DOE Bioenergy Technologies Office (BETO) 2015 Project Peer Review

FY 14-15: Hydrolyzed Lignocellulose as a Feedstock for Fuels Synthesis

25th March 2015

Biochemical Conversion

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Goal Statement

- *Use mild conditions and simple catalysts in chemical processes to convert biomass hydrolysates to fuels and feedstocks as a viable alternative to fermentation routes.*
- This addresses BETO MYPP (July 2015)
  - Bt-H "Cleanup/Separations"
  - Bt-I "Catalyst Efficiency"
  - Tt-L "Knowledge Gaps in Chemical Processes"
- Has potential to utilize a well established feed stream to produce fuel and chemicals in order to reduce our Nation's dependence on petroleum based feedstocks and cut greenhouse gas emissions

Quad Chart Overview

Timeline

- Project start date: Oct 2013
- Project end date: Sept 2015
- Percent complete: 63%

Budget

	Total Costs FY 10 – FY 12	FY 13 Costs	FY 14 Costs	Total Planned Funding (FY 15-Project End Date
DOE Funded	$0	$0	$483k**	$0
Project Cost Share (Comp.)*	N/A	N/A	N/A	N/A

** Carried over $250k into FY 15

Barriers

- Barriers addressed
  - **Bt-H "Cleanup/Separations"**
  - **Bt-I "Catalyst Efficiency"**
  - **Tt-L "Knowledge Gaps in Chemical Processes"**

Partners

- No Partners
- Samples provided by National Renewable Energy Laboratory (NREL) & Joint Bio-Energy Institute (JBEI)

1 - Project Overview

- We aim to apply our recently developed C-C coupling and hydrodeoxygenation (HDO) technologies to molecular feedstocks close to sources of raw biomass (i.e. lignocellulosic hydrolysates). Once a better understanding of our current catalytic HDO systems has been developed, we will move towards improving the process using lower temperatures, lower pressures and cheaper catalysts

2 – Approach (Technical)

- *12 month project with roll-over for 24 months funding*
- *Builds on current LANL results for biomass conversion*
- *Main challenges:*
  - *Utilizing an economically viable feedstock*
  - *Performing the reaction under mild conditions*
  - *Using inexpensive catalysts and reagents*
  - *Optimization of individual transformations for a flow reactor*
  - *Avoid unnecessary separations*
- *Solutions*
  - *Utilize hydrolysate feed streams*
  - *Optimize reactions to minimize energy usage*
  - *Screen non-precious metal catalysts*
  - *Use a continuous process without separations if necessary*

2 – Approach (Management)

- *Critical success factors*
  - *Feedstock cost*
  - *Process cost (pressure, temperature, infrastructure etc.)*
  - *Cost of separations/purification steps*
  - *Demonstration of process scalability*
- *Potential challenges*
  - *Maintaining a reproducible hydrolysate input to allow for confidence in the desired output*
  - *Perform ideal optimized catalytic reactions on a hydrolysate input (non-ideal – acidic, viscous, additional components)*
  - *Catalyst robustness, efficiencies, recyclability*
  - *Connection to WFO partner to aid with commercialization/scalability*
- *Tasks & milestones are constructed to allow for parallel optimization of the two key aspects of this project i.e. chain extension & oxygen removal*

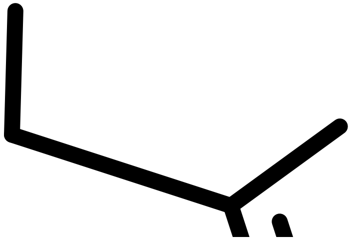
  This will allow us to optimize the overall reaction (pressure, temp., reaction time) more effectively to develop a more complete understanding of the robustness of our catalytic system and to be able to scale this system on real hydrolysate samples.
- *This approach will allow us to develop a more accurate TEA and facilitate scale-up approaches.*

3 – Technical Accomplishments

HMF

- Readily obtainable from sugars
- ~ 60 % yield from corn stover
- Ideal for C-C extension
- Non-enolizable
- Used for similar chemistry

3 – Technical Accomplishments



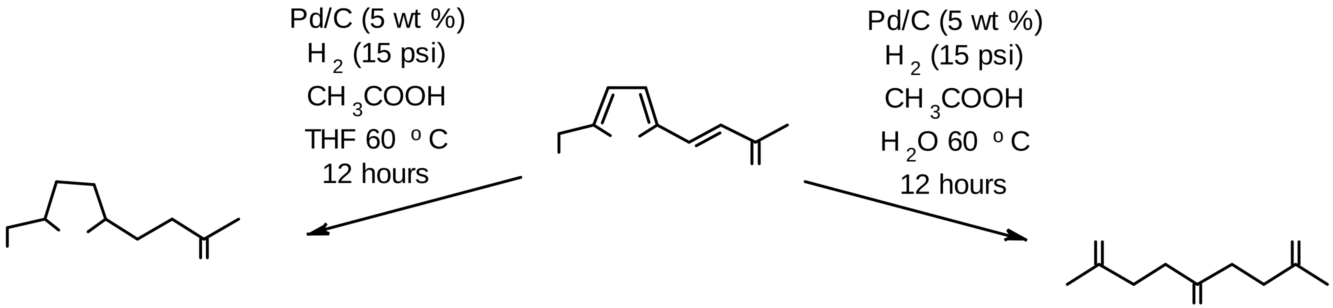
- Up to 99% conversion and 95% isolated yield
- No solvent (neat reactions)
- Room to below room temperature
- Simple work up
- Works on multiple systems
- **Can prepare C_8 to C_{16} precursor molecules**

