Optimization of Aqueous Phase Furfural Hydrogenation Using Pd_1Ni_{15}/Silica Dilute Limit Alloy Catalysts

Md Fakhruddin Patwary*
Leandro De Castro
Christopher Williams
John Regalbuto
University of South Carolina, Columbia, SC 29208 (USA)

UofSC

REGALBUTO RESEARCH GROUP

Motivation: Why Care about this Reaction?

- World energy consumption is projected to raise by **50%** from 2018 to 2050.
- Energy consumption derived from **biomass** accounted for **46%** of the total renewable energy (Remaining from hydro, geothermal, photovoltaic and wind etc).
- **Furfural** is only derived from lignocellulosic biomass which can be converted into solvents, polymers, fuels and other useful chemicals.

- **Cyclopentanone** precursor to fragrances, pesticide, and few valued chemicals.

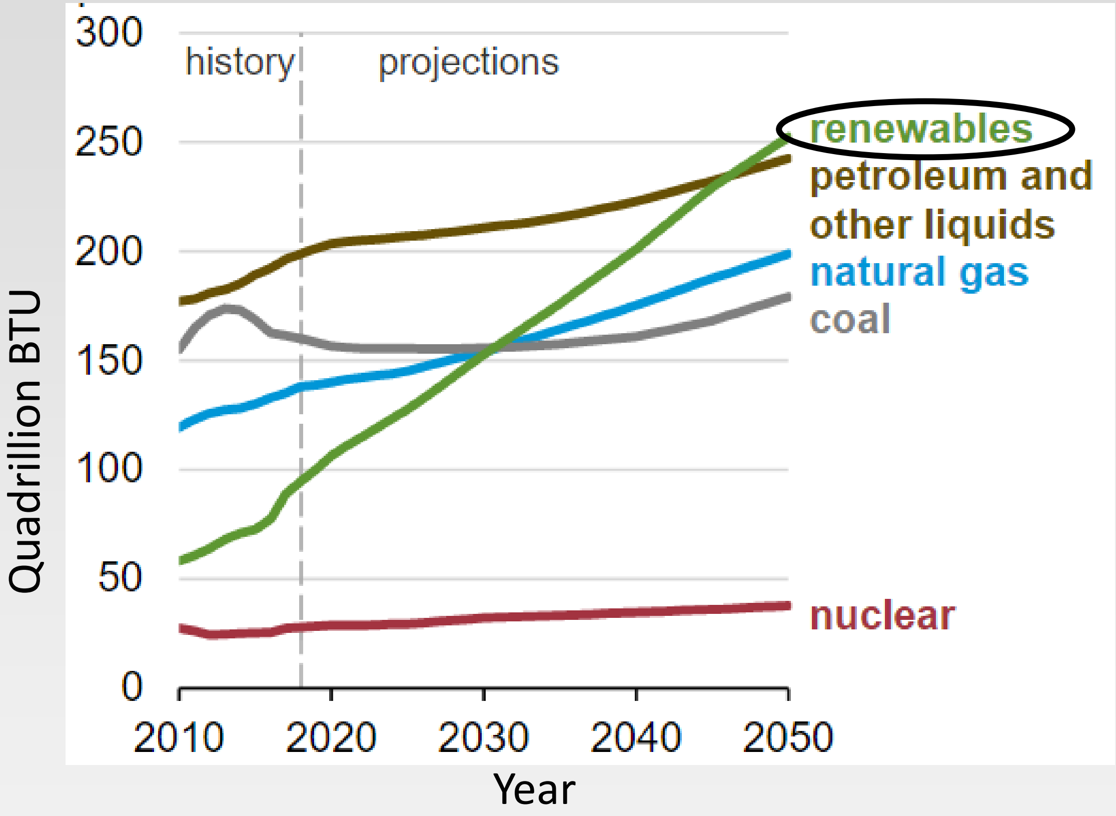


Figure: Global primary energy consumption by energy source.

**International Energy Outlook 2019*

REGALBUTO RESEARCH GROUP

Motivation: Why Bimetallic?

- ❑ Problems: Harmful element, Over reaction, Poor selectivity.

- ❑ Possible solution: Bimetallic Catalyst

    - Lower cost
    - maximizing yield to a specific product
    - increasing the selectivity
    - Improving stability by inhibiting sintering
    - creation of new reaction pathway

Specifications of our Dilute Limit Alloy Catalyst:

❑ <u>Metal Precursors</u>:

- Tetraamine Palladium(II) chloride monohydrate
- Hexaamminenickel(II) chloride

❑ <u>Support</u>: Aerosil300

❑ <u>Synthesis Method</u>: co-Strong Electrostatic Adsorption (co-SEA)

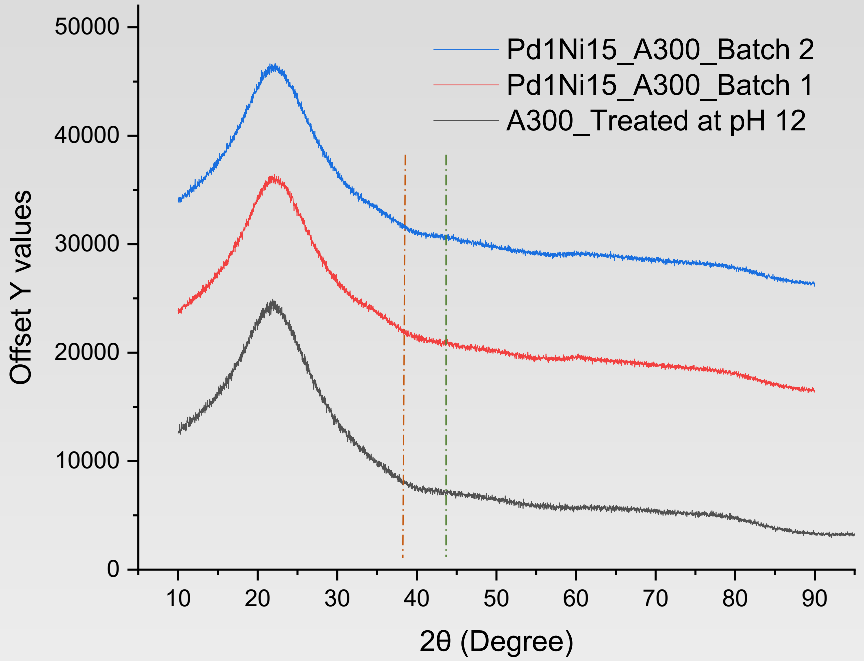
❑<u>Catalyst</u>:

