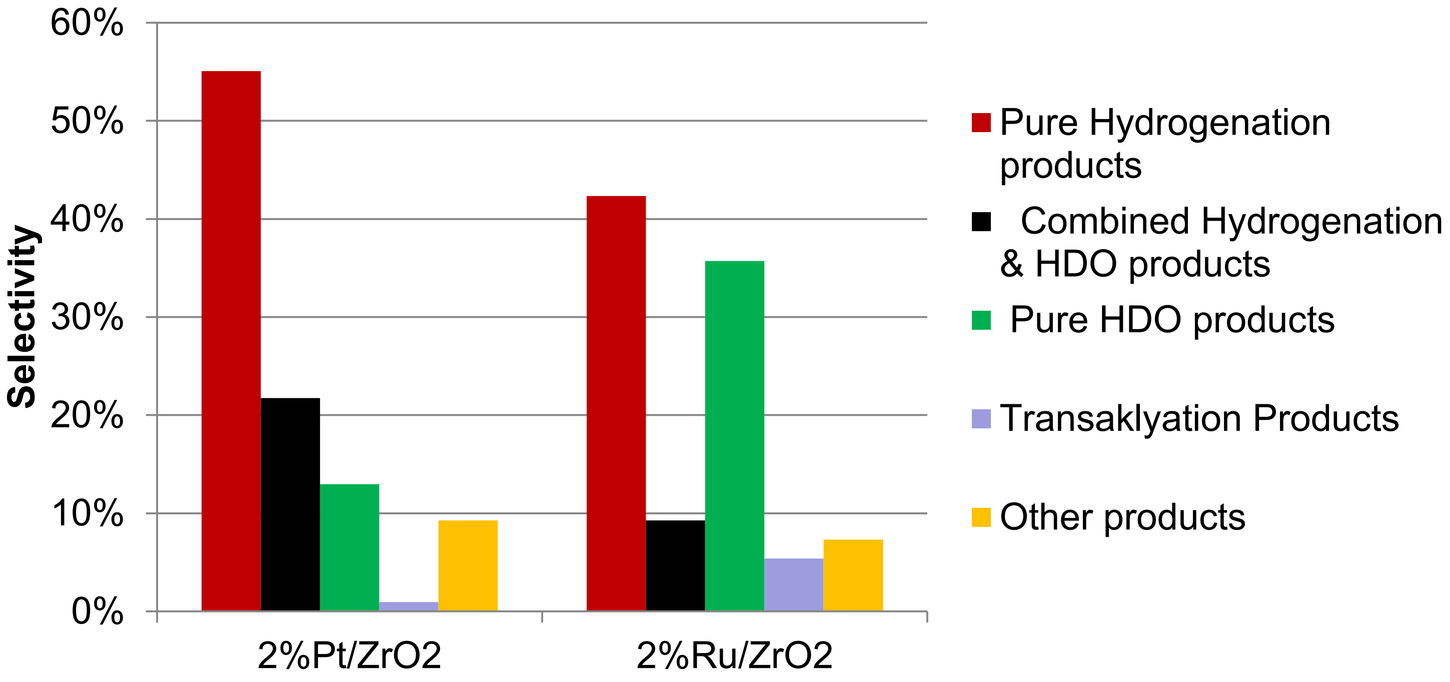
Lignin Model Compound HDO - Catalyst Rates



- 2%Pt/ZrO_2 has **15x** larger than rate on 2%Ru/ZrO_2

- Reaction Conditions of 300°C at 350psig in 2.6 L/min H_2 and 0.06 ml/min Dihydroeugenol
- Rate calculated as mols of product per second per mol of total metal

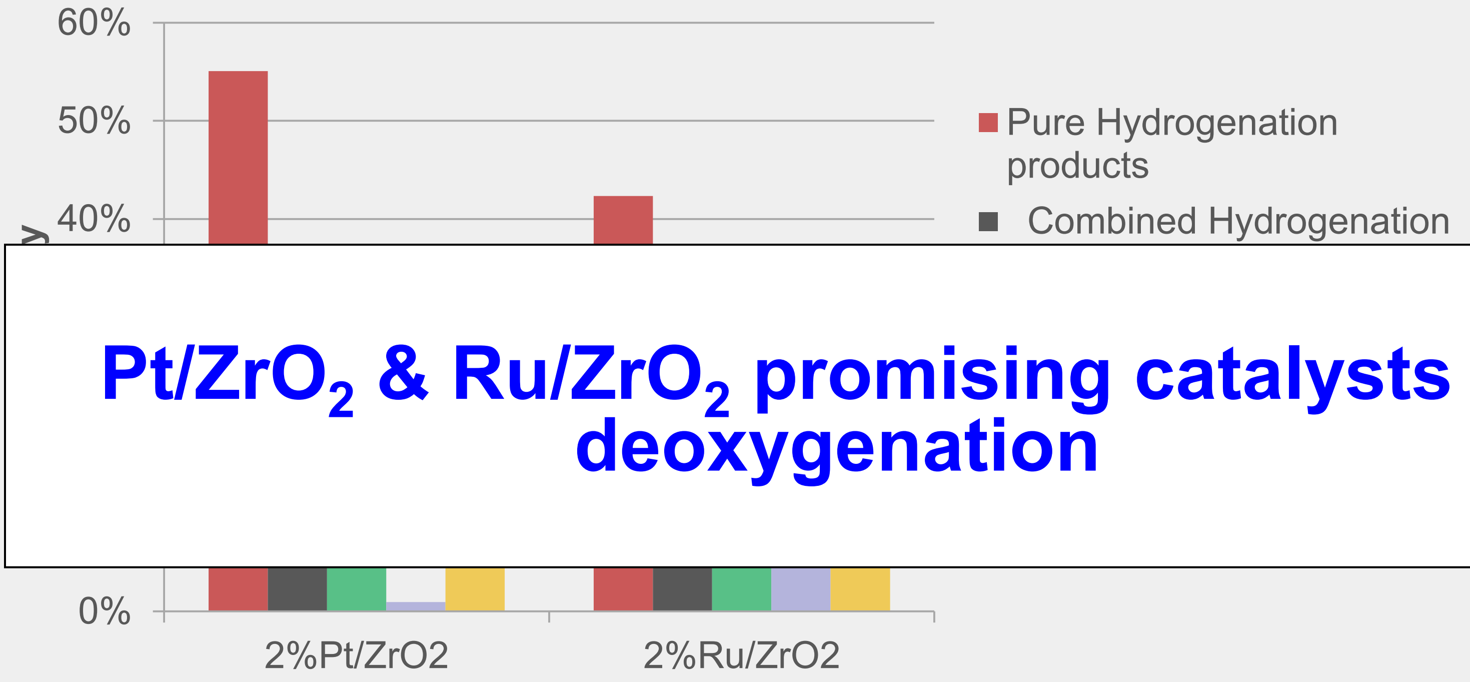
Lignin Model Compound HDO - Catalyst Selectivity



- 2%Pt/ZrO_2 has higher selectivity to hydrogenation products than HDO products
- 2%Ru/ZrO_2 has ~**3x** higher selectivity to HDO products at same conversion than 2%Pt/ZrO_2

- Reaction Conditions of 300°C at 350psig and conversion of 5%
- Rate calculated as mols of product per second per mol of total metal

Lignin Model Compound HDO - Catalyst Selectivity

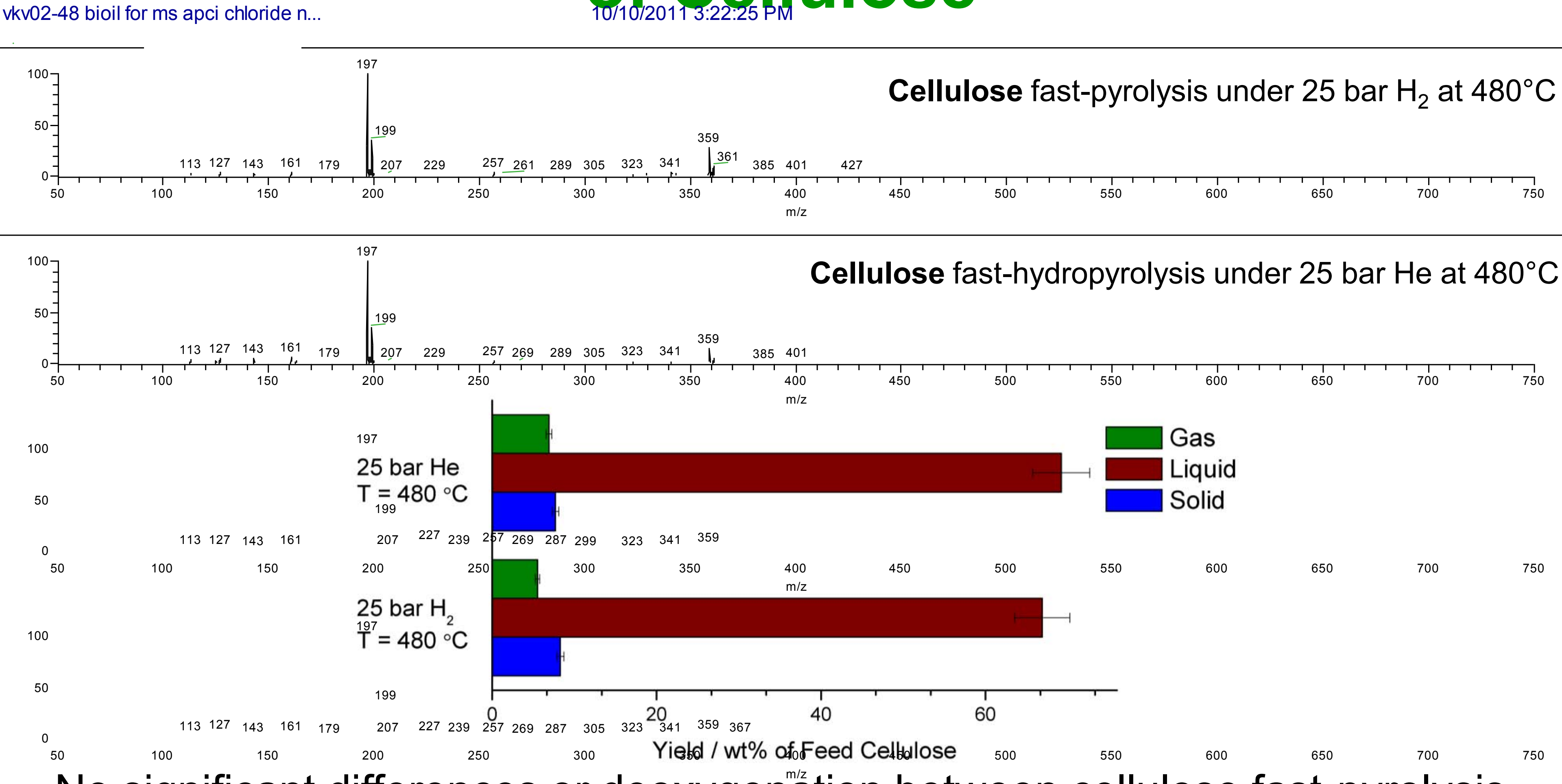


Pt/ZrO$_2$ & Ru/ZrO$_2$ promising catalysts for deoxygenation

- 2%Pt/ZrO$_2$ has higher selectivity to hydrogenation products than HDO products
- 2%Ru/ZrO$_2$ has ~**3x** higher selectivity to HDO products at same conversion than 2%Pt/ZrO$_2$

- Reaction Conditions of 300°C at 350psig and conversion of 5%
- Rate calculated as mols of product per second per mol of total metal

