

Chemical Engineering

TANDEM HYDROTHERMAL DECHLORINATION AND CATALYTIC HYDROGENATION OF PVC WASTE TO HDPE



Oregon State
University

PVC recycling: challenges and opportunities

Traditional areas

- High temperature chemical processes
 - Gasification and pyrolysis require pure product streams
 - HCl is corrosive to gas phase reactors
- Mechanical processes
 - Require extensive cleaning



Opportunities

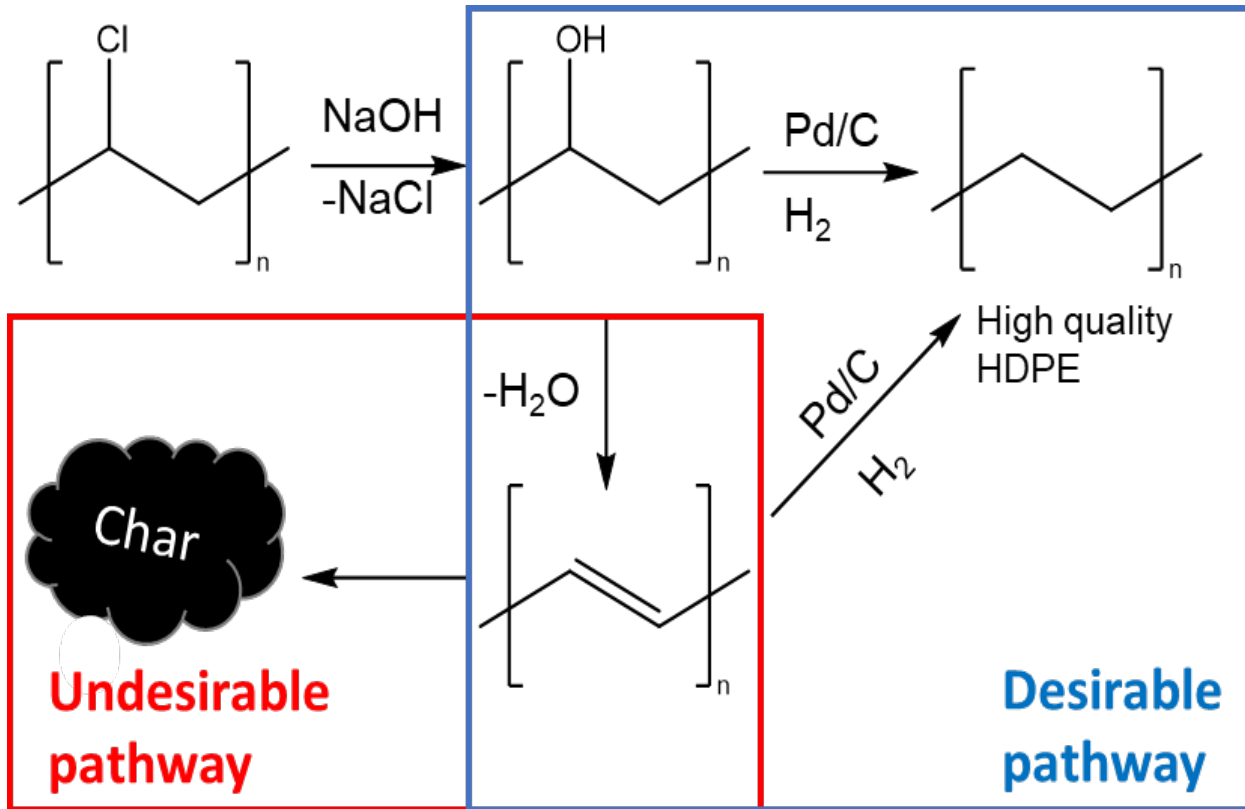
- Low temperature chemical upcycling
 - Extensive cleaning not required
 - Opportunity for UP-cycling → \$\$

Target market: hot melt adhesives

- Proposed Products: Straight-chain hydrocarbon waxes
 - Hot melt adhesive market
 - \$6b market size and growing
 - Can replace portion of the Fischer-Tropsch wax used in HMAs → CO₂ savings