0.16% Pd 1.42% Ni on Silica

or $Pd_1Ni_{15}/A300$

Reduced at 400C for 1.5hr with 10% H_2

XRD indicates formation of very small particles **(<1.5nm)**



Just impregnated → Dried → Reduced catalyst

Confirmation of Dilute Limit Alloy formation:

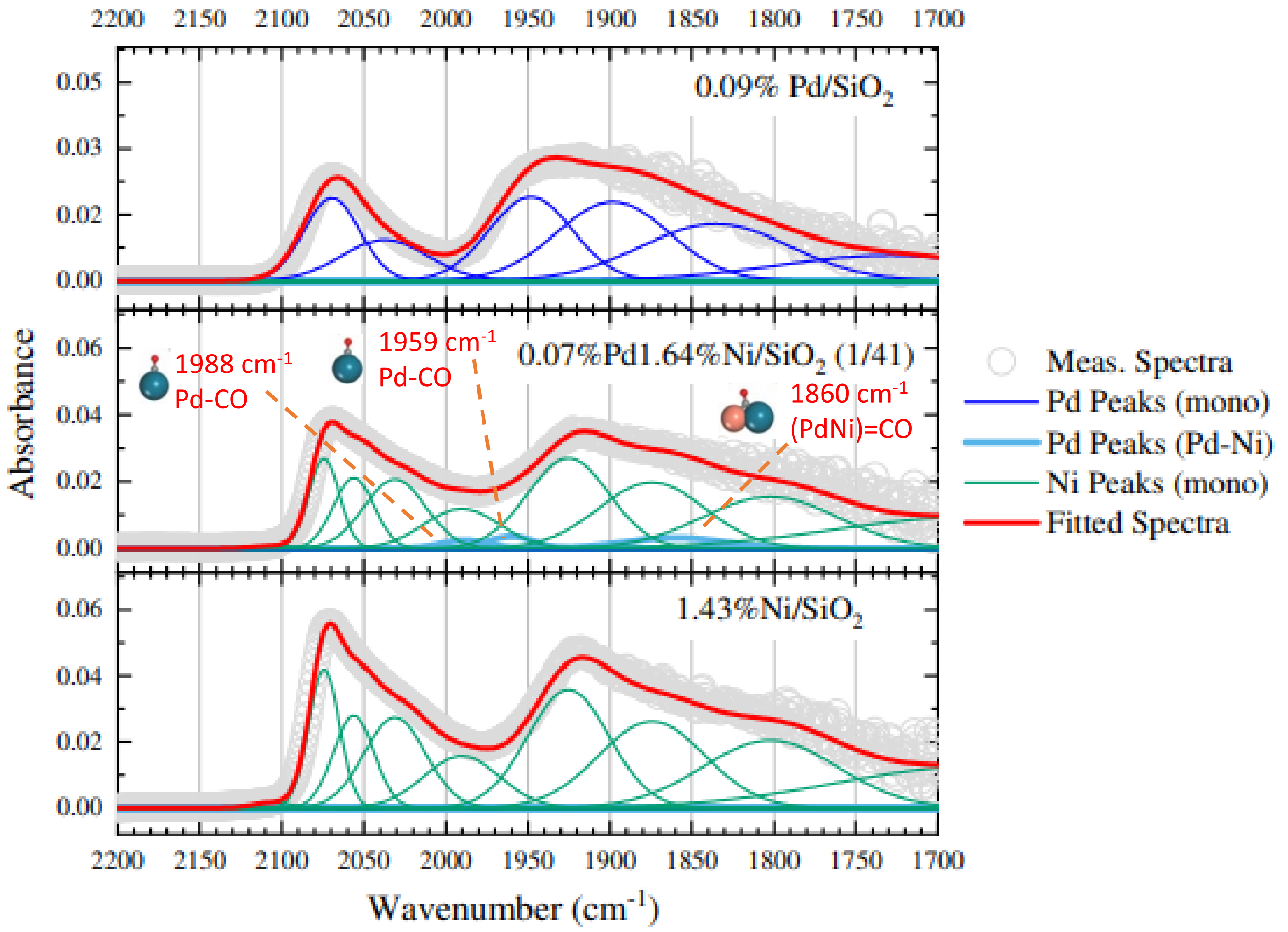


Figure: CO-FTIR study. Comparison of fitted Gaussian functions for monometallic and bimetallic Pd-Ni DLA catalysts – indicating the formation of DLA.