3 – Technical Accomplishments

64 – 93 % isolated yield

Ram & Spicer, *Synthetic Communications*, **1992**, *22(18)*, 2683-2690

~ 85 % isolated yield
Ammonium formate
complicates work up



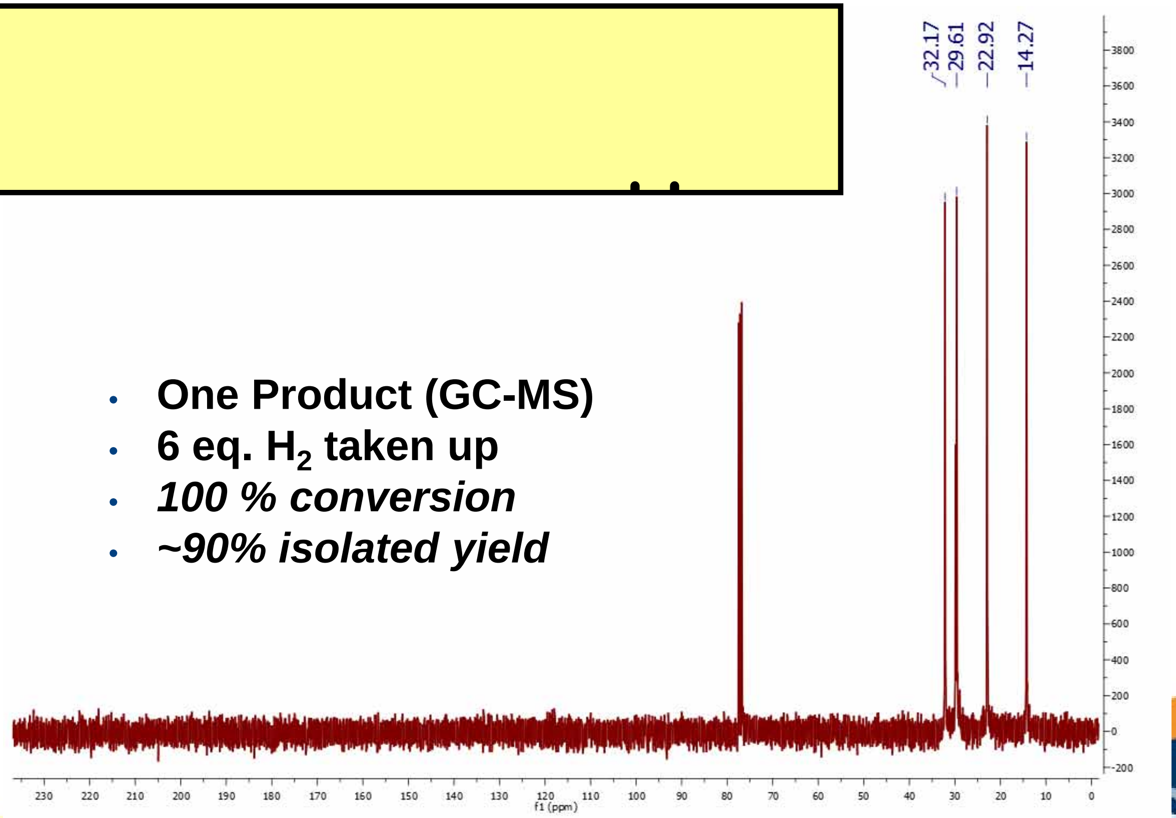
Pd/C (5 wt %)
H_2 (15 psi)
CH_3COOH
THF 60 °C
12 hours

Pd/C (5 wt %)
H_2 (15 psi)
CH_3COOH
H_2O 60 °C
12 hours

3 – Technical Accomplishments

- All attempts to reduce the ketones using standard mild techniques failed.

The HDO is the hardest *i.e.* most energy intensive, step in alkane synthesis

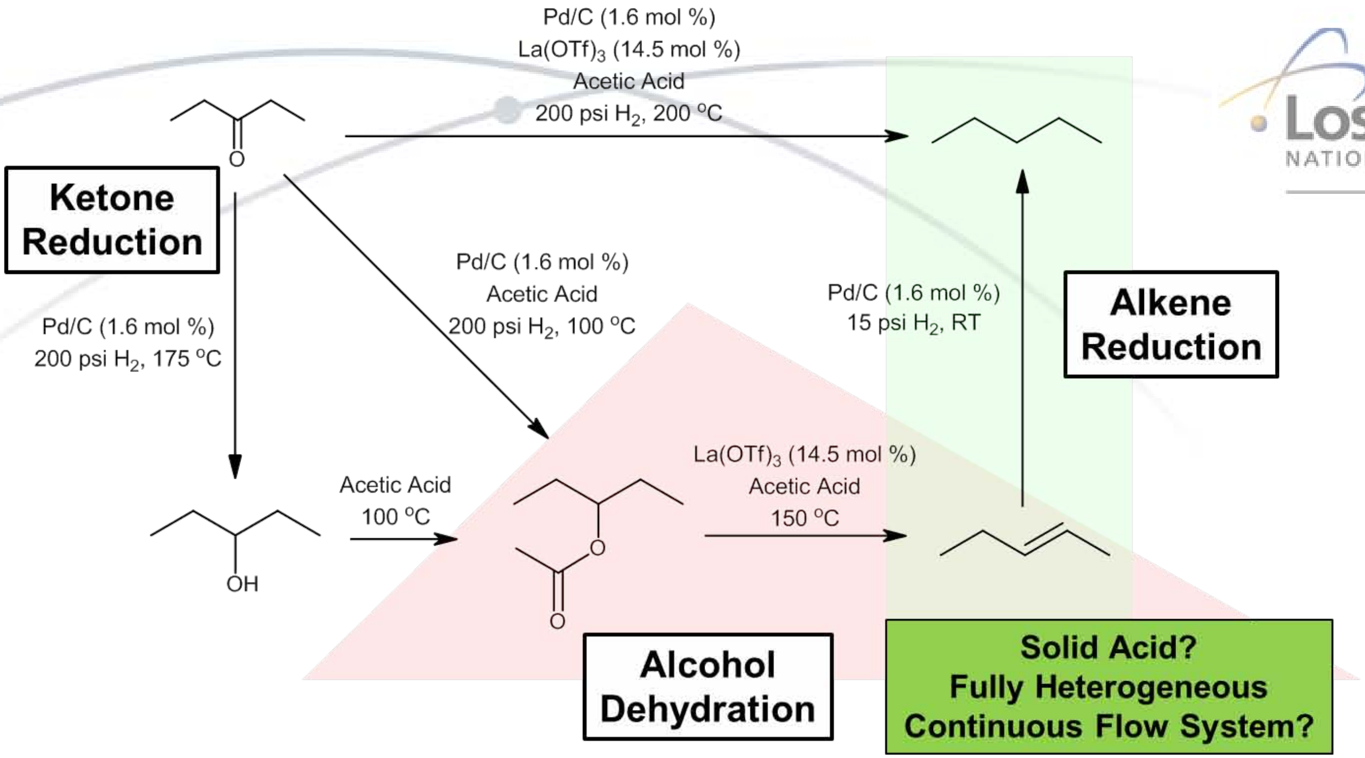


- **One Product (GC-MS)**
- **6 eq. H_2 taken up**
- ***100 % conversion***
- ***~90% isolated yield***

3 – Technical Accomplishments

Method is general to generate other polyketones, which can then be subjected to HDO to make array of alkanes….

Sutton, Gordon et al, *Nature Chemistry*, **2013**, 5, 428.