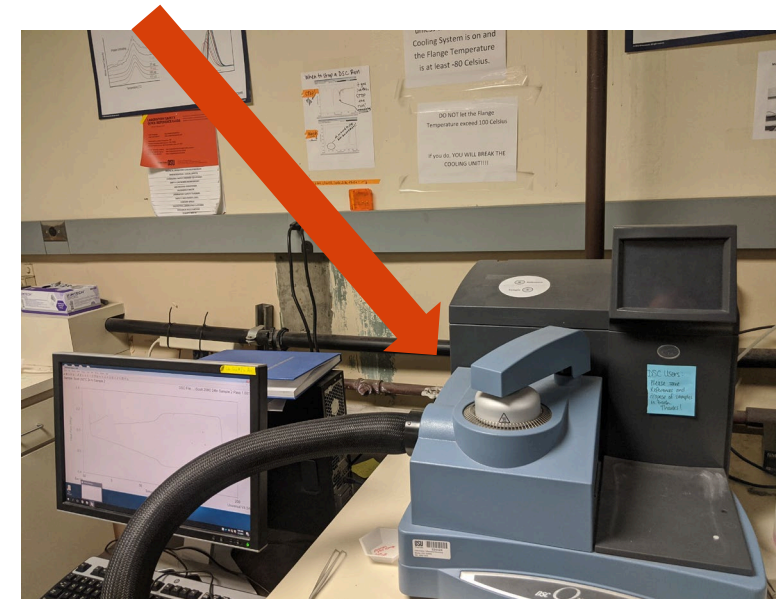
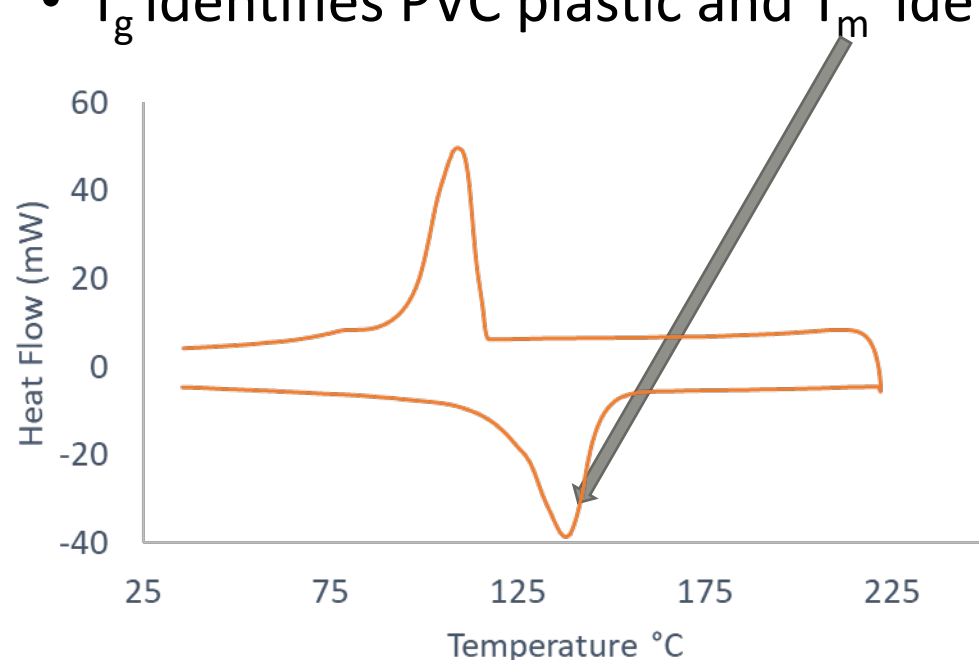
Hydrogenate PVC to HDPE!



- Hypothesis: One-pot, low-temperature conversion to HDPE wax from PVC is possible under reducing conditions
- Under H_2 pressure thermodynamics drives reaction to hydrogenation
- Intermediate PVA type or polyene type is hydrogenated to HDPE
- Addition of strong base may assist dechlorination via $\text{S}_{\text{N}}2$ substitution

Thermal and infrared analysis provides characterization of PVC and HDPE

- Primary tool for identification of HDPE plastic: DSC
 - T_g identifies PVC plastic and T_m identifies PE



- Secondary tool for identification of HDPE plastic: FTIR
 - Peaks identify bonding: C-Cl, C-H, C-O, etc.

Under alkaline conditions some success with known hydrogenation catalysts

Conditions:

24 hrs

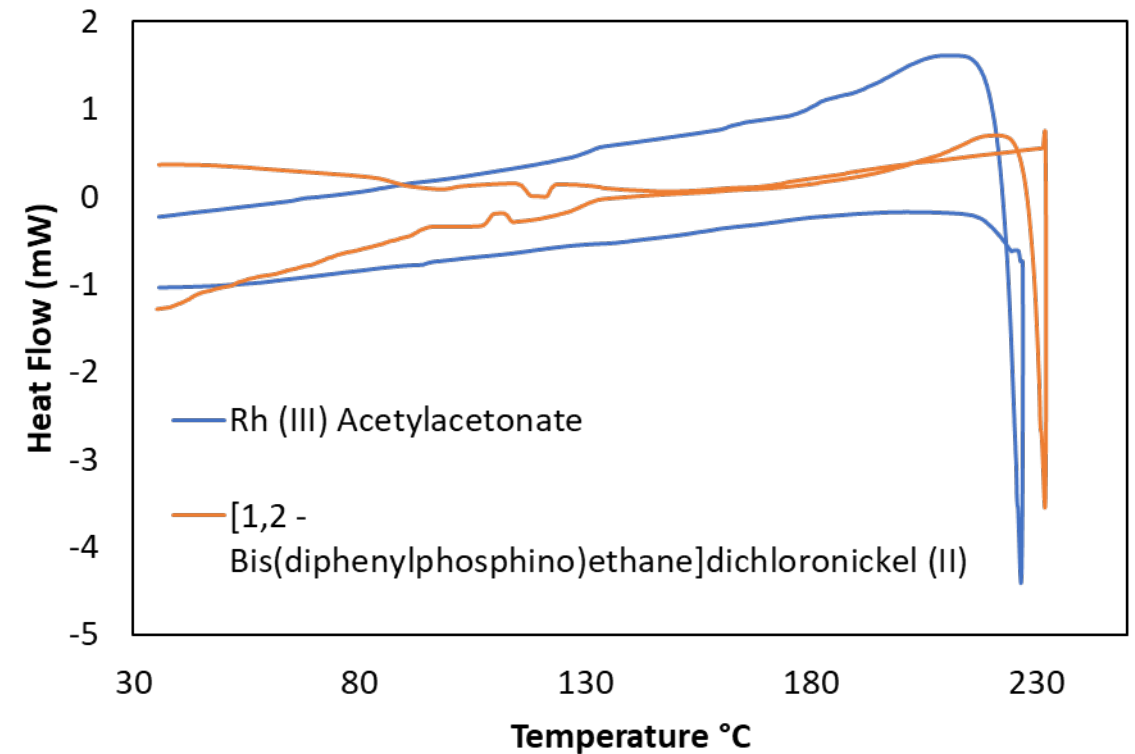
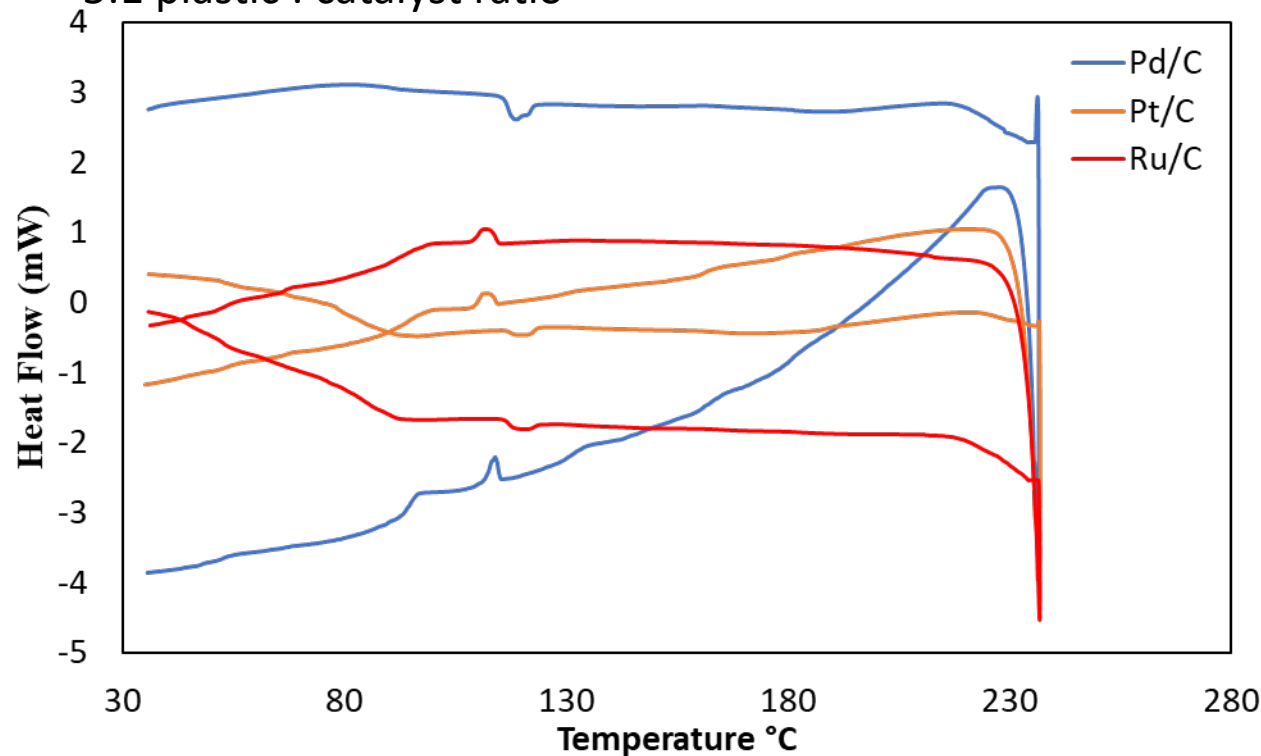
50 PSI H₂