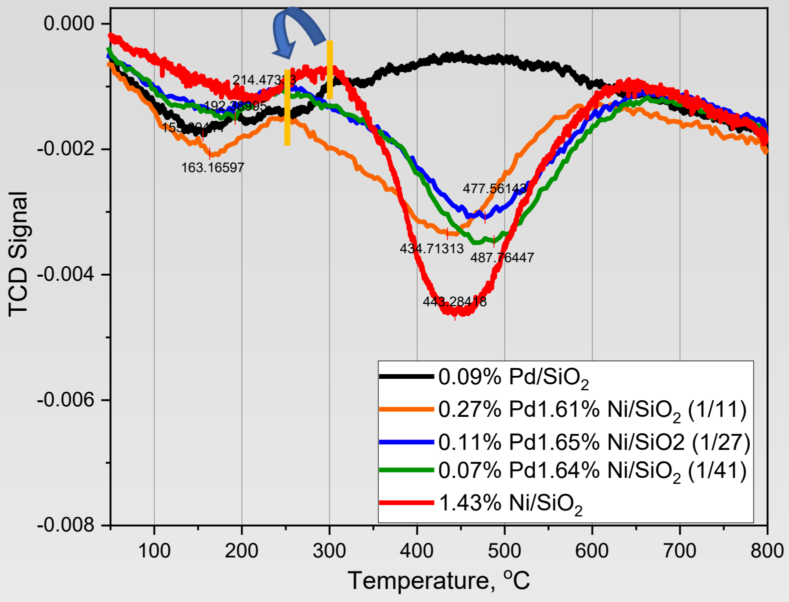


Figure: TPR spectra for Pd, Ni and Pd-Ni DLA catalysts

- ❑ Reduction temperature of Ni/SiO_2 is affected by the presence of Pd – Confirming the presence of dilute limit of Pd.

The Reaction:

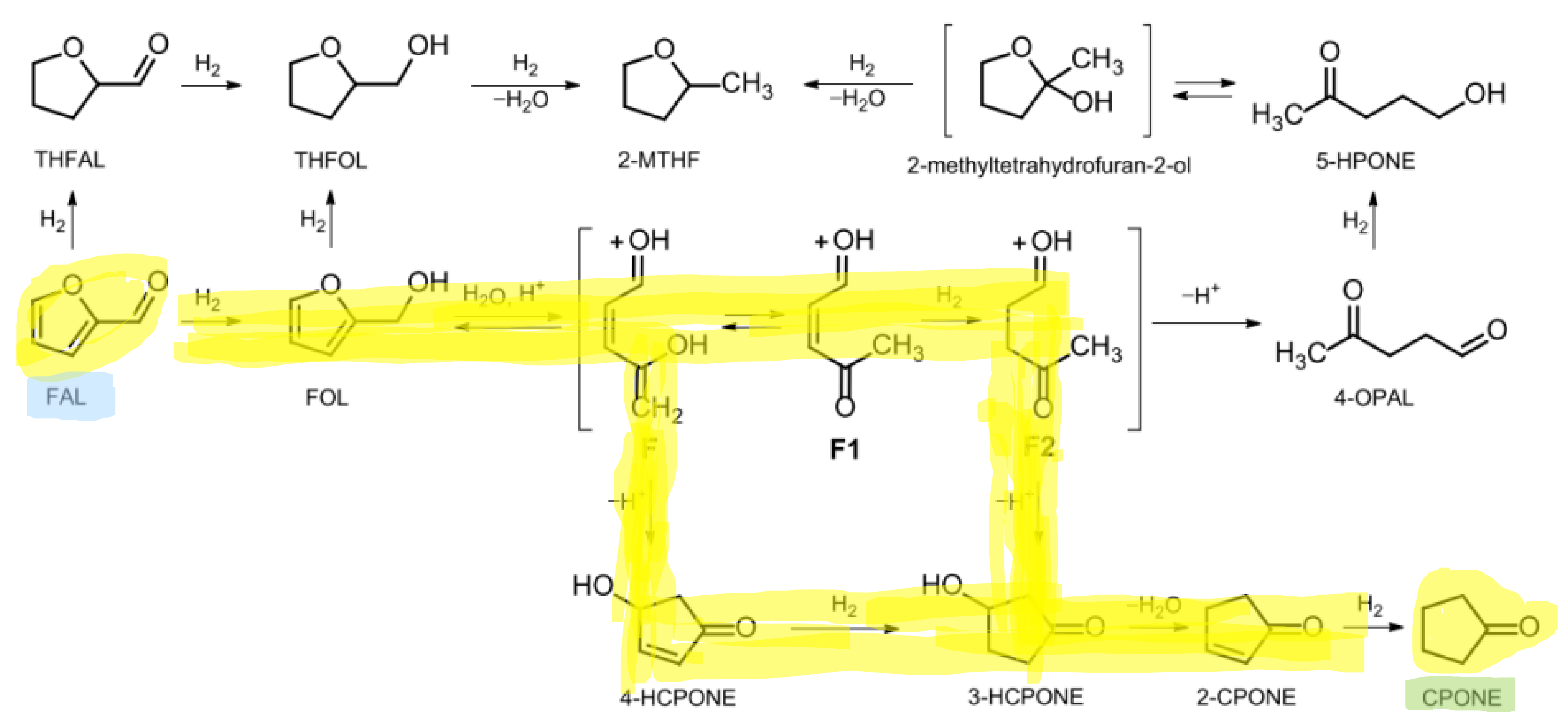


Figure: Proposed reaction network for the aqueous-phase hydrogenation of FAL over supported Pd catalysts

* Mironenko R. M. et. al. ‘ 2019

REGALBUTO RESEARCH GROUP

Reaction Plan:

- Sample collection at 0.5hr, 1.5hr, 3hr, 5hr, 8hr
- Total 15.8 mg metal (1gm catalyst) per batch.
- Temperature range 120 °C to 150 °C
- Pressure range 150psig to 430psig

Pd_1Ni_{15}/Si Cata. (gm)	Temp. (°C)	Pressure (PSIG)
1	120	430
1	150	430
1	180	430
1	120	300
1	150	300
1	180	300
1	120	150
1	150	150
1	180	150