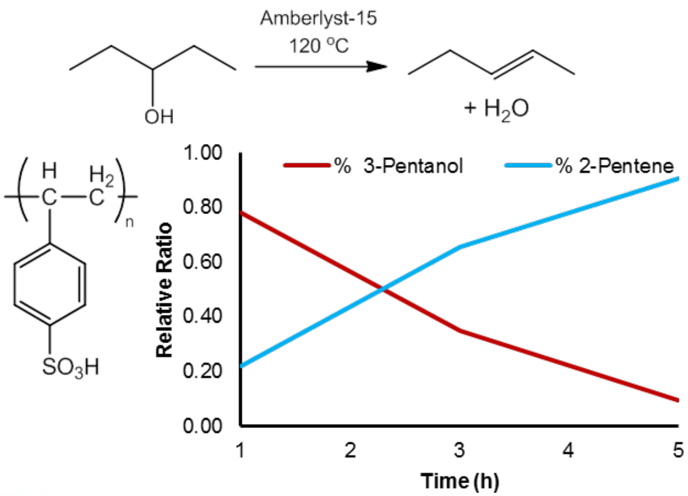


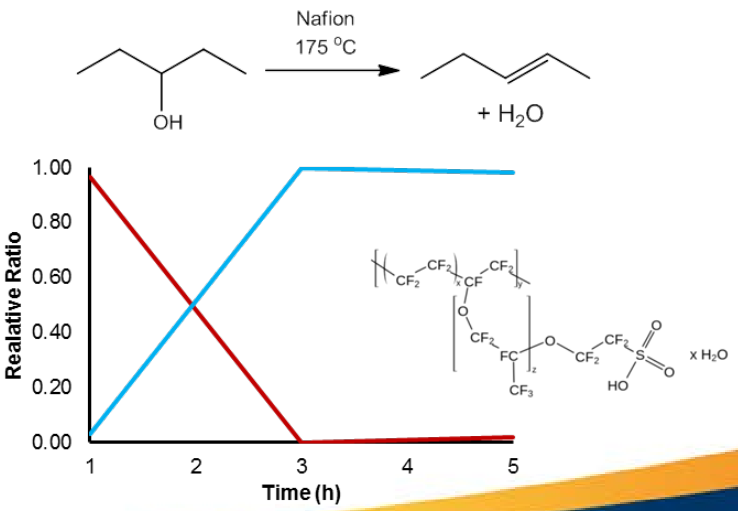
Ketone Reduction

Alcohol Dehydration

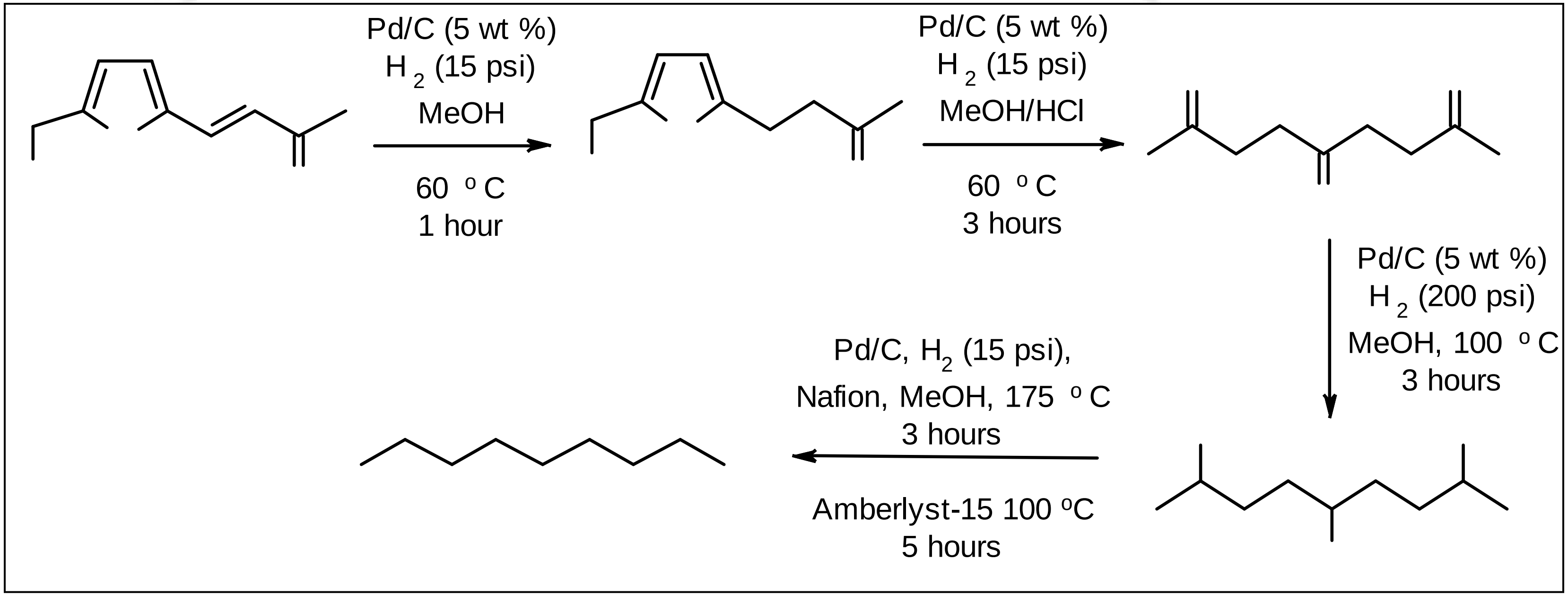
Alkene Reduction

Solid Acid? Fully Heterogeneous Continuous Flow System?



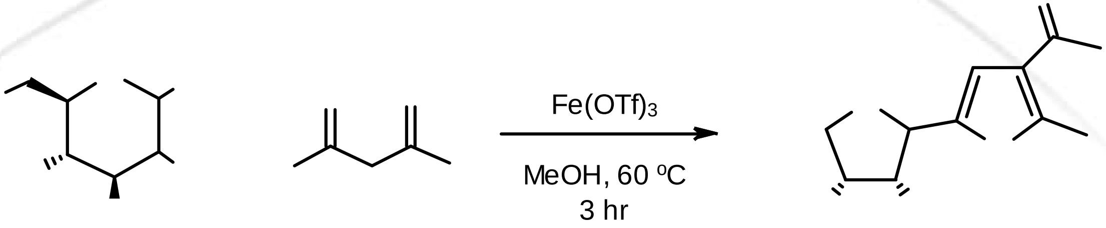


3 – Technical Accomplishments



- **Temperature now 100 ^{o}C for the whole process**
- **No Acetic acid**
- **No $La(OTf)_3$**
- Uses only Pd, HCl & solid acids + H_2
- Can replace Pd with Ni but at higher H_2 pressure