Fast-Pyrolysis and Fast-Hydropyrolysis of Cellulose

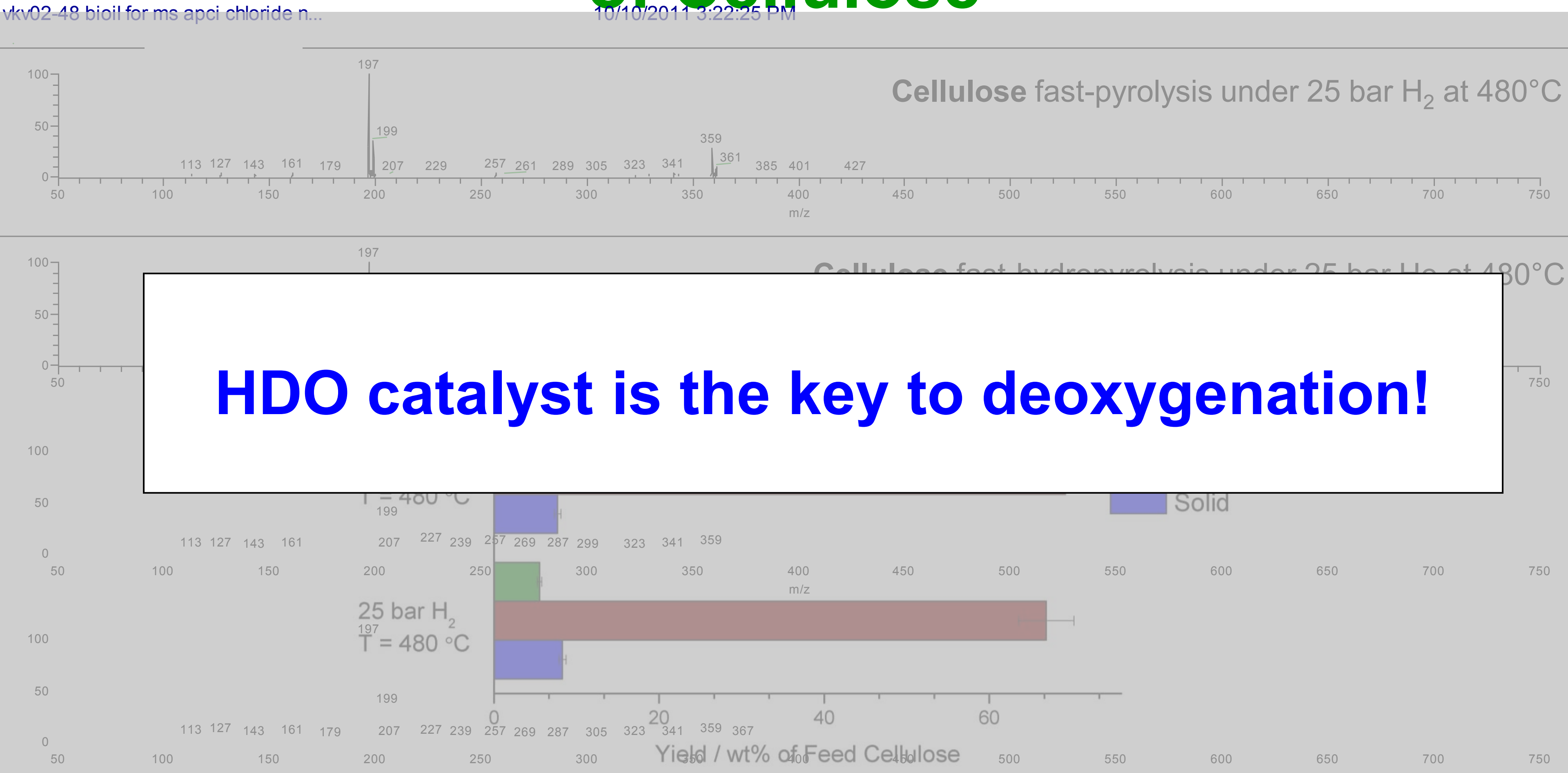


Cellulose fast-pyrolysis under 25 bar H_2 at 480°C

Cellulose fast-hydropyrolysis under 25 bar He at 480°C

No significant differences or deoxygenation between cellulose fast-pyrolysis and fast-hydropyrolysis at 25 bar He and 25 bar H_2 respectively

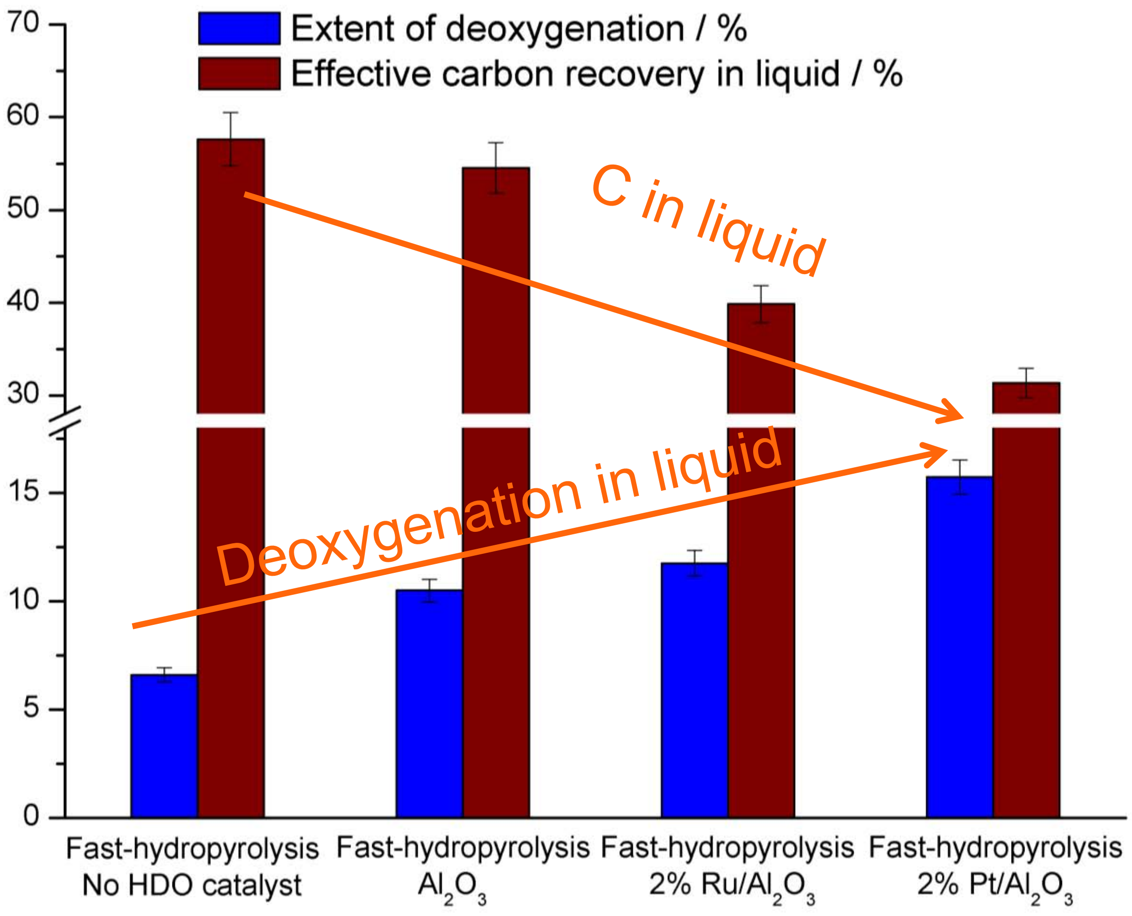
Fast-Pyrolysis and Fast-Hydropyrolysis of Cellulose



HDO catalyst is the key to deoxygenation!

No significant differences in the liquid product composition or the product yields between cellulose fast-pyrolysis and fast-hydropyrolysis at 25 bar He and 25 bar H_2 respectively

Cellulose FHP - Candidate HDO catalysts



Improvement of deoxygenation in the liquid with Pt and Ru catalysts

But, loss of carbon to gas phase as CO and CH_4

Balance of metal and acid function is essential

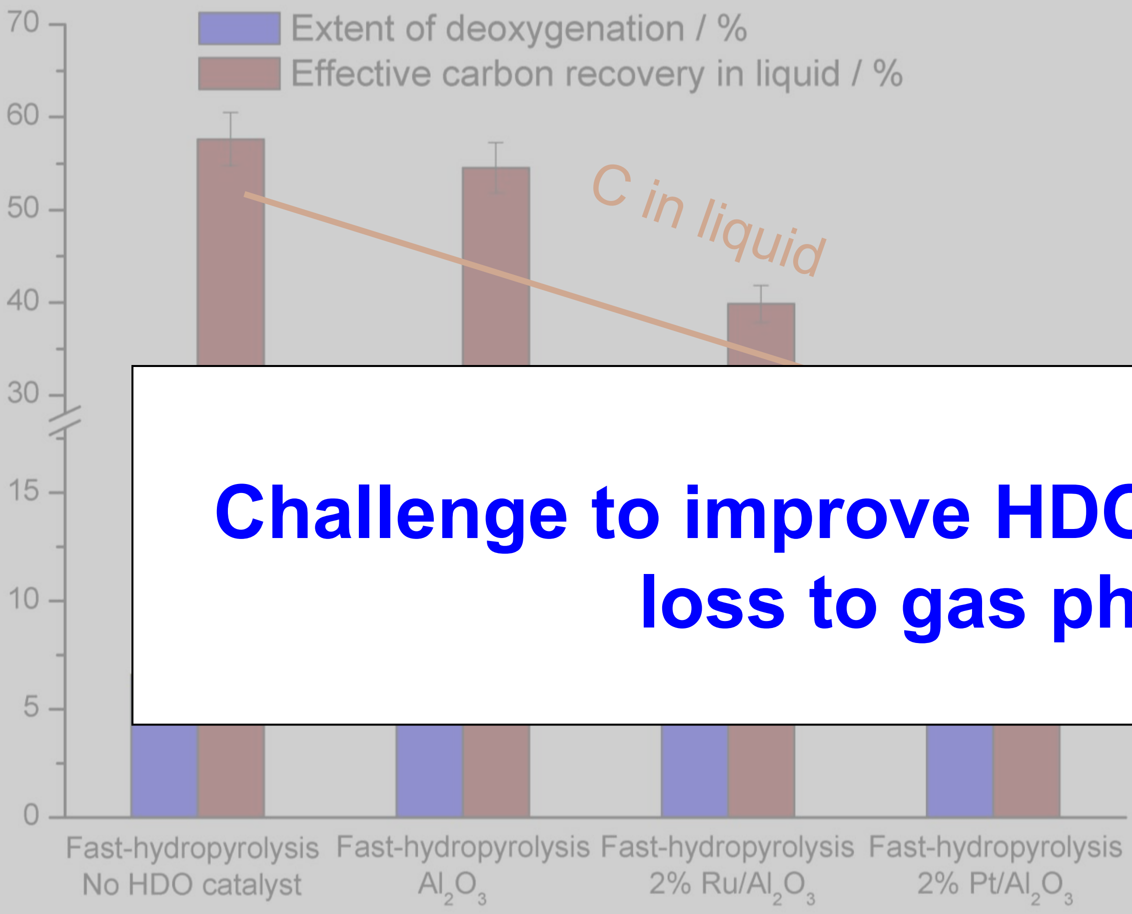
Challenge is to

Improve deoxygenation in the liquid as compared to the feed

Retain carbon in the liquid product

P_{H_2} = 9 bar, P_{total} = 27 bar
Hydropyrolysis Temp. ~ 550 °C, HDO Temp. ~ 375 °C , WHSV ~ 9.7 hr^{-1}

Cellulose FHP - Candidate HDO catalysts



Improvement of deoxygenation in the liquid with Pt and Ru catalysts

Challenge to improve HDO without carbon loss to gas phase!