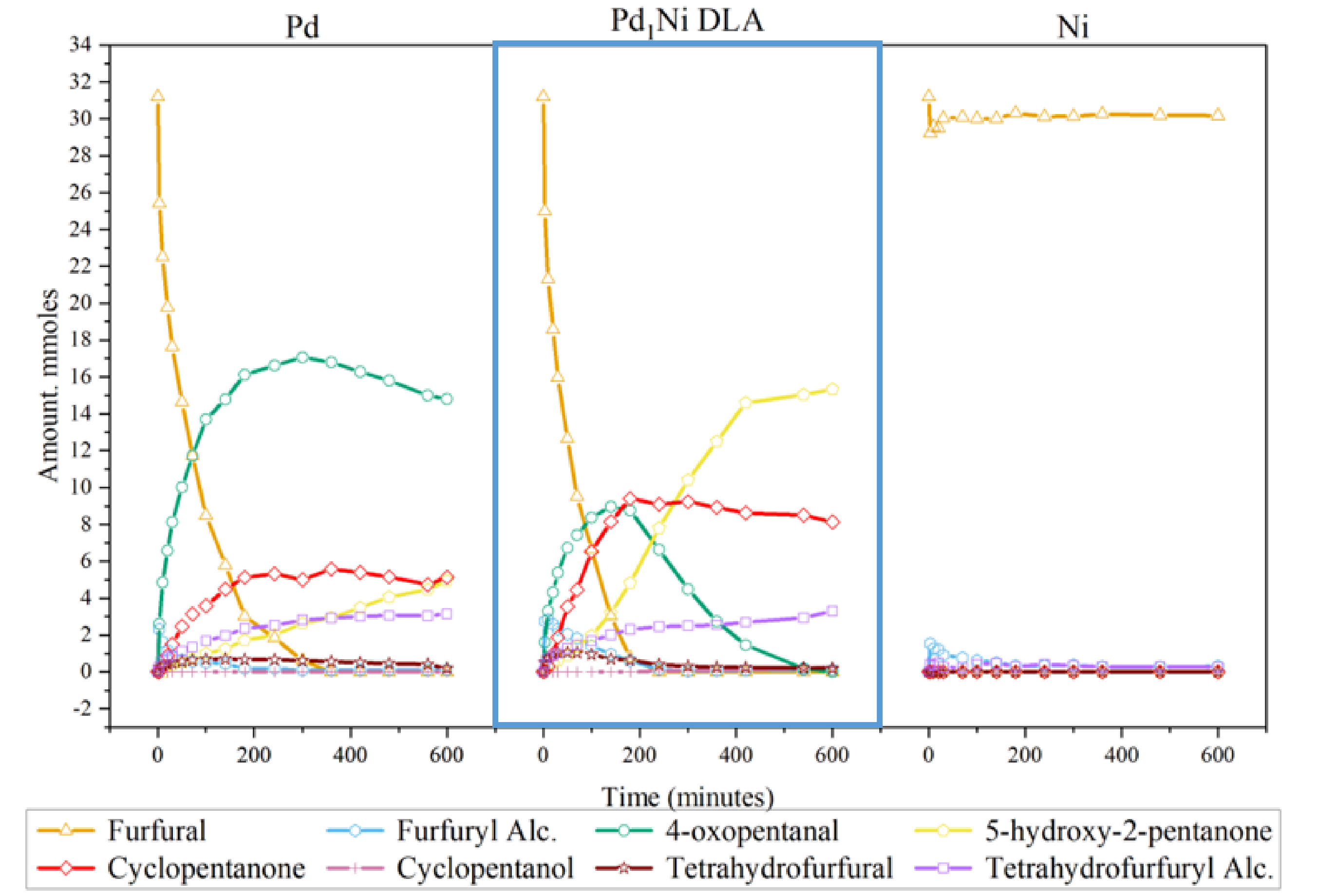


Figure: Aqueous phase furfural hydrogenation Concentration profile comparison using monometallic Pd, monometallic Ni and Pd1Ni DLA. Condition: 150°C, 430PSIG

Previous work

UofSC

REGALBUTO RESEARCH GROUP

Reaction Setup:

- 100 mL stainless-steel autoclave batch reactor
- 1000 rpm propeller speed
- Total 60ml reaction solution
- Reaction duration 8hrs

- HP 5890 Series II gas chromatogram

Figure: Batch Reactor

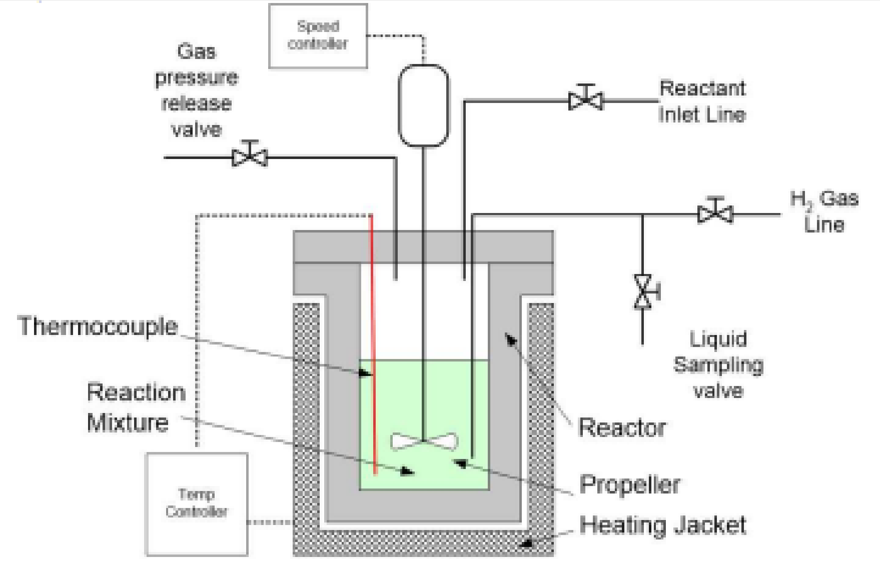


Figure: Reactor schematic diagram

Results: Furfural Hydrogenation by Pd1Ni15/A300

We reproduced the Pd_1Ni_{15}/A300 and using that we got similar results for Furfural conversion.