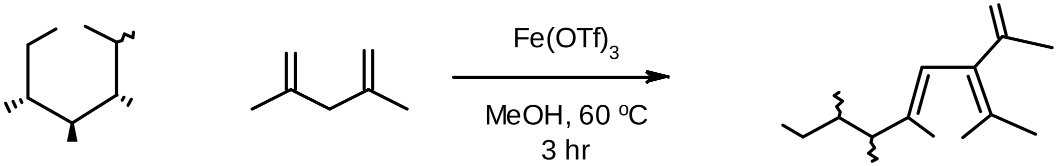
3 – Technical Accomplishments



Fe(OTf)3

MeOH, 60 ºC
3 hr

glucose 2,4-pentanedione Glucose Garcia-Gonzales Product (G-GG)

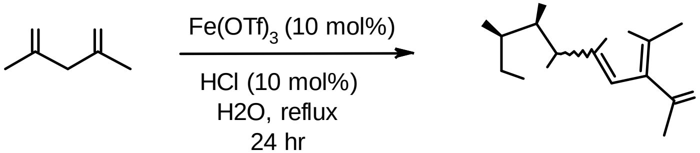


$Fe(OTf)_3$

MeOH, 60 ºC
3 hr

xylose 2,4-pentanedione Xylose Garcia-Gonzales Product (X-GG)

Starch



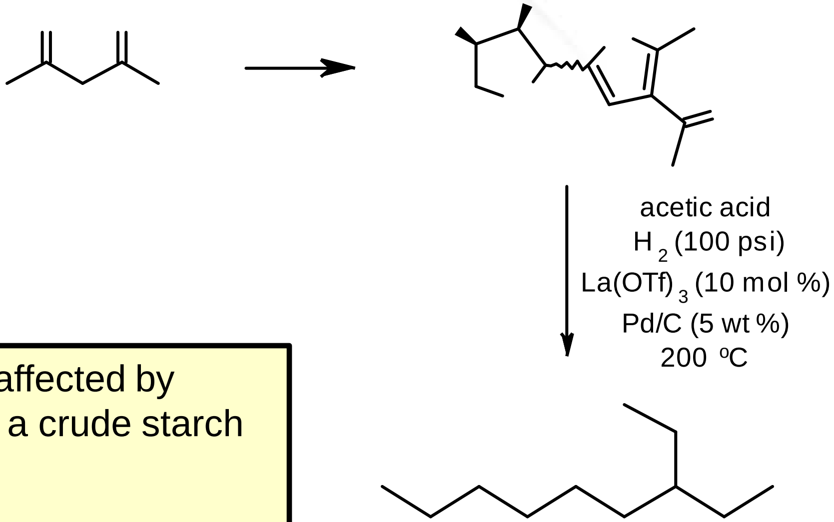
$Fe(OTf)_3$ (10 mol%)

HCl (10 mol%)
H2O, reflux
24 hr

>99% conversion
ca. 75% isolated yield.

85 % isolated yield

3 – Technical Accomplishments



acetic acid
H_2 (100 psi)
$La(OTf)_3$ (10 mol %)
Pd/C (5 wt %)
200 ºC

- Catalysis doesn't appear to be adversely affected by proteins and other materials isolated from a crude starch extraction
- Alkanes produced in good yield from soluble starch
- Potato serves as an illustrative example of our ability to access desirable fuel synthons *directly from biomass* (algae could also be used to access starch..)

C_{10}-C_{12} alkanes are in the carbon chain length appropriate for diesel fuel applications

3 – Technical Accomplishments/ Progress/Results FY14

Milestone	Date Completed	Task
1	Q1 12/31/13	Obtain a minimum of one hydrolysate sample from a DOE partner and analyze its composition (use GC-MS, HPLC, NMR and EA).
2	Q2 3/31/14	Conduct HDO catalysis studies on chosen hydrolysate mixture(s)
3	Q3 6/31/14	Use results from Q2 to determine what clean-up/separations steps have to be applied to the hydrolysate in order to promote catalyst longevity/activity
4	Q4 9/31/14	Based on results of Q2 and Q3, investigate the use of a non-precious metal hydrogenation catalyst to supplant use of Pd (e.g. Raney Ni)

3 – Technical Accomplishments/ Progress/Results FY14

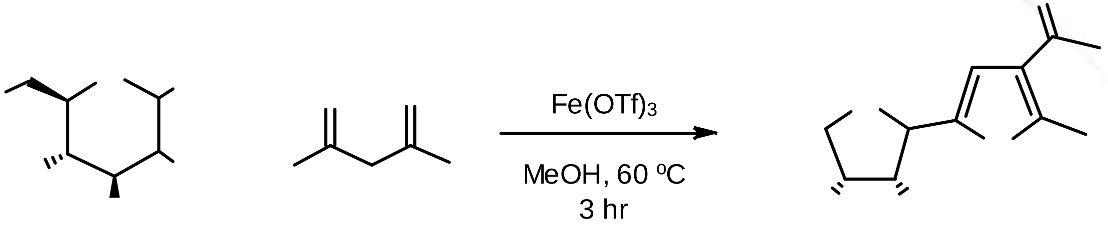
- *Milestone 1: Hydrolysate samples received from NREL*

			Monomeric Sugars						Total Sugars					Organic Acids					
Sample Type	Total Solids, %	Density, g/ml	Cellobiose	**Glucose (mg/ml)**	**Xylose (mg/ml)**	Galactose	Arabinose (mg/ml)	Fructose	**Glucose (mg/ml)**	**Xylose (mg/ml)**	Galactose	Arabinose (mg/ml)	Fructose	Lactic Acid	Glycerol	Acetic Acid	Ethanol (mg/ml)	HMF (mg/ml)	Furfural
Acid Pretreatment Liquid	14%	1.05	0.8	**15.9**	**74.9**	5.9	11.2	0.0	**16.6**	**82.1**	6.3	12.1	0.0	0.0	0.7	8.7	0.0	0.3	4.4
Enzymatic Hydrolysis Liquid	19%	1.08	2.8	**80.2**	**49.3**	3.9	7.4	0.0	**88.2**	**55.5**	4.2	8.5	0.4	0.0	0.4	6.3	0.0	0.2	3.2