Balance of metal and acid function is essential

Challenge is to

Improve deoxygenation in the liquid as compared to the feed

Retain carbon in the liquid product

P_{H_2} = 9 bar, P_{total} = 27 bar

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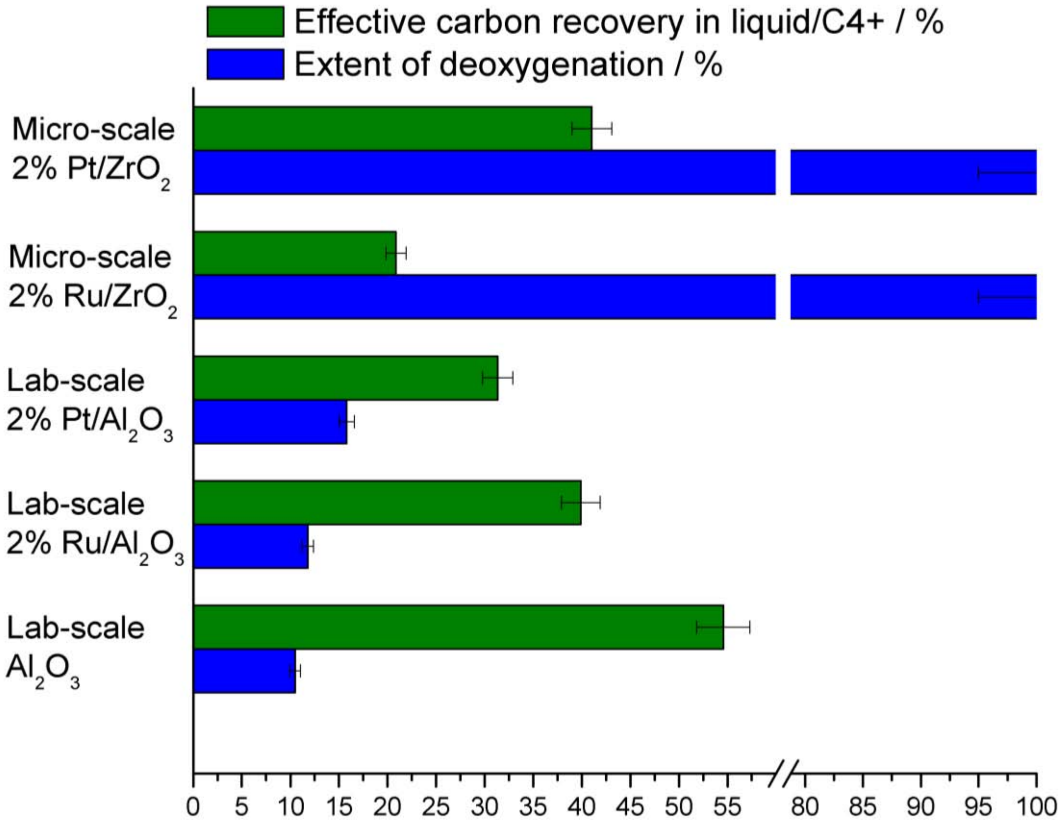
Cellulose FHP - Candidate HDO catalysts Lab-scale and Micro-scale comparison



100% deoxygenation with catalyst-to-feed ratios of ~20 in micro-scale batch reactor

< 20% deoxygenation at high space velocities ~10 hr^{-1} (low catalyst-to-feed rate ratios) in lab-scale continuous reactor

- Need to explore lower space velocity regimes (or higher catalyst to feed rate ratios) in lab-scale continuous reactor for improving extent of HDO
- Catalyst needs to be selective for HDO without C-C cleavage to make a deoxygenated liquid product with high carbon recoveries

Micro-scale: P_{H_2} **= 25 bar, Hydropyrolysis Temp. ~ 500 °C**
HDO Temp. ~ 300 °C , Catalyst: Feed ratio= 22 (2%Pt/ZrO$_2$), 18 (2%Ru/ZrO$_2$)
Lab scale: P_{H_2} **= 9 bar,** P_{total} **= 27 bar Hydropyrolysis Temp. ~ 550 °C**
HDO Temp. ~ 375 °C , WHSV ~ 9.7 hr^{-1}

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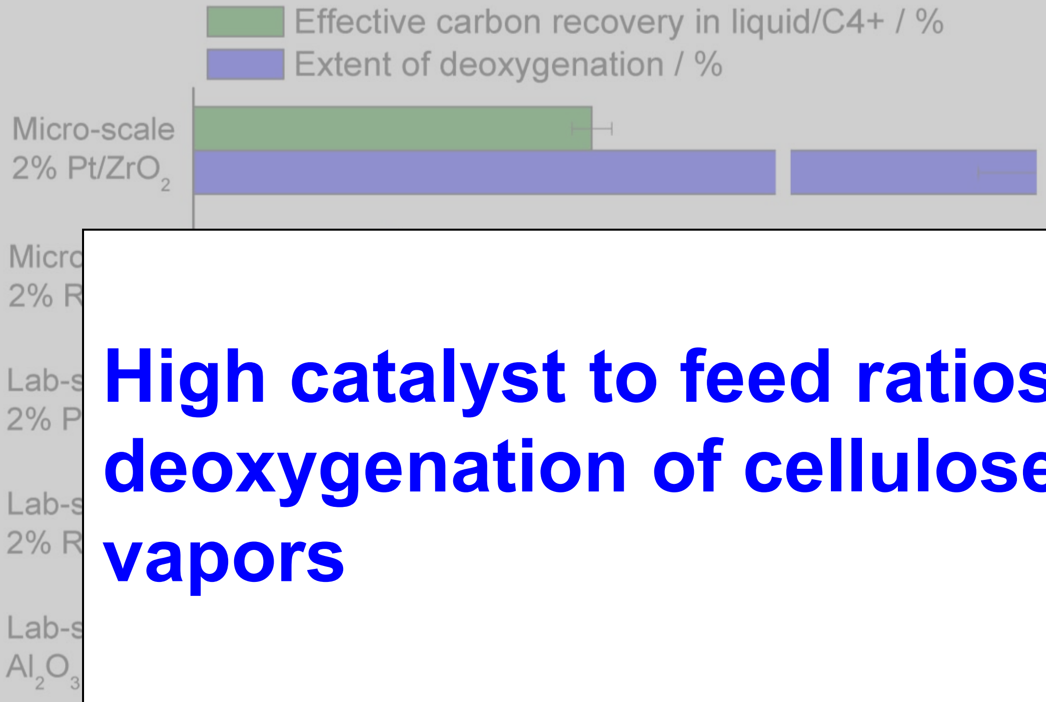

100% deoxygenation with catalyst-to-feed ratios of ~20

High catalyst to feed ratios can achieve 100% deoxygenation of cellulose fast-hydropyrolysis vapors

Challenge to develop catalyst that is selective to improve HDO, but retain carbon in liquid

- Need to explore lower space velocity regimes (or higher catalyst to feed rate ratios) in lab-scale continuous reactor for improving extent of HDO
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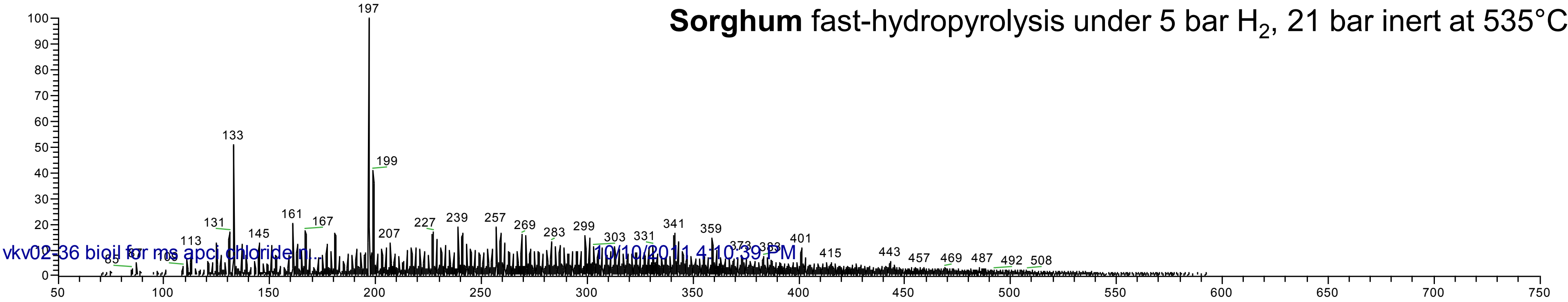
Lab scale: P_{H_2} = 9 bar, P_{total} = 27 bar Hydropyrolysis Temp. ~ 550 °C
HDO Temp. ~ 375 °C , WHSV ~ 9.7 hr^{-1}

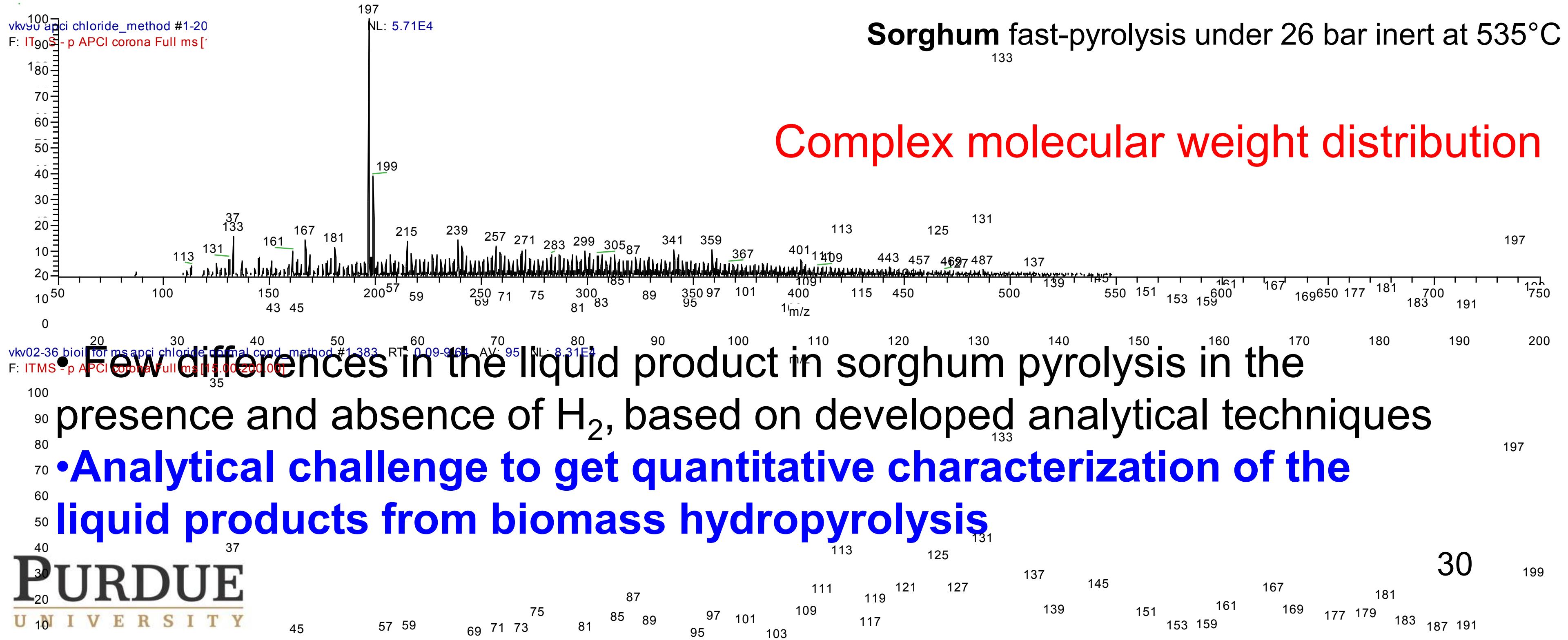
Technical Accomplishments/ Progress/Results