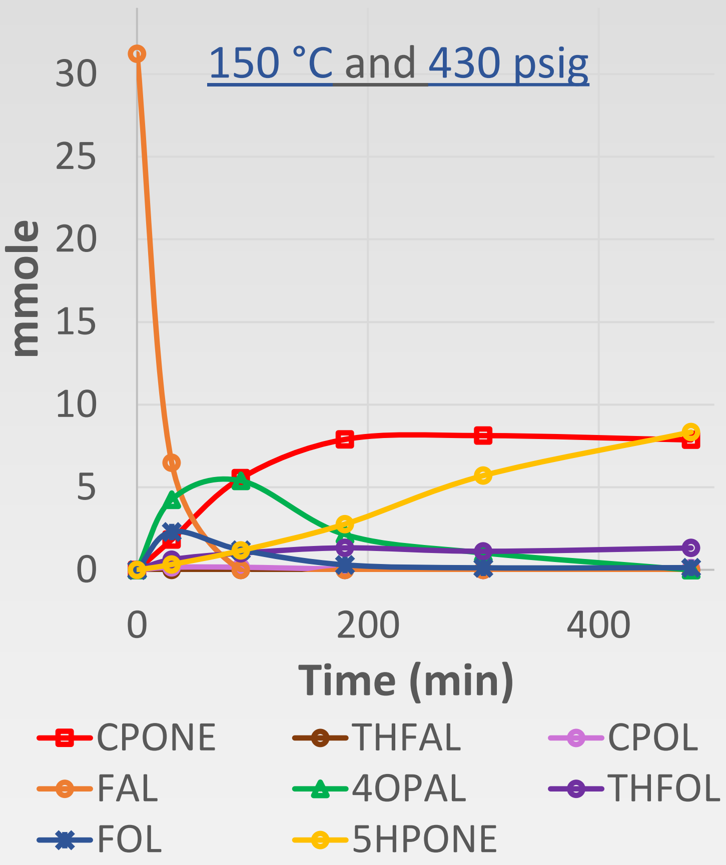


Figure: Current work

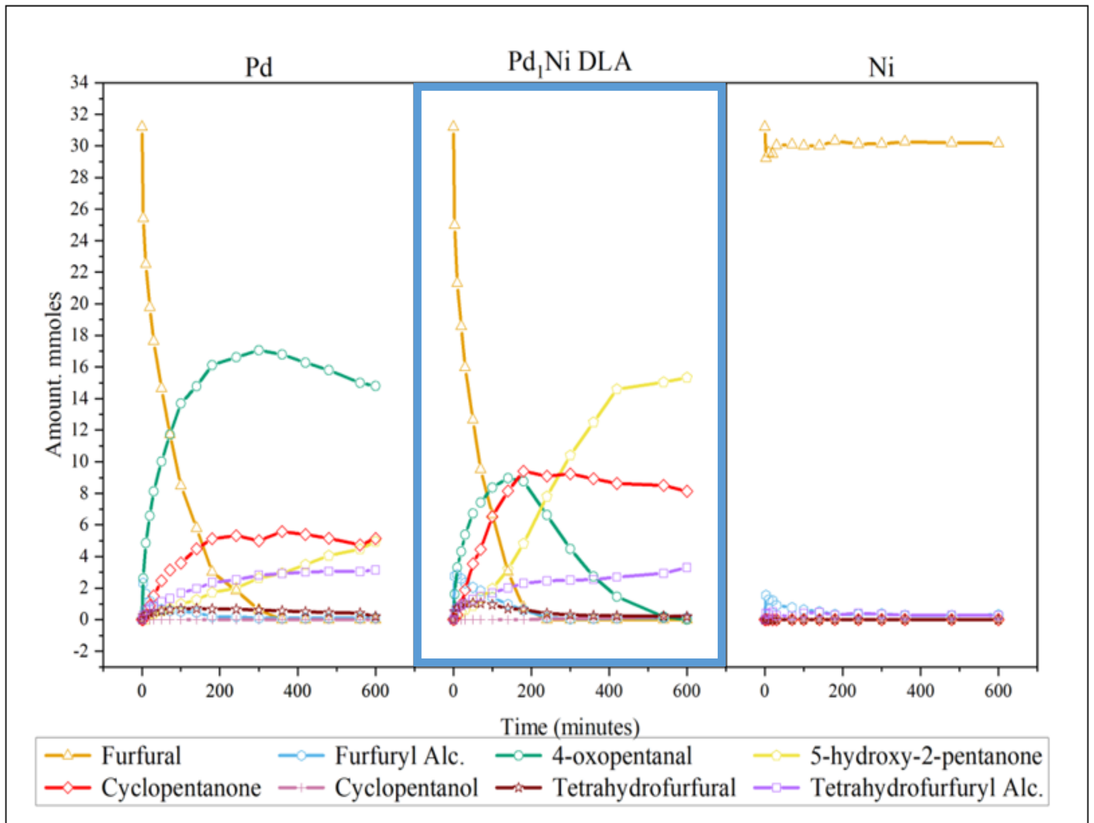


Figure: Aqueous phase furfural hydrogenation Concentration profile comparison using monometallic Pd, monometallic Ni and Pd1Ni DLA. Condition: 150°C, 430PSIG