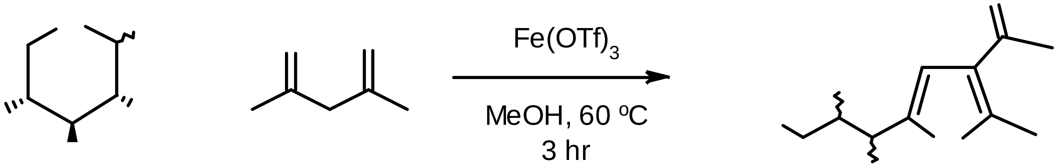
- *Techniques*
  - *GC-MS – not appropriate for sugars; NMR – indicates sugars are present but due to overlapping resonances, individual species cannot be identified; EA – Elemental analysis would also be unhelpful*
- ***However, all these techniques will be useful to determine new products formed in the conversion process and to determine the degree of conversion***

3 – Technical Accomplishments/ Progress/Results FY14

- *Milestone 2:* HDO catalysis studies on chosen hydrolysate mixture(s)



glucose 2,4-pentanedione Glucose Garcia-Gonzales Product (G-GG)

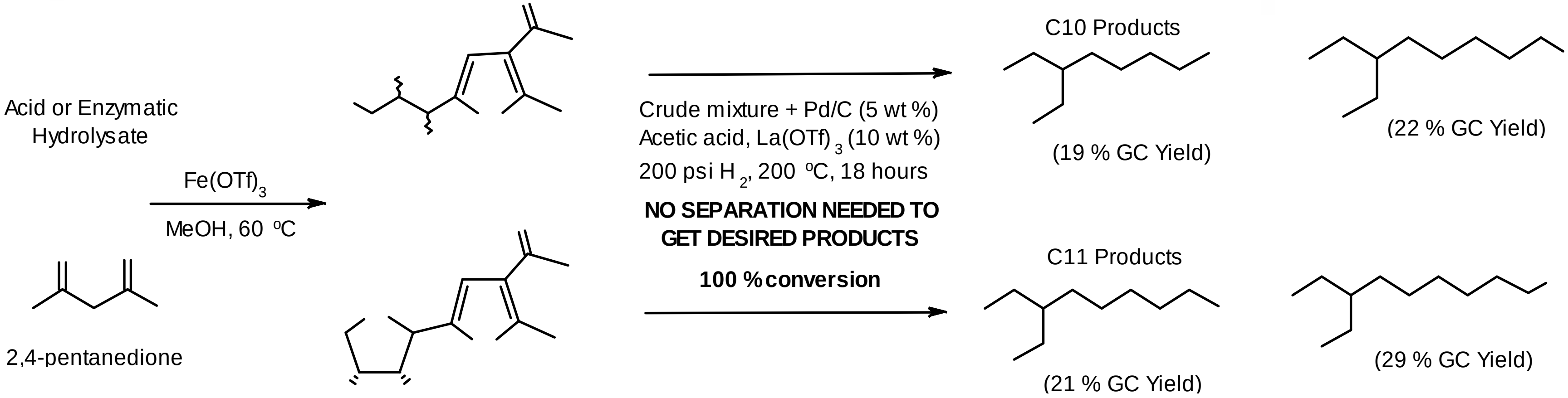


xylose 2,4-pentanedione Xylose Garcia-Gonzales Product (X-GG)

- *Milestone 3:* No separation or purification required in benchtop scale experiments
  - Some separations may be eventually be advantageous to improve yield/selectivity
- *Milestone 4:* Raney Ni performs as well but at increased pressure (300 psi H_2)
  - Gets us away from precious metal Nickel - $7.70/100g, Palladium - $2800/100g

3 – Technical Accomplishments/ Progress/Results FY14

- *Milestone 2:* HDO catalysis studies on chosen hydrolysate mixture(s)



Acid or Enzymatic Hydrolysate

2,4-pentanedione

$Fe(OTf)_3$

MeOH, 60 ºC

Crude mixture + Pd/C (5 wt %)
Acetic acid, $La(OTf)_3$ (10 wt %)
200 psi H_2, 200 ºC, 18 hours

NO SEPARATION NEEDED TO GET DESIRED PRODUCTS

100 % conversion

C10 Products

(19 % GC Yield)

(22 % GC Yield)

C11 Products

(21 % GC Yield)

(29 % GC Yield)

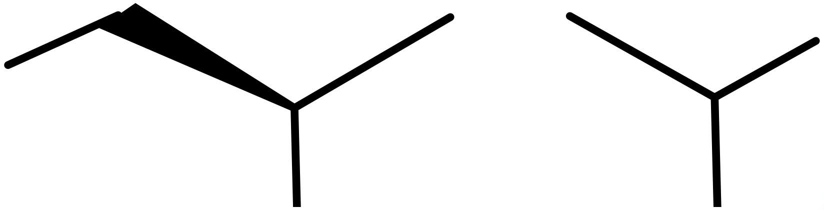
- *Milestone 3:* No separation or purification required in benchtop scale experiments
  - Some separations may be eventually be advantageous to improve yield/selectivity
- *Milestone 4:* Raney Ni performs as well but at increased pressure (300 psi H_2)
  - Gets us away from precious metal Nickel - $7.70/100g, Palladium - $2800/100g

3 – Technical Accomplishments/ Progress/Results FY15

Milestone	Date Completed	Task
1	Q2 3/31/15	Optimize chain extension chemistry for xylose. Apply this to mixed glucose/xylose sugar inputs to generate mixed G-GG and X-GG solutions.
2	Q2 3/31/15	Optimize pressure and temperature for HDO reaction of X-GG /G-GG mixtures. Use this to minimize residence time and demonstrate catalyst reuse.
3	Q3 6/31/15	Apply optimized chain extension chemistry to hydrolysate feed streams and optimize GG-like product outputs.
4	Q3 6/31/5	Apply optimized HDO chemistry from Milestone 2 to GG-extended hydrolysate feedstream.
5	Q4 9/31/15	Demonstrate the use of mixed X-GG/G-GG feed on a 5g HDO scale.
6	Q4 9/31/15	Demonstrate at least 1g sugar hydrolysate input conversion to alkane using optimized system to allow calculation of overall yield from raw biomass.