- Task C: Biomass Samples Study (M 4.20.1)
  - Conventional pyrolysis and hydropyrolysis in a single stage with biomass samples
  - Catalyst testing and development for catalytic pyrolysis and second stage upgrading

Fast-Pyrolysis and Fast-Hydropyrolysis of Sorghum



Sorghum fast-hydropyrolysis under 5 bar H_2, 21 bar inert at 535°C



Sorghum fast-pyrolysis under 26 bar inert at 535°C

Complex molecular weight distribution

- Few differences in the liquid product in sorghum pyrolysis in the presence and absence of H_2, based on developed analytical techniques

•Analytical challenge to get quantitative characterization of the liquid products from biomass hydropyrolysis

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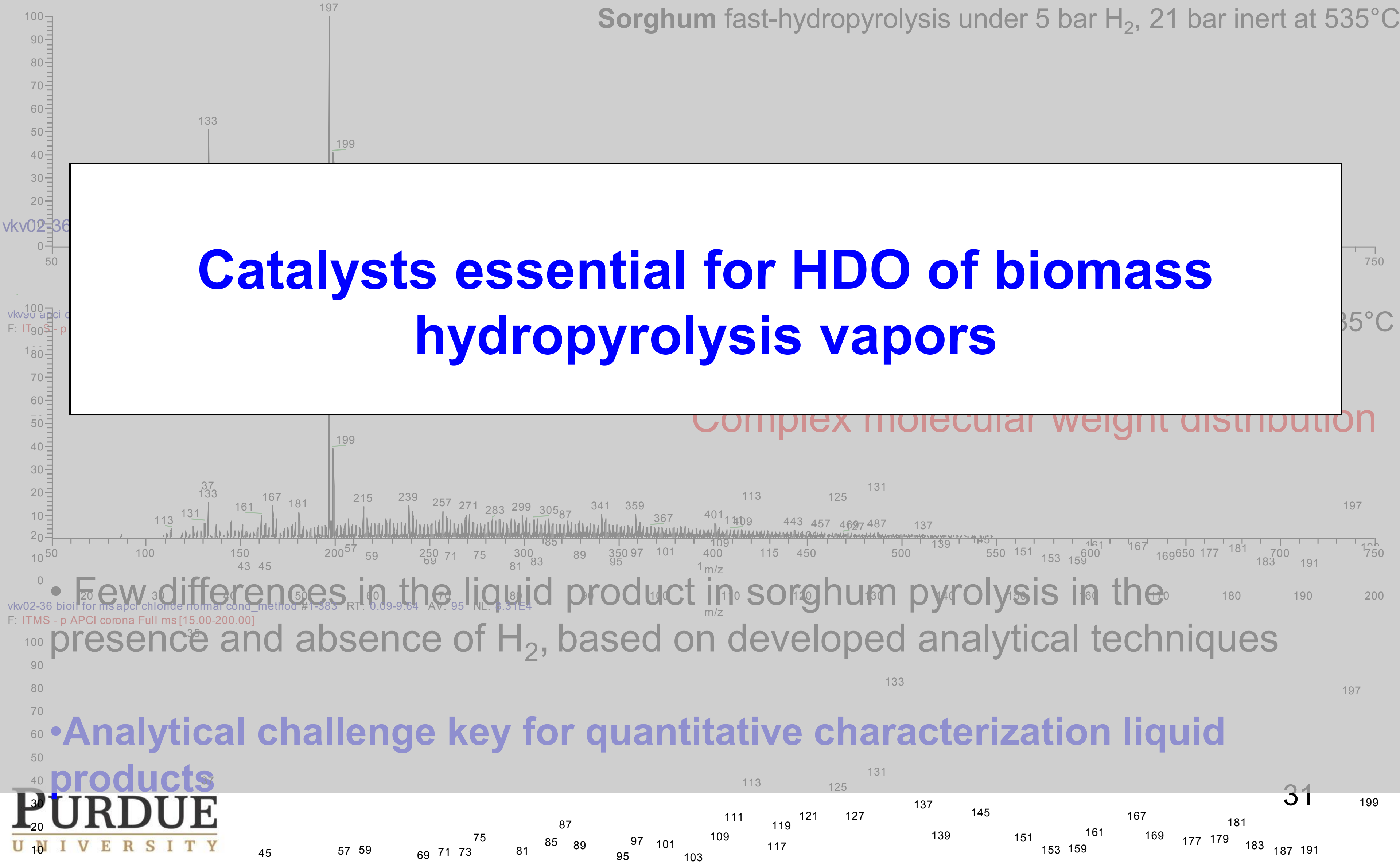
Fast-Pyrolysis and Fast-Hydropyrolysis of Sorghum



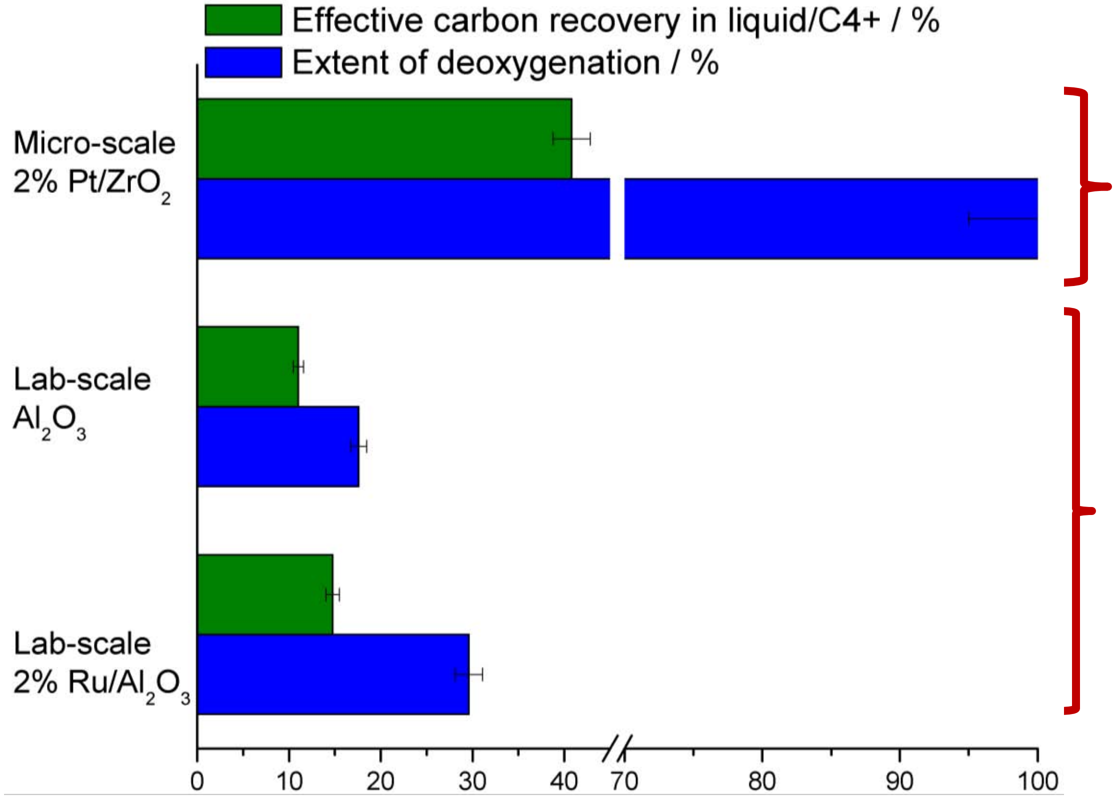
Sorghum fast-hydropyrolysis under 5 bar H_2, 21 bar inert at 535°C

Catalysts essential for HDO of biomass hydropyrolysis vapors

Complex molecular weight distribution

- Few differences in the liquid product in sorghum pyrolysis in the presence and absence of H_2, based on developed analytical techniques
- Analytical challenge key for quantitative characterization liquid products

Sorghum FHP - Candidate HDO catalysts Lab-scale and Micro-scale comparison



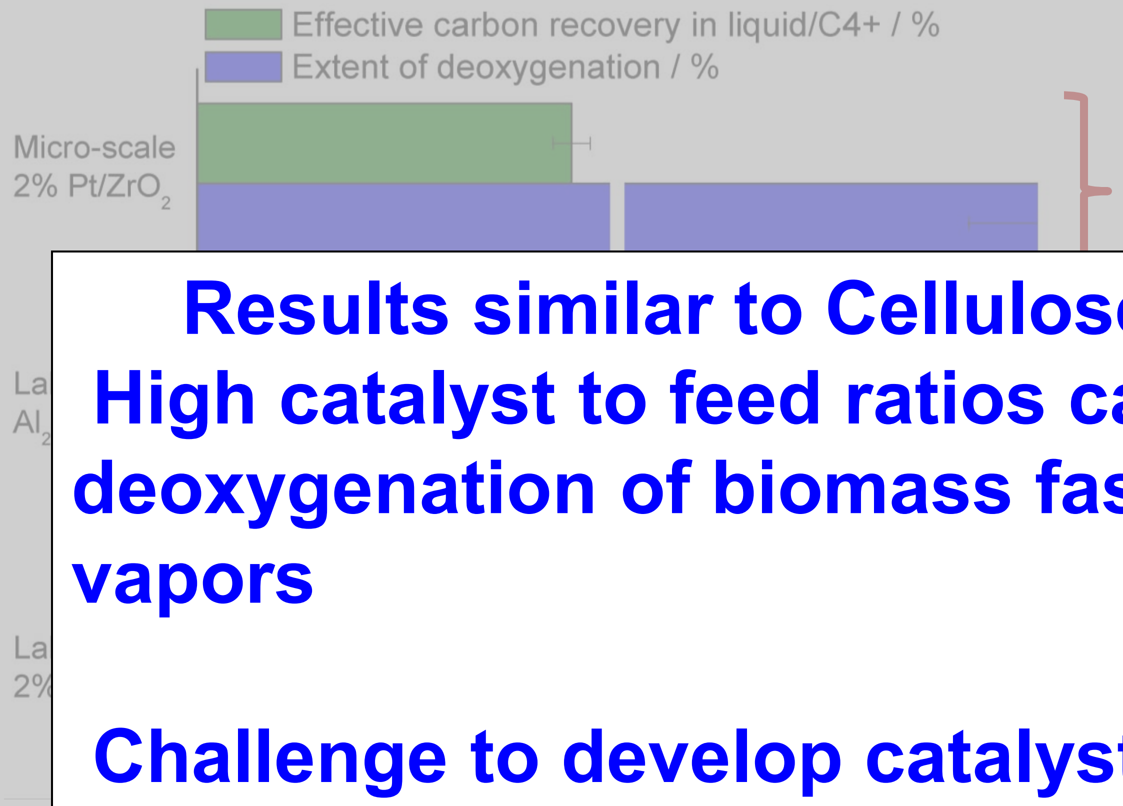
100% deoxygenation with catalyst-to-feed ratios of ~19 in micro-scale batch reactor

< 30% deoxygenation at space velocities ~3 hr^{-1} in lab-scale continuous reactor

Similar to results from Cellulose FHP and HDO
Higher catalyst-to-feed rate ratios required for improving extent of deoxygenation

Micro-scale: P_{H_2} = 25 bar, Hydropyrolysis Temp. ~ 500 °C
HDO Temp. ~ 300 °C , Catalyst: Feed ratio= 19 (2%Pt/ZrO_2)
Lab scale: P_{H_2} = 5 bar, P_{total} = 27 bar Hydropyrolysis Temp. ~ 535 °C
HDO Temp. ~ 375 °C , WHSV ~ 3 hr^{-1} (Al_2O_3), 4.5 hr^{-1} (2% Ru/Al_2O_3)

Sorghum FHP - Candidate HDO catalysts Lab-scale and Micro-scale comparison



100% deoxygenation with catalyst-to-feed ratios of ~19

Results similar to Cellulose FHP and HDO

High catalyst to feed ratios can achieve 100% deoxygenation of biomass fast-hydropyrolysis vapors