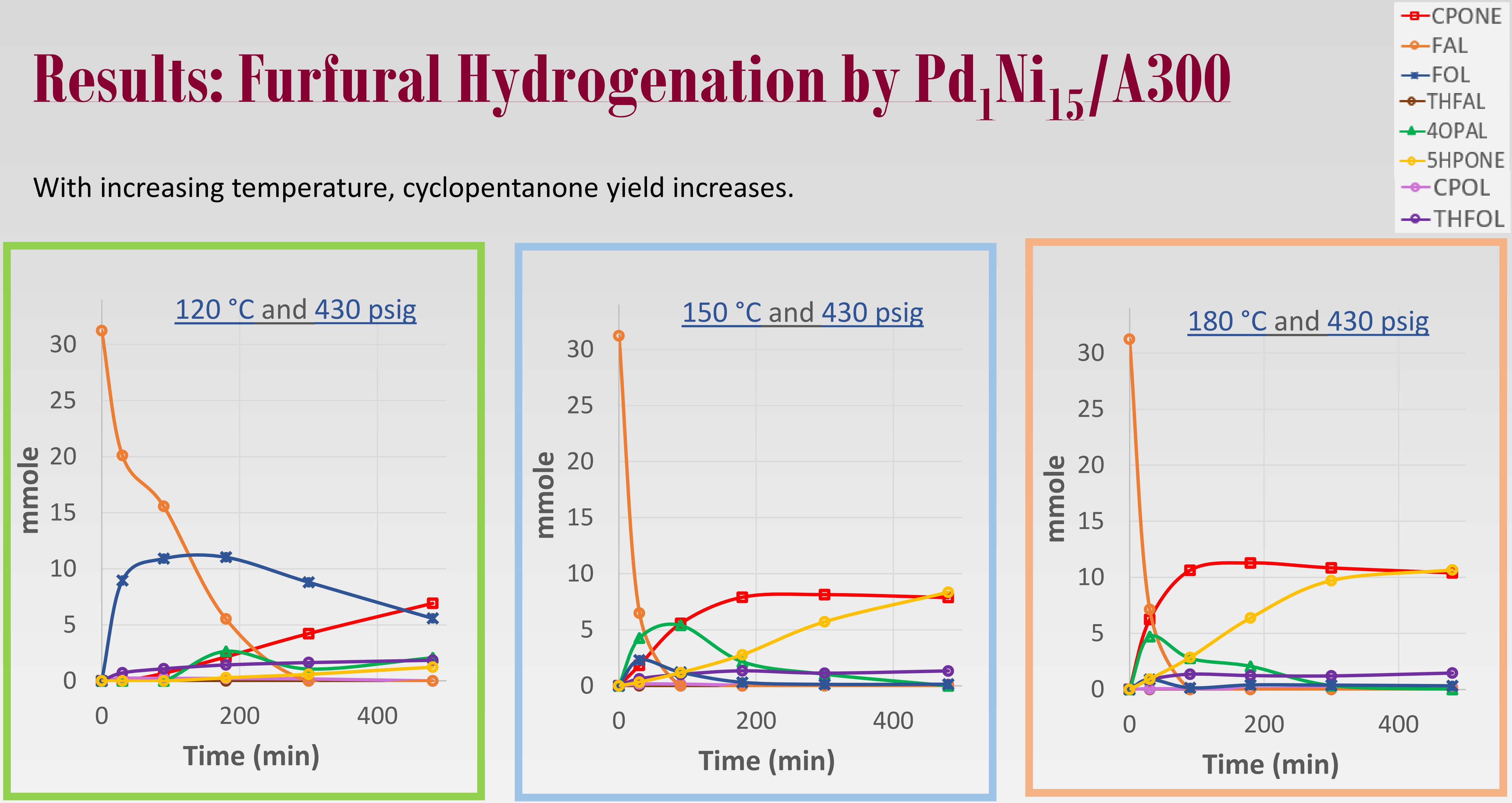
Figure: Previous work by Dr. Decastro

UofSC

REGALBUTO RESEARCH GROUP

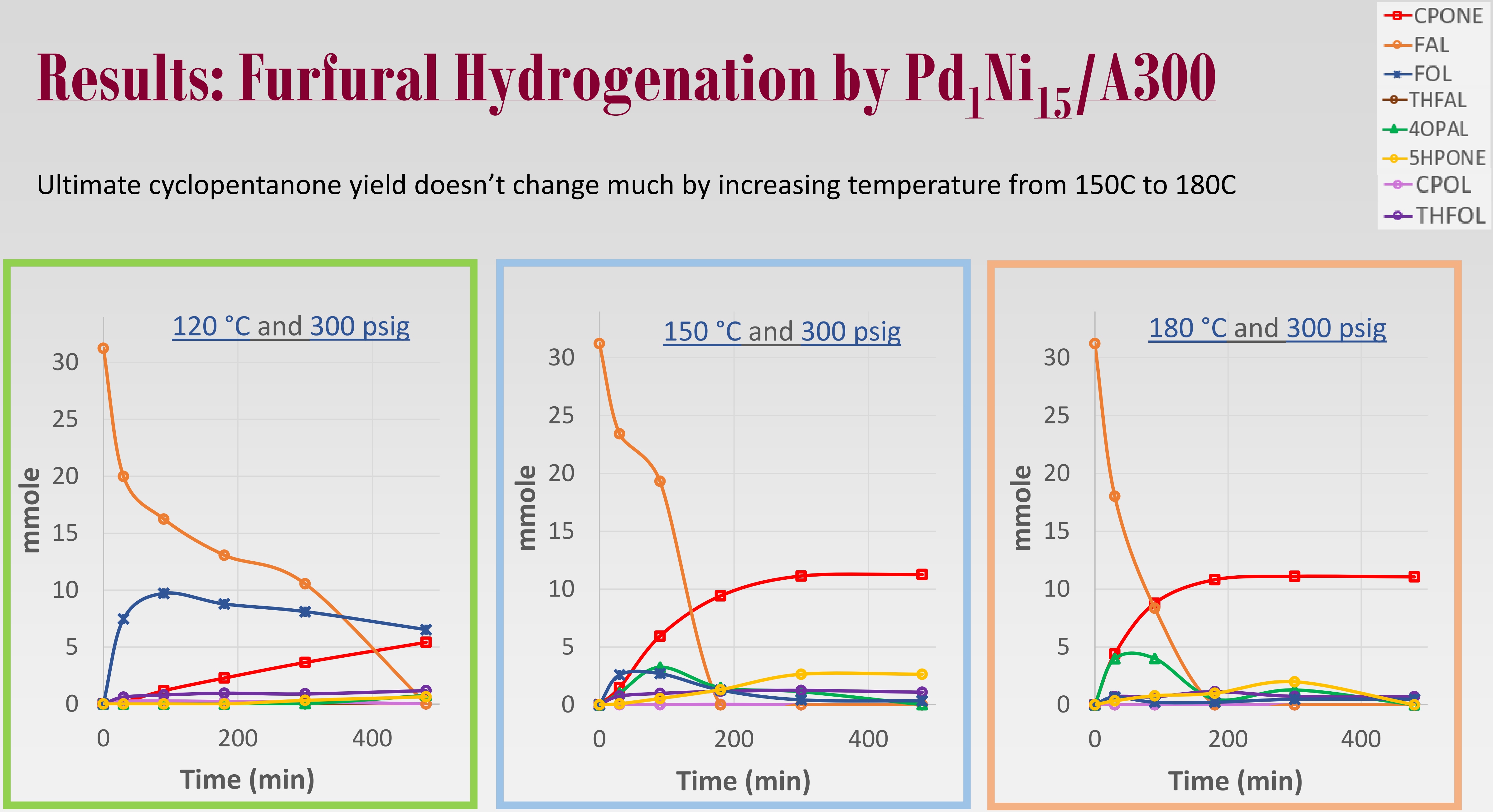
Results: Furfural Hydrogenation by $Pd_1Ni_{15}/A300$