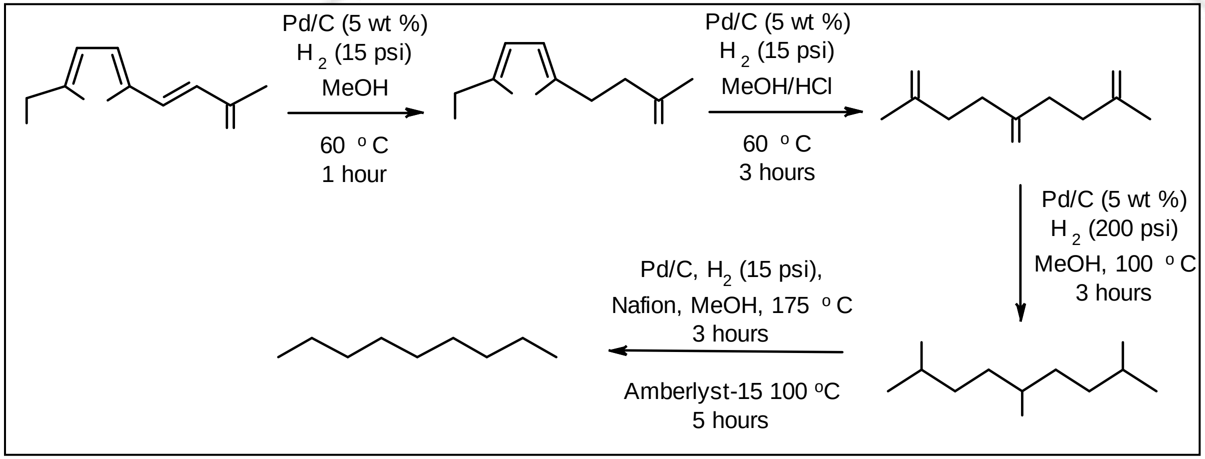
3 – Technical Accomplishments/Progress/Results FY15

- *Milestone 1:* Optimize chain extension chemistry for xylose. Apply this to mixed glucose/xylose sugar inputs to generate mixed G-GG and X-GG solutions (Due 3/31/15).



- Done on 1g total sugar input
- No longer need rare earth catalyst
- Using non-precious metal
- Mixed sugars work well
- 99 % conversion
- Work to increase rate ongoing

Application to "Real" Molecules



- **Temperature now 100 °C for the whole process**
- **No Acectic acid**
- **No La(OTf)$_3$**
- Uses only Pd, HCl & solid acids + H_2
- Can replace Pd with Ni but at higher H_2 pressure

Currently testing the applicability to the GG products but initial tests look promising

4 – Relevance

- This project addresses **Bt-H "Cleanup/Separations" Bt-I "Catalyst Efficiency", Tt-L "Knowledge Gaps in Chemical Processes" from BETO MYPP**
- We aim to eliminate processing steps and lower operating conditions and use cheaper catalysts to produce drop-in fuel replacements to reduce cost **(Bt-H & Bt-I)**
- Currently no separations are needed (although this may be modified to extend catalyst and infrastructure lifetime) **(Bt-H)**
- By understanding the molecular transformations, we know what is required for each transformation so we can rationally design better catalysts **(Bt-I & Tt-L)**
- This is applicable to range of different bio-derived molecules resulting in a range of different potential transport applications (i.e. autos, trains, planes, military etc.)
- The retention of functional groups has been demonstrated and application to chemical feedstock industry is being explored.
- Our catalytic cycle can be applied to multiple feedstock inputs and as a result produces multiple products which builds in an inherent robustness to this flexible catalytic system **(Bt-I & Tt-L)**

5 – Future Work

- Optimize pressures and temperatures for HDO reaction of X-GG /G-GG mixtures. Use this to minimize residence time and **demonstrate catalyst reuse**.
- Apply optimized chain extension chemistry to hydrolysate feed streams and optimize GG-like product outputs.
- Do HDO on this product mix from hydrolysate feed stream
- Scale-Up: Demonstrate the use of mixed X-GG/G-GG feed on a 5g HDO scale & 1g total sugar input.
- Move to flow reactor with new catalyst/reaction conditions to fully optimize the reaction steps
- Vary the diketone in order to generate a range of alkane products.

3 – Technical Accomplishments/ Progress/Results FY15

Milestone	Date Completed	Task
1	Q2 3/31/15	Optimize chain extension chemistry for xylose. Apply this to mixed glucose/xylose sugar inputs to generate mixed G-GG and X-GG solutions.
2	Q2 3/31/15	Optimize pressure and temperature for HDO reaction of X-GG /G-GG mixtures. Use this to minimize residence time and demonstrate catalyst reuse.
3	Q3 6/31/15	Apply optimized chain extension chemistry to hydrolysate feed streams and optimize GG-like product outputs.
4	Q3 6/31/5	Apply optimized HDO chemistry from Milestone 2 to GG-extended hydrolysate feedstream.
5	Q4 9/31/15	Demonstrate the use of mixed X-GG/G-GG feed on a 5g HDO scale.
6	Q4 9/31/15	Demonstrate at least 1g sugar hydrolysate input conversion to alkane using optimized system to allow calculation of overall yield from raw biomass.

Summary

1. Overview
   - C-C extension and oxygen removal catalysis for the production of fuels and feedstocks
2. Approach
   - Builds on current results towards an optimized scaled-up process using flow reactors
3. Technical Accomplishments/Progress/Results
   - Removed acetic acid, lanthanum, cerium and potentially palladium catalyst from processes
   - Replaced these with commercially available or earth abundant metals
   - Can perform the production of alkanes from hydrolysate without the need for separations
4. Relevance
   - Increasing catalyst efficiencies, reducing catalyst cost, reducing separations and reducing energy input (temperature, infrastructure)
5. Future work
   - Catalyst longevity, scale-up, further optimization with hydrolysates

Acknowledgments

- John Gordon (PI)
- Pete Silks
- Ruilian Wu
- Richard Elander (NREL)
- Anthe George (JBEI)
- BETO