Challenge to develop catalyst that is selective to improve HDO, but retain carbon in liquid

of deoxygenation

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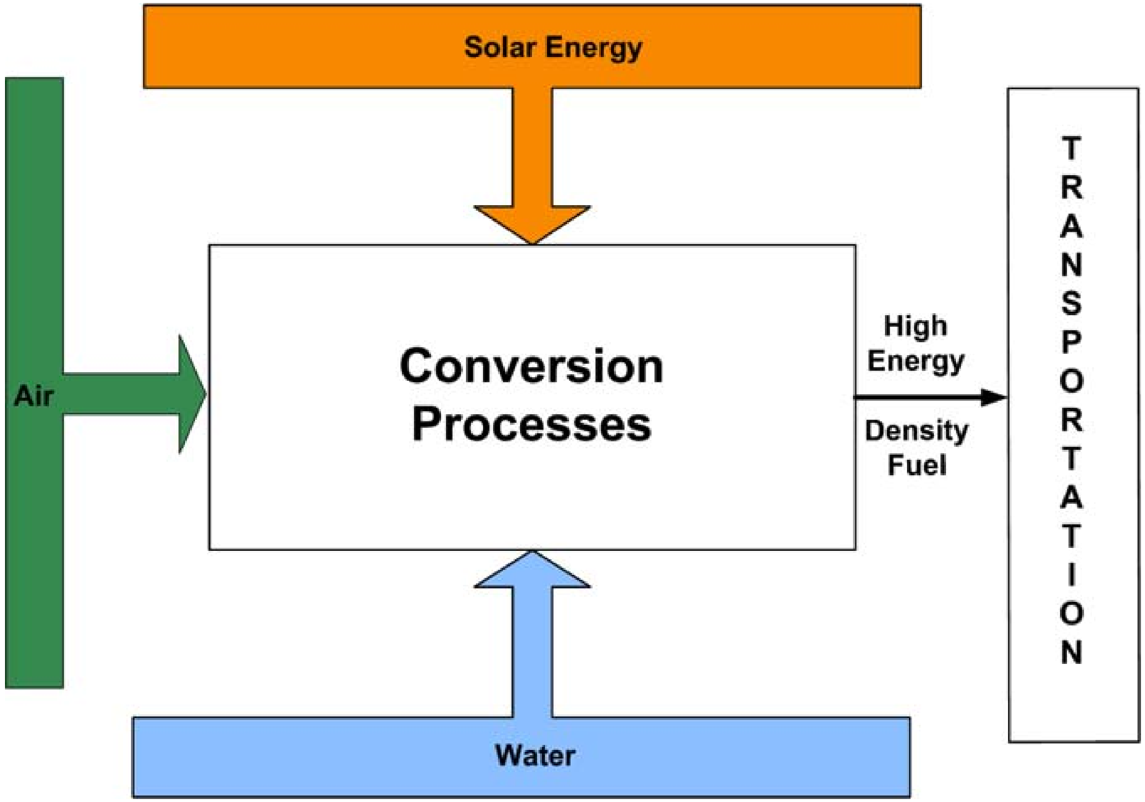
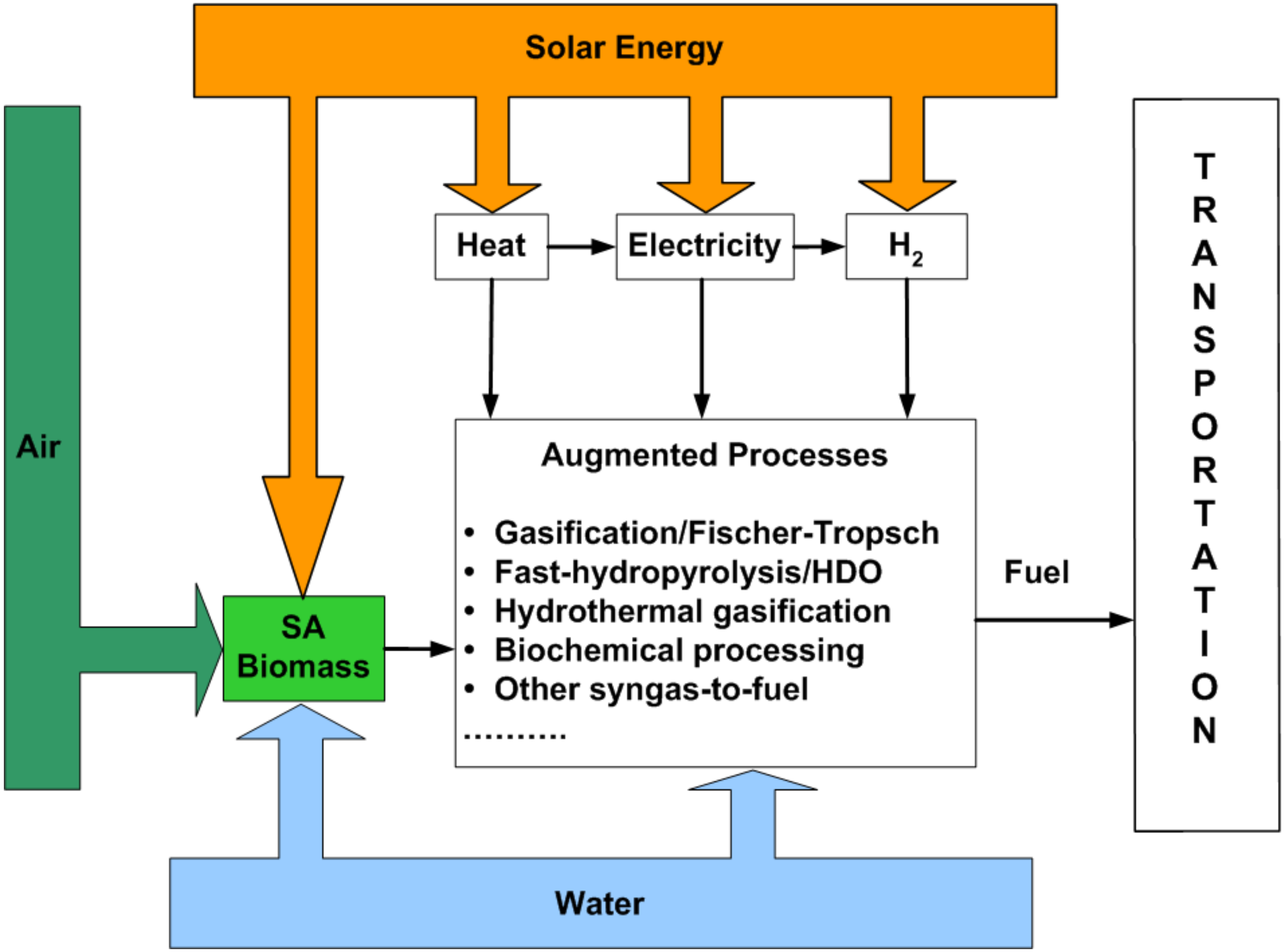
Technical Accomplishments/ Progress/Results

Task E: Energy Systems Analysis (M.4.19.7)



Augmented processes



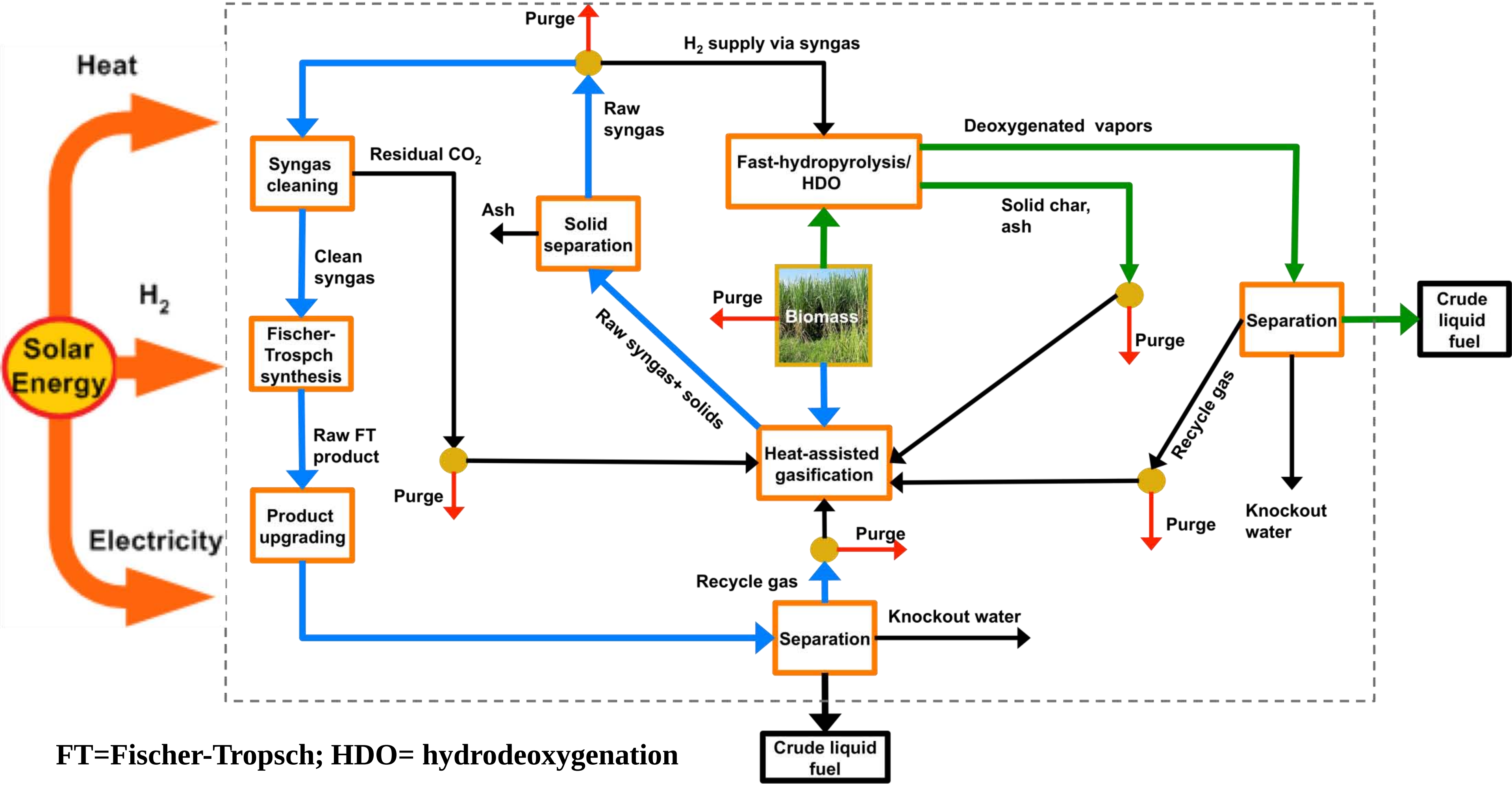
Up to 100% biomass carbon recovery possible