With increasing temperature, cyclopentanone yield increases.



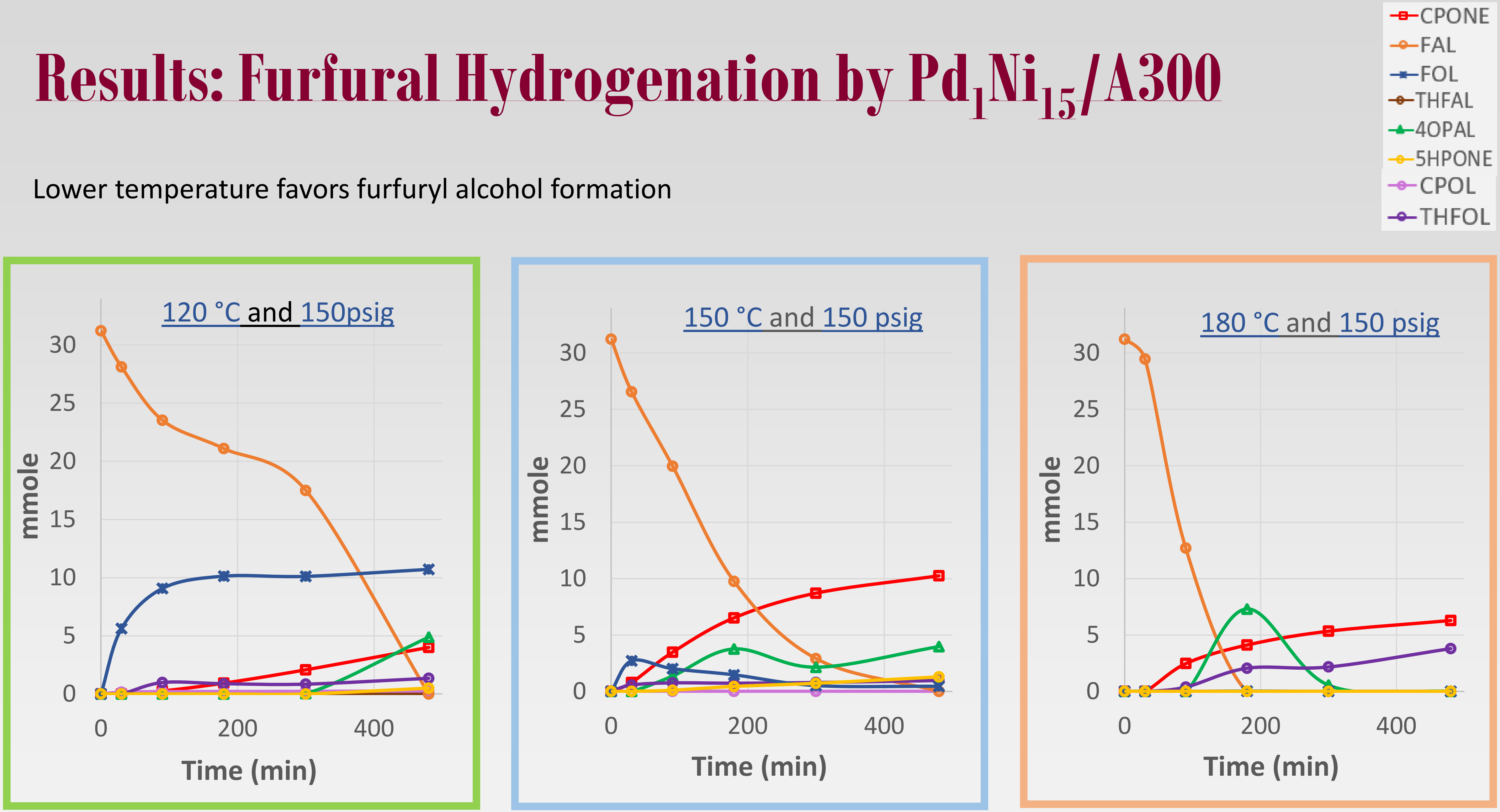
Results: Furfural Hydrogenation by $Pd_1Ni_{15}/A300$

Ultimate cyclopentanone yield doesn't change much by increasing temperature from 150C to 180C