Additional Slides

Publications, Patents, Presentations, Awards, and Commercialization

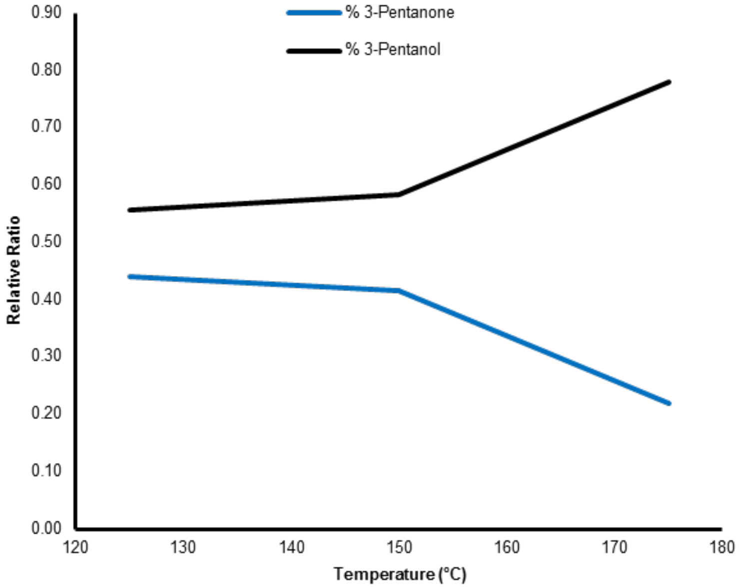
PRESENTATIONS

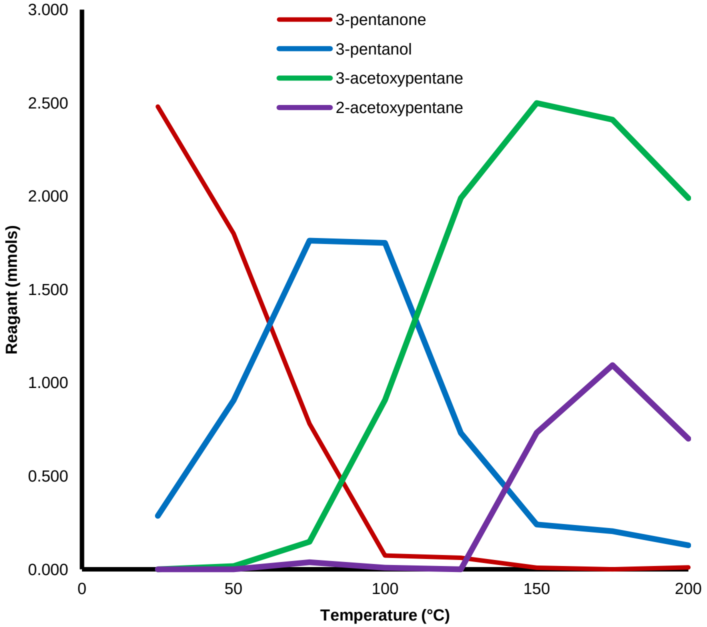
- Andrew D. Sutton, Amanda E. King, Ty Brooks, Pete Silks, Ruilian Wu, John. C. Gordon, Enrique Batista, Marcel Schlaf, Fraiser Waldie, “Conversion of Oligosaccharides into Alkanes For Fuels and Feedstocks” Gordon Research Conference – Organometallic Chemistry, Salve Regia University, RI, July 6th – 11th 2014
- Andrew D. Sutton, Amanda E. King, Ty Brooks, Pete Silks, Ruilian Wu, John. C. Gordon, Marcel Schlaf, Fraiser Waldie, “Conversion of Oligosaccharides into Alkanes” Biomass 2014, Washington DC, July 29th – 30th 2014
- Amanda E. King, John C. Gordon, Andrew D. Sutton “Hydrodeoxygenation of bioderived furans into alkanes: Process development” 248th ACS National Meeting, San Francisco, CA, August 10th - 14th 2014.
- John C. Gordon, Amanda E. King, Pete Silks, Andrew D. Sutton, Ruilian Wu, “Upgrading carbohydrates into hydrocarbons for fuels applications” 248th ACS National Meeting, San Francisco, CA, August 10th - 14th 2014.
- *Andrew D. Sutton, Amanda E. King, Ty Brooks, Thomas Huegle, “Adding Value to Biomass - Green Gold!” Gordon Research Conference – Inorganic Reaction Mechanisms, Hotel Galvez, Galveston, TX, March 1st – 6th 2015*

PUBLICATIONS

- Amanda E. King, John C. Gordon, Andrew D. Sutton “Hydrodeoxygenation of bioderived furans into alkanes: Process development” Preprints - American Chemical Society, Division of Energy & Fuels (2014), 59(2), 49-50.
- John C. Gordon, Amanda E. King, Pete Silks, Andrew D. Sutton, Ruilian Wu, “Upgrading carbohydrates into hydrocarbons for fuels applications” Preprints - American Chemical Society, Division of Energy & Fuels (2014), 59(2), 118-119.
- Andrew D. Sutton, Jun K. Kim, Caroline B. Hoyt, Ruilian Wu, David B. Kimball, Louis. A. Silks III, John C. Gordon, “Conversion of Oligosaccharides to Branched Alkanes.” *To be submitted, 2015.*
- Thomas Huegle, Ty J. Brooks, Andrew D. Sutton “Low temperature routes to fuels and feedstock molecules from