Singh, Delgass, Ribeiro and Agrawal, *Environ. Sci. Tech.*, 2010

Screening for carbon & energy efficient augmented processes

Process superstructure optimization

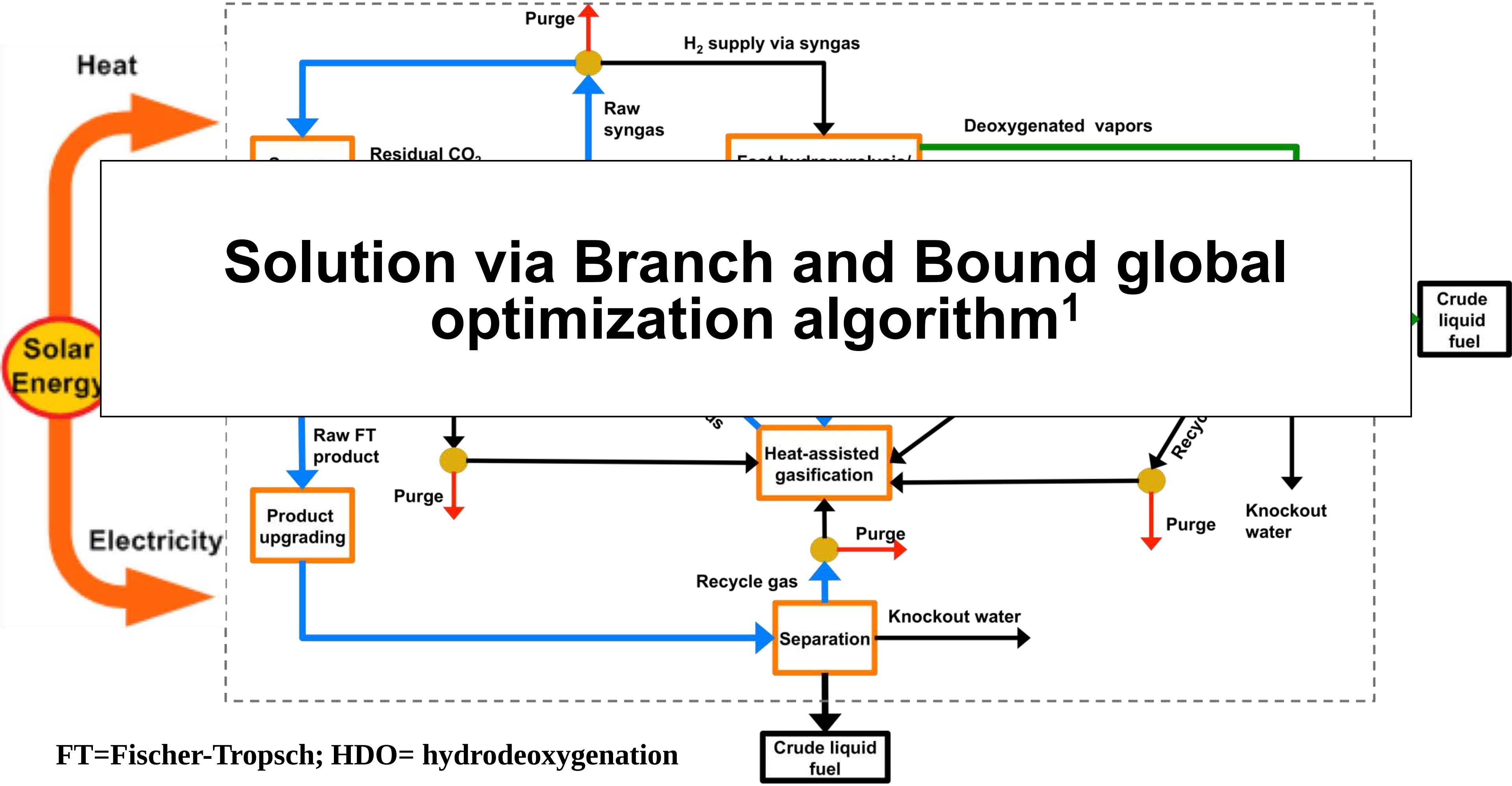
An example superstructure: gasification +fast-hydropyrolysis



FT=Fischer-Tropsch; HDO= hydrodeoxygenation

1. Tawarmalani and Sahinidis, Convexification and Global optimization of Mixed-Integer Nonlinear Programming, 2002

An example superstructure: gasification +fast-hydropyrolysis



Solution via Branch and Bound global optimization algorithm[1]

FT=Fischer-Tropsch; HDO= hydrodeoxygenation

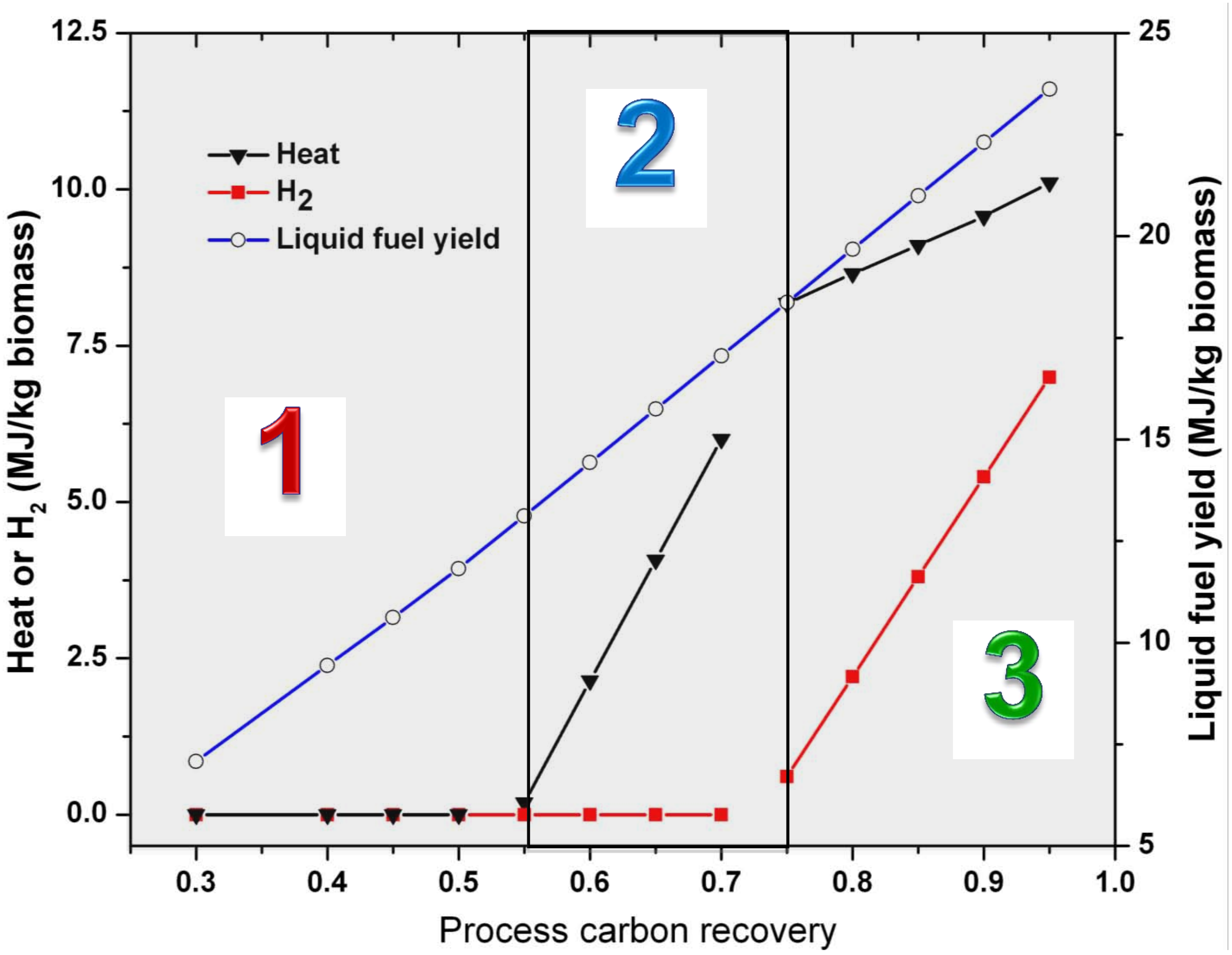
[1] Tawarmalani and Sahinidis, Convexification and Global optimization of Mixed-Integer Nonlinear Programming, 2002

Three different process regimes

- **Region 1**:
self-sufficient

- **Region 2**:
solar heat

- **Region 3**:
solar heat+H_2



Relevance

- Our research is aimed at discovery of novel process technologies that will maximize fuel production from biomass
  - Synergistic interactions between existing technologies
  - Discovery of new process technologies and chemical routes to liquid fuels via a joint modeling and experimental approach
- Current research: TRL-1 though TRL-4

Success Factors

- Success Factors
  - Smooth operation of FHP and FBR
  - Direct conversion of biomass to a low oxygen content, high energy density liquid.
- Research Impact
  - Developed understanding of pyrolysis of biomass at high-pressure H_2 and high-temperature
  - Developed HDO catalysts to remove oxygen from a variety of oxygen functional groups present in the hydropyrolysis product mixture
  - Developed H2Bioil process which can produce larger quantities of oil from a given quantity of biomass, reducing demand on land area for more biomass

Challenges

- Major Challenges Solved
  - High Pressure Reactors
    - Designed safe, high-pressure reactors that will fulfill the challenging and demanding operating conditions needed for fast-pyrolysis and upgrading
      - Solid biomass feeding at high pressure
      - Rapid heating and quenching
      - High hydrogen pressure
      - High temperature
    - Achieved 50% conversion of real biomass sample into liquids and gases via pyrolysis (Milestone C.ML.1)
  - Catalyst development for oxygen removal
    - Development of catalysts and reaction schemes for upgrading FHP oil that will selectively remove oxygen.
    - Achieved 35% wt reduction in oxygen of lignin model compound via catalytic HDO (Milestone B.ML.1)
    - Achieved 35% wt reduction in oxygen of cellulose model compound via pyrolysis and catalytic HDO (Milestone B.ML.2)
    - Achieved 35% wt reduction in oxygen of biomass via pyrolysis and catalytic HDO (Milestone C.ML.2)
  - Quantitative analysis of products
    - Developed variety of analytical methods for product identification and analysis

Future Work

- Have successfully completed all grant tasks and milestones
- Based on equipment developed and knowledge gained via this project, have identified areas for future work
  - Further HDO catalyst development
  - Reactor design for scalable reactor
  - Further analysis method development
  - Studies on greater variety biomass feedstocks

Summary

- Relevance
  - We explored new process and chemical (catalytic) technologies that could result in greater utilization of existing biomass resources to transportation fuels (increased stability and higher energy content))
- Approach
  - Developed versatile lab-scale equipment to explore new pyrolysis conditions and upgrading catalysts
  - Utilized model compounds to help simplify inherent chemical complexity of real biomass and bio-oil
  - Applied knowledge gained from model compounds to overcome challenges with real biomass feedstocks

Summary

- Technical Accomplishments since 2009
  - Explored several FHP reactor designs
  - Built second generation cyclone reactor rated for high-pressure H_2
  - Built stand-alone, high-pressure FBR for HDO studies.
  - Achieved 50% conversion of real biomass sample into liquids and gases via pyrolysis (Milestone C.ML.1)
  - Developed catalysts and reaction schemes for upgrading FHP oil that will selectively remove oxygen
  - Achieved 35% wt reduction in oxygen of lignin model compound via catalytic HDO (Milestone B.ML.1)
  - Achieved 35% wt reduction in oxygen of cellulose model compound via pyrolysis and catalytic HDO (Milestone B.ML.2)
  - Achieved 35% wt reduction in oxygen of biomass via pyrolysis and catalytic HDO (Milestone C.ML.2)
- Research provides proof-of-concept for future process / reaction scheme optimization and for techno-economic analysis

Additional Slides

Responses to Previous Reviewers' Comments from 2011

- **Comments** Economic Modeling
  - Although energy systems modeling is a useful tool in guiding research, it seems to be over emphasized here without equal recognition to systems economic modeling.
  - Essentially no economics, simple energy balances, without any real consideration for costs. The team did not seem to understand the DOE targets or the details of how their data needed to fit in.
  - The cost-effective production of biofuel which is asked for in the DOE research plan cannot be met so far. Economic information is missing.
  - Too much emphasis ($?) placed on energy-systems modeling and use of solar power. Really need some high level techno-economic assessment to go along with this rather than just energy balances - thermodynamically viable does not necessarily translate to economic and/or technically viable.
- **Response**
  - We have carried out an economic analysis for the proposed biomass fast-hydropyrolysis/hydrodeoxygenation (H_2Bioil) process relying on H_2 derived different primary energy sources (Ref. 1). The break-even crude oil price for a delivered biomass cost of $94/metric ton when H_2 is derived from coal, natural gas or nuclear energy ranges from $103 to $116/bbl for no carbon tax scenarios. This break-even crude oil price compares favorably with the literature estimated prices of fuels from alternative biofuel production routes. The break-even crude oil prices is found to be most sensitive to a 20% reduction in the liquid fuel output (~$28/bbl), increase in biomass cost from $94/metric ton to $121/metric ton (~10/bbl), and 25% increase in capital cost (~$5 bbl) in that order.
  - The economic analysis also revealed much higher break-even crude oil prices when using H_2 from renewable energy sources like wind ($139/bbl) and solar energy ($219/bbl). However, it should be noted that the technologies relevant to harnessing renewable energy (e.g. solar hydrogen production) are at an early stage of development. Therefore, current economic parameters (capital cost, operating costs etc.) for these technologies are often poor indicators of their future cost. While mature future costs are bound to be useful, the current cost projections as a metric for comparison may not be a true indicator of the technology viability in the future. We have continued to focus on identifying novel solar augmented biomass to liquid fuel process designs achieving high carbon and energy efficiency, which can potentially translate into reduced operating cost associated with the process.
  - Reference: 1. Singh, N. R., Mallapragada D., Agrawal R., Tyner W. E. (2012). "Economic analysis of novel synergistic biofuel (H_2Bioil) processes" Biomass Conv. Bioref. **2**: 141-148.