Results: Furfural Hydrogenation by $Pd_1Ni_{15}/A300$

Lower temperature favors furfuryl alcohol formation

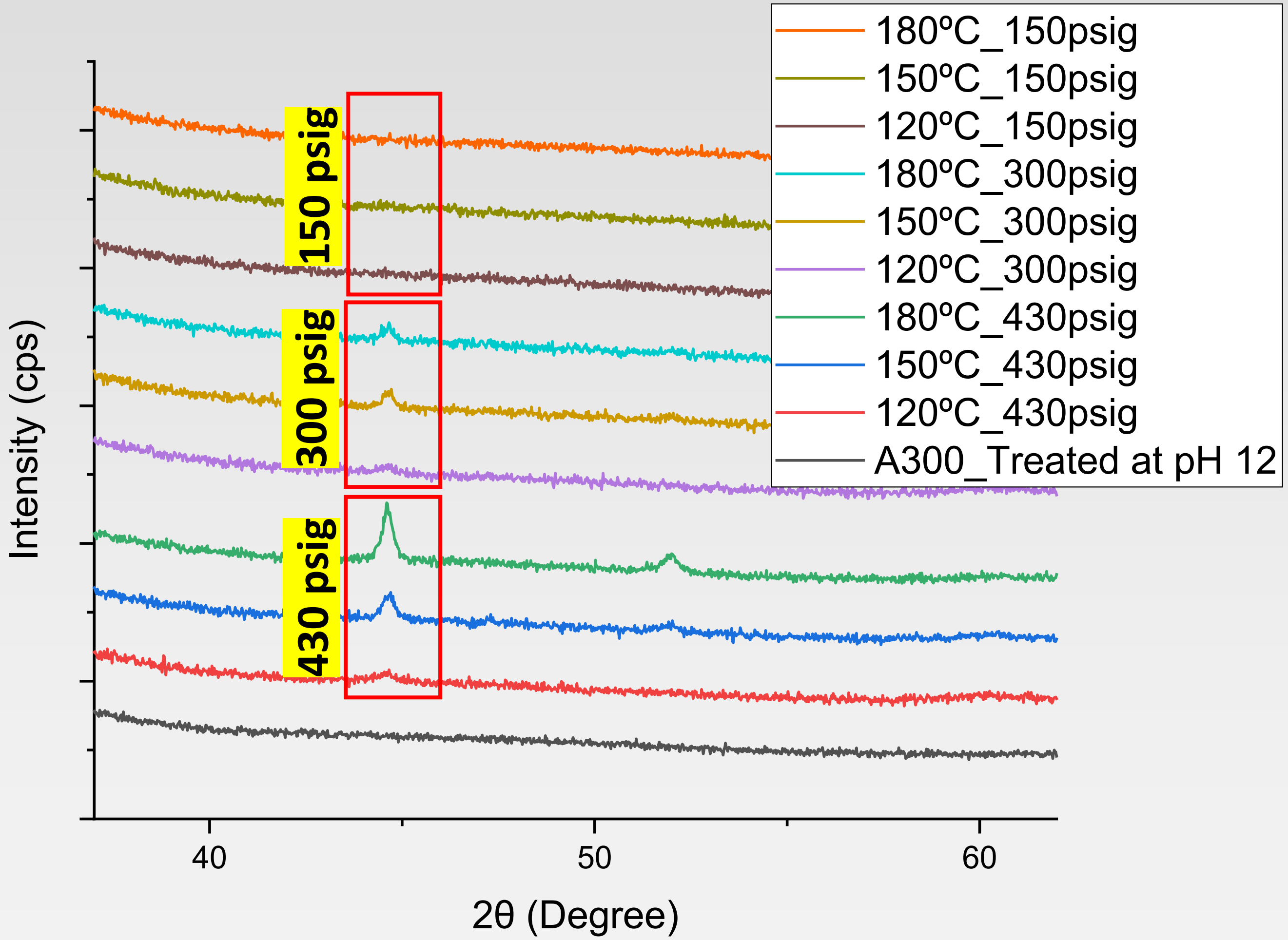


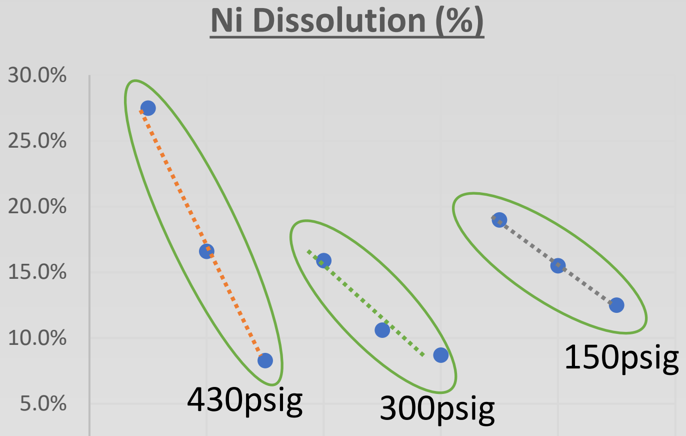
UofSC

REGALBUTO RESEARCH GROUP

Post Reaction Catalyst Characterization:

- Pd dissolution was practically zero (<0.07ppm)
- As the temperature increase (at const. pressure at/above 300psig), particles sinter and dissolve less.





Temp. (°C)	Pressure (PSIG)	Ni dissolved %
120	430	**27.5%**
150	430	**16.6%**
180	430	**8.3%**
120	300	**15.9%**
150	300	**10.6%**
180	300	**8.7%**
120	150	**19.0%**
150	150	**15.5%**
180	150	**12.5%**

Conclusions & Possible Outcomes:

- DLA catalyst of Pd_1Ni_{15}/A300 prepared successfully
- Characterization by X-ray diffraction showed ultrasmall nanoparticles
- Operating at lower temperature favors FOL formation.
- Higher temperature favors cyclopentanone formation and selectivity
- Lowering pressure from 430PSIG to 300PSIG don't significantly affect the cyclopentanone yield
- Under the range of this study, 180°C and 300psig was the optimum operating condition for cyclopentanone production
- As the temperature increase (at const. pressure at/above 300psig), particle sinter and dissolves less.

- Future work:
  - Investigate effect of temperature above 180 on cyclopentanone yield.

THANKS