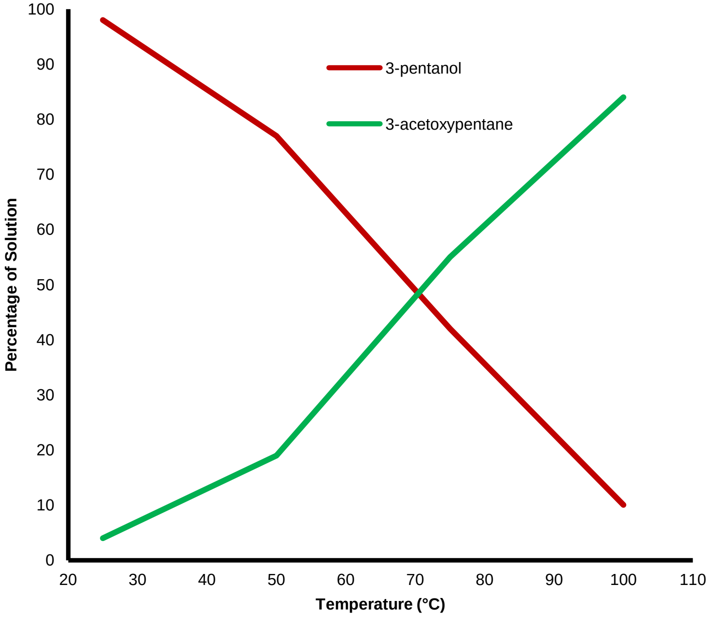
Stage 1 – Ketone Reduction

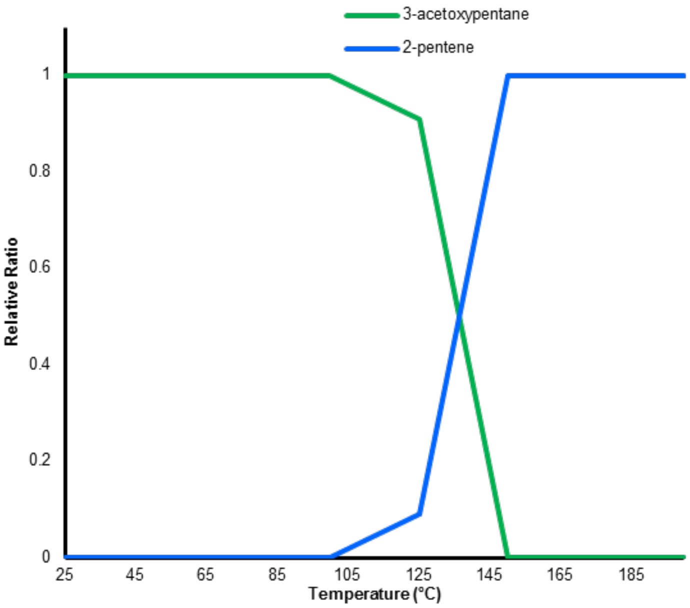




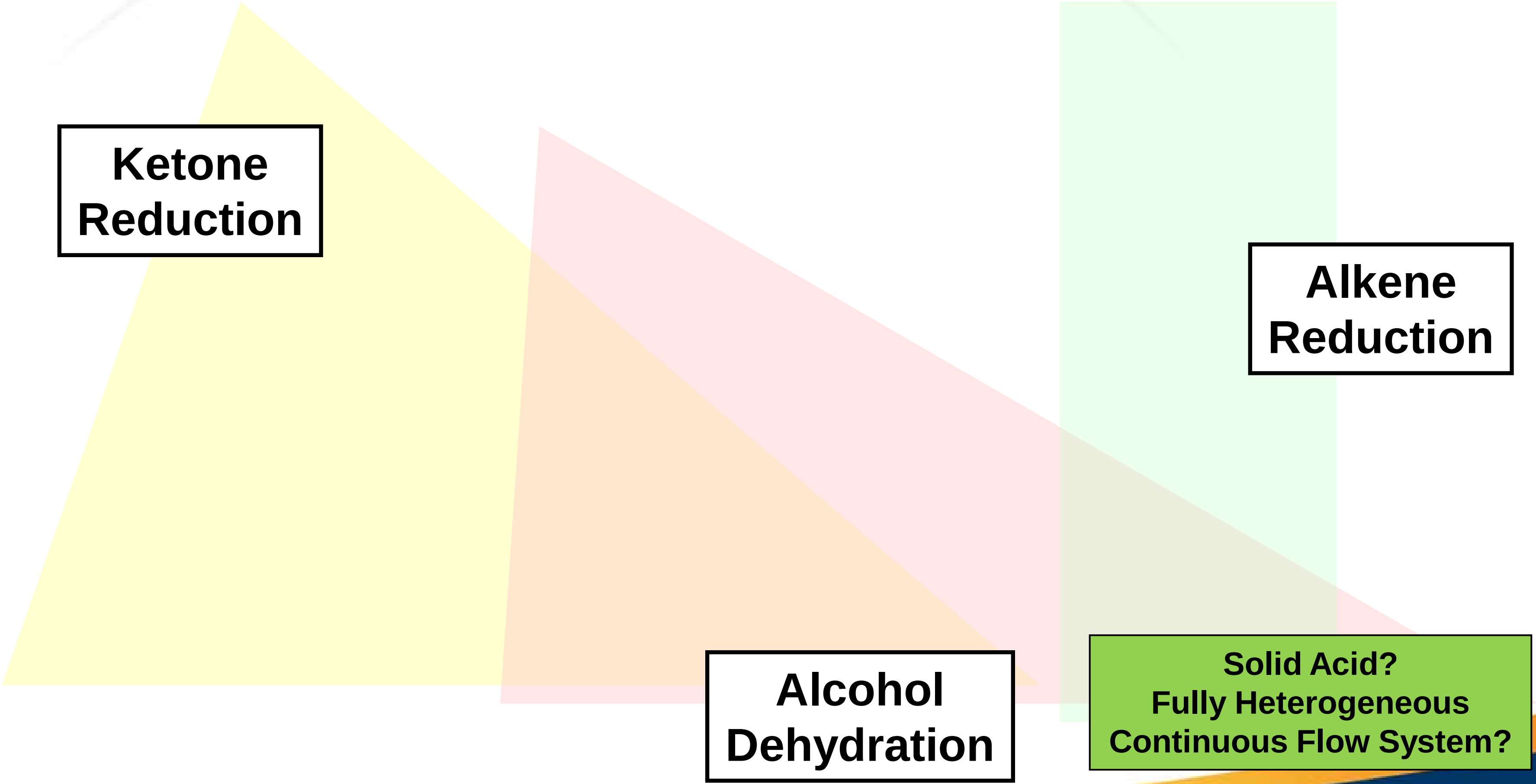
Stage 2 – Acetoxylation

Stage 3 – C-O Cleavage





Where could we improve the most?



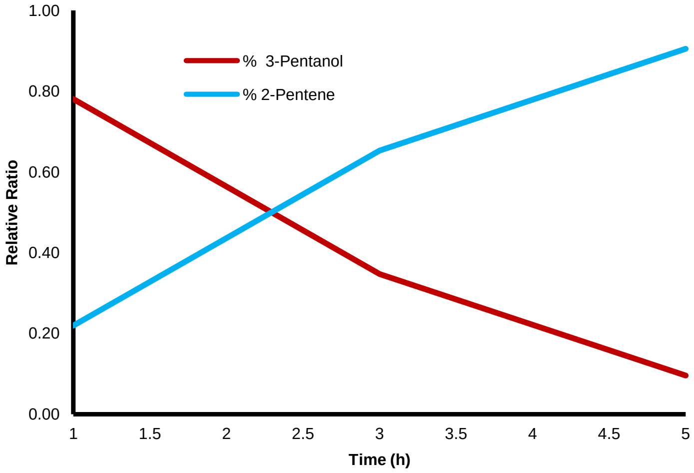
Ketone Reduction

Alkene Reduction

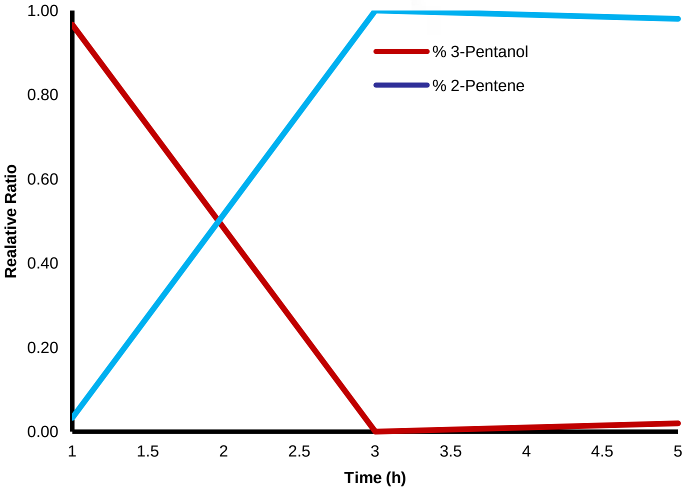
Alcohol Dehydration

Solid Acid?
Fully Heterogeneous Continuous Flow System?

Alcohol Dehydration with Solid Acids



Low Temperature – 120 ^{o}C



Fast – Complete in 3 hours!