Responses to Previous Reviewers' Comments from 2011

- **Comments** Hydrogen costs
  - They are focused on retaining carbon in product, but did not clearly consider the cost of the H2.
- **Response**
  - We agree with the reviewer regarding the importance of the cost of H_2 on the economic viability of the process. With this in mind, we have carried out an economic analysis for the proposed biomass fast-hydropyrolysis/hydrodeoxygenation (H_2Bioil) process relying on H_2 derived different primary energy sources (Ref. 1). The break-even crude oil price for a delivered biomass cost of $94/metric ton when H_2 is derived from coal, natural gas or nuclear energy ranges from $103 to $116/bbl for no carbon tax scenarios. This break-even crude oil price compares favorably with the literature estimated prices of fuels from alternative biofuel production routes. Among the different options, the H_2Bioil process using H_2 from natural gas is particularly interesting, given the recent expansion in US natural gas reserves.
  - The economic analysis also revealed much higher break-even crude oil prices when using H_2 from renewable energy sources like wind ($139/bbl) and solar energy ($219/bbl). However, it should be noted that the technologies relevant to harnessing renewable energy (e.g. solar hydrogen production) are at an early stage of development. Therefore, current economic parameters (capital cost, operating costs etc.) for these technologies are often poor indicators of their future cost.
  - At the process level, we have also investigated the H_2 requirement for different amounts of biomass carbon recovered as liquid fuel. For example, at ~50% carbon recovery, the optimal H_2Bioil process configuration doesn't require any external energy (heat or H_2) input. Here, the H_2 requirement is met by gasifying a portion of the char and gas produced from the process. Thus, depending on the cost of H_2 and other economic factors, the H_2 requirement can be traded-off against the fraction of biomass carbon recovered as liquid fuel. In this manner, the cost of H_2 has been addressed in our analysis.
  - Reference: 1. Singh, N. R., Mallapragada D., Agrawal R., Tyner W. E. (2012). "Economic analysis of novel synergistic biofuel (H_2Bioil) processes" Biomass Conv. Bioref. **2**: 141-148.

Responses to Previous Reviewers' Comments from 2011

- **Comments** Process Modeling
  - Their system modeling was weak and did not appear to have a clear process for validation of costs or state of technology.
  - The energy systems analysis task is not integral to the thermochem program. It could be done as a stand-alone project leaving more focus on the stabilization of the bio-oils.
- **Response**
  - We disagree with the reviewer's assertion regarding the validity of our modeling results. We have employed a unique process design approach of representing a process superstructure as a mixed integer nonlinear programming (MINLP) model. The MINLP model, allowing for simultaneous process heat, mass and power integration, is subsequently solved using state-of-the-art global optimization tools to identify lucrative process configurations. Literature data has been used to develop the models for each unit operation considered in the process superstructure. For modeling fast-hydropyrolysis/HDO, we have developed a stoichiometric model considering the reactants of woody biomass and H_2, producing a high energy density liquid fuel, gas, water and solids. The resulting product distribution estimated from our stoichiometric model provides a reasonable approximation of the available experimental product distribution. Further, the stoichiometric model can be easily adjusted when more information regarding production composition yields becomes available from the experimental work of this project. In this manner, the energy systems analysis task ties in with the experimental work of the project.
  - As stated in the project proposal, the energy systems analysis task has focused on identifying new ideas to guide the development of biofuel processes that maximize energy efficiency and minimize resource requirements. The results of the modeling work guide the experimental investigations, through identification of critical process pinch points, optimal operating conditions and long-term targets to be achieved. Therefore, we disagree with the reviewer's assertion that the systems analysis task can be carried out independently.

Responses to Previous Reviewers' Comments from 2011

- **Comments** Solar Availability
  - There are still a lot of open questions especially related to the energy balance of this approach. Does the whole concept will work in the US especially in relation to the solar availability?
- **Response**
  - Our modeling work considers the overall energy balance by accounting for the different process energy inputs (e.g. H_2, heat or electricity) involved. With regard to solar availability, we refer the reviewer to a previous publication where we have presented the case in favor of using solar energy forms (H_2, heat or electricity) along with biomass to supply liquid fuel for the US transportation sector:
  - Agrawal R, Singh NR, Ribeiro FH, & Delgass WN (2007) "Sustainable fuel for the transportation sector". *Proc. Natl. Acad. Sci. U. S. A.* **104** (12):4828-4833.

Responses to Previous Reviewers' Comments from 2011

- **Comments** Solar Thermal for Heat
  - I also question the practicality of using solar thermal for heat since this resource is typically not located where the biomass is. I recommend not using more project time or resources on this type of analysis. Instead, focus on seeing if your basic concept of high pressure, H2-assisted pyrolysis has potential.
- **Response**
  - We have focused on identifying alternative augmented biofuel process configurations, capable of recovering a greater fraction of biomass carbon atoms as liquid fuel through the efficient use of supplemental energy forms (like H_2, heat, and electricity) derived from solar energy. The use of solar heat, which is available at higher solar conversion efficiency than H_2 or electricity, is presented as one possible option to supply the process heat requirements. In the absence of solar heat, a portion of the char and gas products of biomass fast-hydropyrolysis/hydrodeoxygenation could be combusted to provide process heat. This is similar to the current practice for biomass fast-pyrolysis based processes. Alternatively, additional solar H_2, produced via solar driven water electrolysis, could be combusted to provide the process energy requirements.

Responses to Previous Reviewers' Comments from 2011

- **Comments** <u>High Pressure Safety & Economic issues</u>
  - Safety features related to the high pressure process might be able to kill the project from an economic point of view. Also the fact that the whole process is under high pressure causes some questions related to energy efficiency.
  - Hard to imagine widespread use of a pyrolysis process involving hydrogen at 50-bar (safety issue).
  - The project has appropriately identified the safe operation of the high pressure process as a major challenge.
- **Response**
  - Safety features for use of high pressure hydrogen have been successfully installed and tested in our laboratories. Processes involving higher than 50 bar H_2 are widespread in the petroleum refining industry. Similarly, in our process, results have shown that high pressures of H_2 are necessary for high hydrodeoxygenation reaction rates.
  - We are aware that the safety issues associated with high pressure hydrogen use in widespread distributed or mobile pyrolysis units would need to be carefully considered. Of course, the mobile pyrolysis units would need to be operated by trained operators. However, methane reformers used for hydrogen fueling stations face similar issues. We agree this is an concern, but we believe the safety issues could be addressed and would not prevent potential implementation of the process.
  - From an operational viewpoint, higher pressures reduce the volume of the reactor and the associated heat losses. In addition, the energy required for gas compression to enable high pressure operation, is only a small fraction of the overall process energy requirement. Therefore, the impact of high pressure operation on the energy efficiency of the process is expected to be small.

Responses to Previous Reviewers' Comments from 2011

- **Comments** Scale-Up:
  - Also the commercial practicality of feeding biomass into 100 bar reactor seems to be overlooked.
  - The reactor, e.g., screw feeder, high pressure, with H2, fixed bed reactor, may not be suitable for large scale.
- **Response**
  - Commercially, high pressure screw feeders have been used for handling solids e.g. in the coal processing industry. Coal gasifiers typically operate at ~69 bar.
  - Use of high pressure hydrogen and fixed bed reactors are widespread in the petroleum refining industry and hence are suitable for large scale.

Responses to Previous Reviewers' Comments from 2011

- **Comments** Biomass feedstock particle size
  - Need very small particle-size biomass (50 micron) to achieve high mass & heat transfer in the reactor.
- **Response**
  - We have tested biomass particles up to a size of 420 microns and our results compare well with fast-pyrolysis literature and theoretical calculations that validate high heat and mass transfer rates in the reactor. Ability to process large particle sizes of biomass would also help in the overall economics of the process due to smaller milling costs.

Responses to Previous Reviewers' Comments from 2011

- **Comments:** Testing of real biomass
  - The project has made good progress with equipment - development of a high pressure biomass pump and development of the cyclone reactor. However, more progress on testing with real biomass and analysis of bio-oil quality is needed.
- **Response**
  - All grant tasks related to testing of biomass samples (sorghum) have been completed. Methods for analysis of resulting bio-oil have been developed and utilized to test the bio-oil quality.

Responses to Previous Reviewers' Comments from 2011

- **Comments** Technology Transfer
  - Technology transfer and industrial validation was limited.
  - This project appears to be operating largely in isolation. The PI should find opportunities beyond publications to interact with other elements of the TC platform.
- **Response**
  - The project has not worked in isolation. We have engaged outside groups, including GTI. Our presentation of technology to GTI resulted in their developing a pilot scale process.
  - Significant progress has been made on the development of the H_2Bioil process. However, as shown on the future work slide, further work is need in HDO catalyst development, reactor design for a scalable reactor, further analysis method development, and studies on a greater variety biomass feedstocks before the process would be ready for technology transfer out of the lab to an industrial setting.

Responses to Previous Reviewers' Comments from 2009

Comments

- Reliance on solar hydrogen is unrealistic and makes this program of marginal relevance
- No addressing of intermittent hydrogen feed from renewables.

- **Response**
  - The source of hydrogen is irrelevant for the success of this project. The novelty of this process does not lie in the fact that hydrogen from solar energy is being used. At present, hydrogen could be supplied from coal or natural gas until an economical carbon-free hydrogen source is available. Because it is very inefficient to grow and transport biomass, we believe there is a potential benefit to convert more biomass to high-energy-density fuel by the addition of hydrogen

Responses to Previous Reviewers' Comments from 2009

Comment

This project really needs a detailed Thermodynamic (1st and 2nd law) analysis

Response

The overall process energy efficiency of the proposed process is 81%, while that for gasification/Fischer-Tropsch processes is 40.6% and that of fast pyrolysis processes is 77%[1]. This comparative advantage in efficiency along with the significant improvements in yield mentioned earlier, make this process thermodynamically feasible to produce high energy density liquid fuel.

[1] Agrawal R., Singh N.R., "Synergistic Routes to Liquid Fuel for a Petroleum Deprived Future", AIChE J 55 7 2009 p1898-1905.

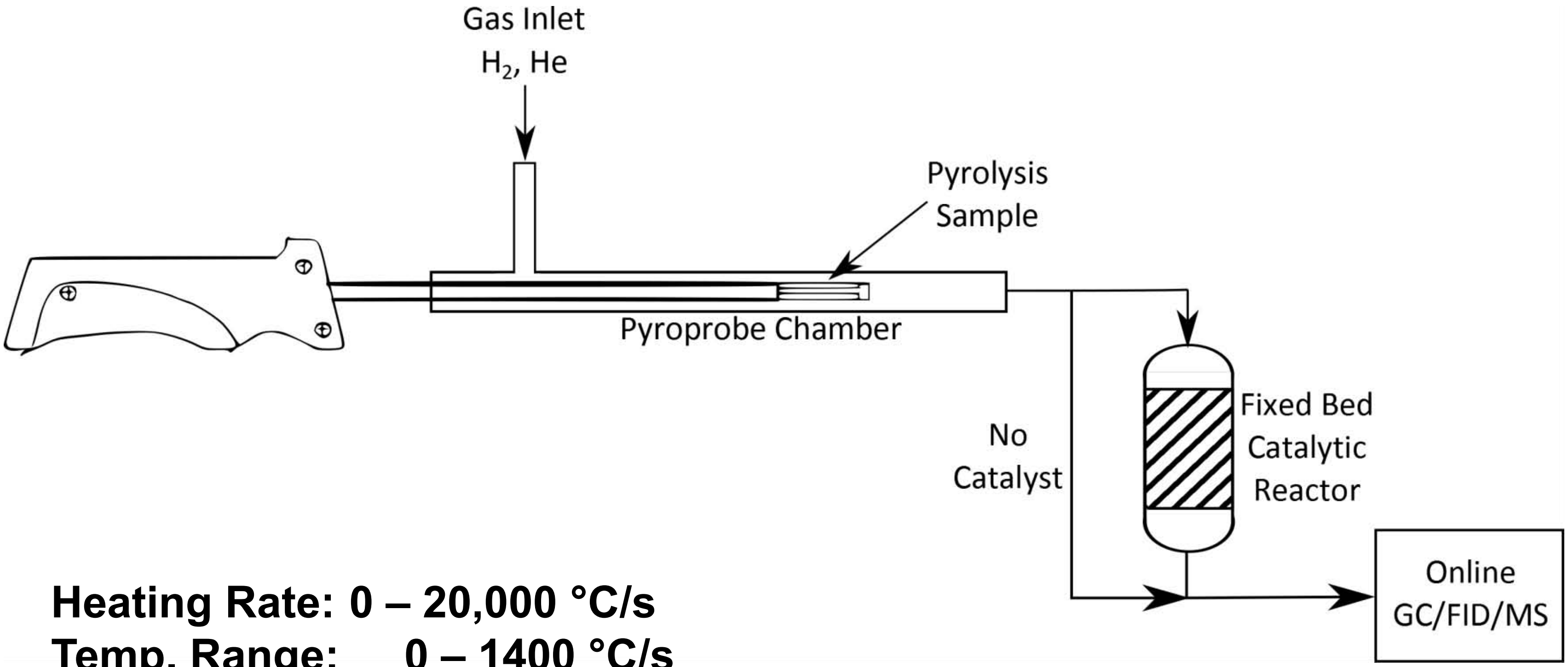
Publications

- Publications
  - Singh, N.R., Delgass, W.N., Ribeiro, F.H., Agrawal, R., “Estimation of Liquid Fuel Yields from Biomass”, Environmental Science and Technology 44 13 2010 p5298-5305
  - Agrawal, R., Singh, N.R., “Solar Energy to Biofuels”, Review of Chemical and Biomolecular Engineering 11 2010 p343-364
  - Agrawal R., Singh N.R., ”Synergistic Routes to Liquid Fuel for a Petroleum Deprived Future”, AIChE J 55 7 2009 p1898-1905.
  - Agrawal, R., Singh, N.R., Ribeiro, F.H., Delgass, W.N., Perkis, D.F., Tyner, W.E., ”Synergy in the hybrid thermochemical–biological processes for liquid fuel production”, Computers and Chemical Engineering 33 12 2009 p2012-2017.
  - Agrawal, R., Mallapragada, D.S., “Chemical Engineering in a Solar Energy Driven Sustainable Future”, AIChE J 56 11 2010 p2762-2768.

Presentations

- Presentations
  - Mallapragada,D.S., Singh, N.R., Curteanu, V., Agrawal, R., Sun-to-Fuel Assessment of Routes for Fixing CO_2 as Liquid Fuel, Ind Eng Chem Res 52 14 2013 p5136-5144.
  - Sara L. Yohe, W. Nicholas Delgass, Fabio H. Ribeiro, Rakesh Agrawal, Kinetics of High Pressure Catalytic Reaction Pathways for Dihydroeugenol of Pt/ZrO2, American Institute of Chemical Engineers National Meeting, 2012, *Pittsburgh, PA*
  - Singh, N. R., Mallapragada D., Agrawal R., Tyner W. E., "Economic analysis of novel synergistic biofuel (H_2Bioil) processes", Biomass Conv. Bioref. 2 2012 p141-148
  - Mallapragada D. S., Singh, N.R., Agrawal, R., "Energy Systems Analysis for a Renewable Transportation Sector", in 21st European Symposium on Computer Aided Process Engineering-ESCAPE 21, eds. E. N. Pistikopoulos, M. C. Georgiadis and A. Kokossis, Elsevier B.V, Chalkidiki, Greece, 2011.
  - Sara L. Yohe, W. Nicholas Delgass, Fabio H. Ribeiro, Rakesh Agrawal, High Pressure Catalytic Hydrodeoxygenation of Hydro-pyrolysis Vapor Lignin Model Compounds, American Institute of Chemical Engineers National Meeting, 2011, *Minneapolis, MN*
  - Vinod Kumar Venkatakrishnan, Andrew D. Smeltz, Sergey V. Semikolenov, Fabio H. Ribeiro, W. Nicholas Delgass and Rakesh Agrawal, High Pressure Fast-Pyrolysis and Fast-Hydropyrolysis for Conversion of Biomass to Liquid Fuels, American Institute of Chemical Engineers National Meeting, 2011, *Minneapolis, MN*
  - Mallapragada, D.S., Delgass, W.N., Ribeiro, F.H., Agrawal, R., The Scope of Using Concentrated Solar Energy to Produce Liquid Fuels from Biomass, American Institute of Chemical Engineers National Meeting, 2010, Salt Lake City, UT.
  - Agrawal, R., Transportation Fuel in a Solar Economy, Foundations of Computer-Aided Process Design Meeting, 2009, Breckenridge, CO
  - Singh, N.R., Agrawal, R., Synergistic Routes to Liquid Fuel for a Petroleum Deprived Future, American Institute of Chemical Engineers National Meeting, 2009, Nashville, TN
  - Singh, N.R., Ribeiro, F.H., Delgass, W.N., Agrawal, R., Synergistic Use of Solar Hydrogen with Biomass to Produce Biofuels, American Institute of Chemical Engineers National Meeting, 2008, Philadelphia, PA.

Micro-scale Batch Fast-Hydropyrolysis Reactor



Heating Rate: 0 – 20,000 °C/s
Temp. Range: 0 – 1400 °C/s
Pressure Range: 0 – 34 bar

Screening for carbon & energy efficient augmented processes

Process superstructure optimization

Systematic augmented process synthesis

- **Step 1:** Construct a superstructure of process alternatives
- **Step 2:** Formulate Mixed Integer Nonlinear Program (MINLP)
- **Step 3:** Define target carbon recovery level
- **Step 4:** Process optimization to minimize solar energy use

Augmented process synthesis: MINLP model

Minimize $Q_{solar} = \frac{Q_{H2}}{h_{STH_2}} + \frac{Q_{Heat}}{h_{STHe}} + \frac{W_{elec}}{h_{STE}}$ **…. Objective function**

subject to,

$f\left(\mathbf{x},\mathbf{y}\right) = 0$ **…. Mass, Energy balance, thermodynamic models**

$h\left(\mathbf{x},\mathbf{y}\right) \pounds 0$ **…. Inequalities (split fractions, conversion etc.)**

$carbon_{eff} \ ^{3} \ carbon_{\mathbf{target}}$ **…. Target carbon recovery level**

$\mathbf{x}^{L} \pounds \mathbf{x} \pounds \mathbf{x}^{U}$

…. Variable bounds

$\mathbf{y} = \{0,1\}$

- **Traditional solvers (e.g. Aspen Plus SQP) yield local solutions close to initial point**

Impact: SA biomass+ Augmented Processes for US transportation

- Sustainably available biomass potential= 498 Million tons/yr[1]

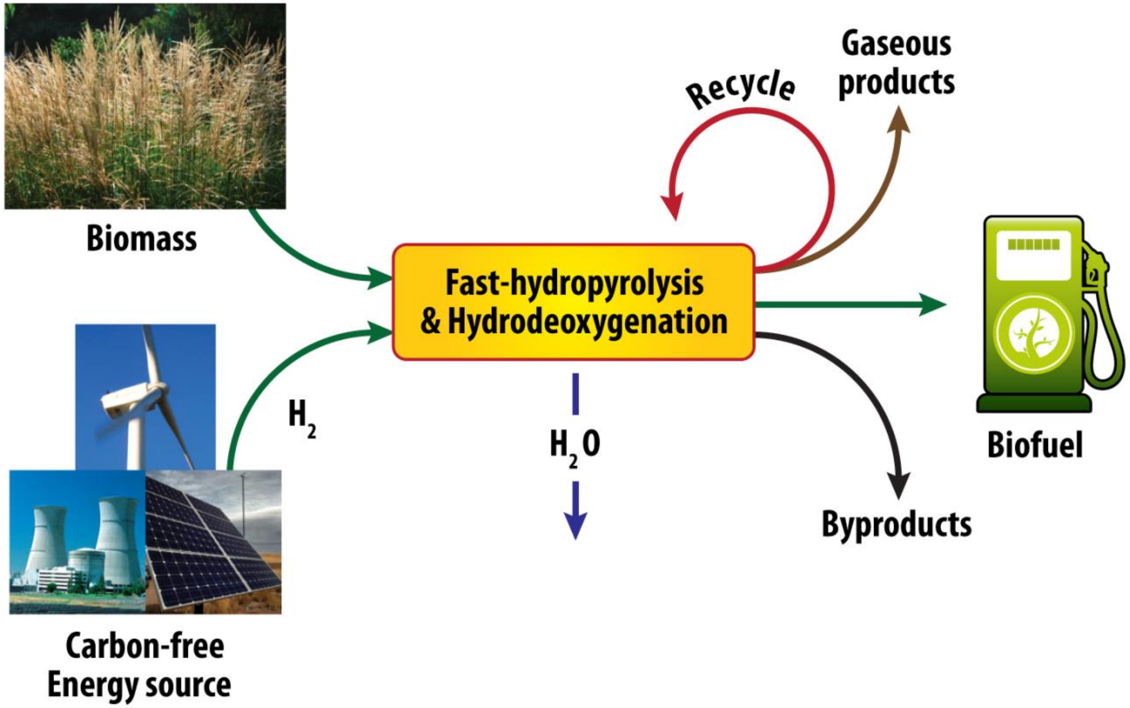
- Transportation fuels use in the USA, 2011 =12.68 Mbbl/day[2]

~100% biomass carbon conversion to liquid fuel

~47 % (5.9 Mbbl/day) of current US transportation demand produced from SA biomass

1. **Liquid transportation fuels NRC report, 2010**
2. **Davis *et al.*, Transportation energy data book, 2012**

Short-term outlook: process economics



- H_2 from coal, natural gas or nuclear
  - Without carbon tax: $103-$116/bbl
  - With carbon tax: $99-$111/bbl
- H_2 from wind, no carbon tax → $139/bbl

Singh, Mallapragada, Agrawal and Tyner, *Bio. Conv. Biorefin.*, 2012