200 °C

2.5 M KOH solution

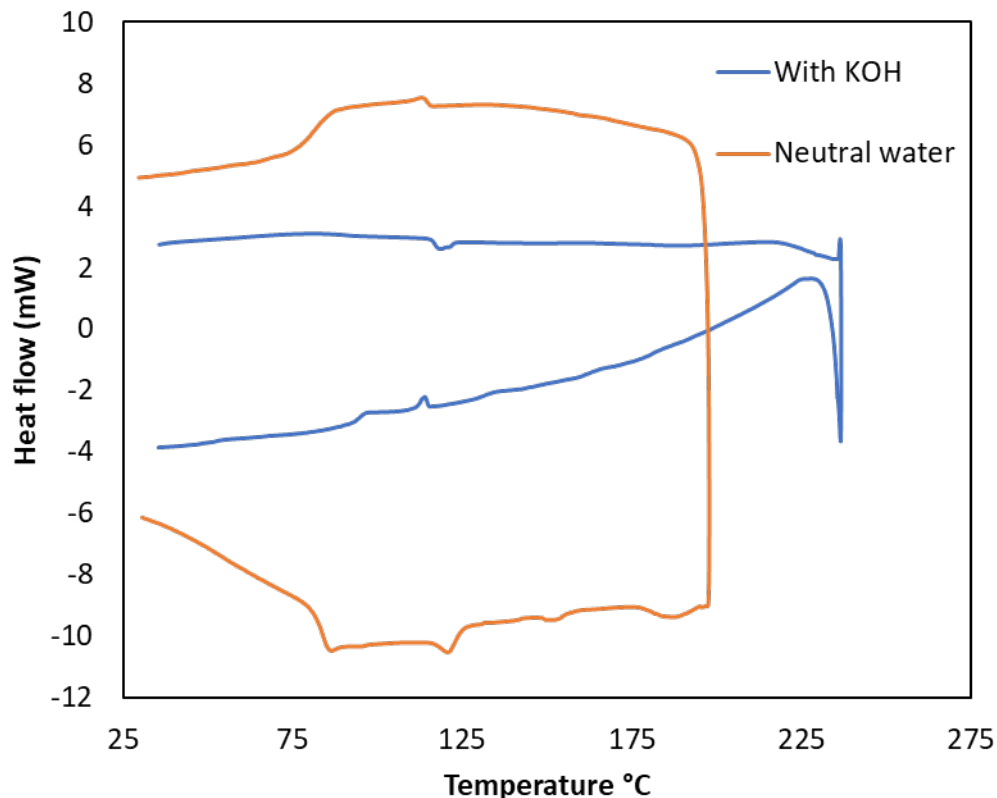
5:1 plastic : catalyst ratio

Wilkinson like catalysts appear less active than traditional hydrogenation heterogeneous catalysts



Comparison of alkaline to neutral hydrothermal conditions: just add water!

We posited that the reaction works better in strong base, but initial results show the opposite



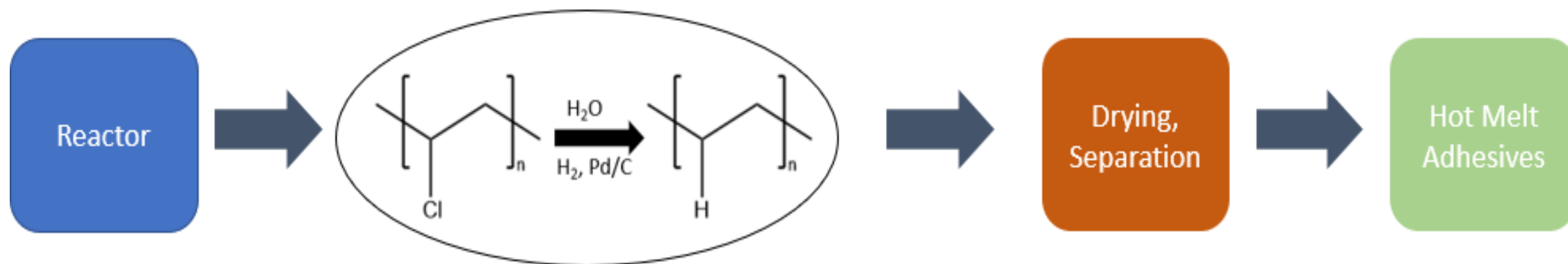
200 °C
50 PSI H₂
5:1 ratio plastic : Pd/C

More prominent T_g in neutral water suggests less dechlorination

More prominent T_m in neutral water suggests better HDPE yields

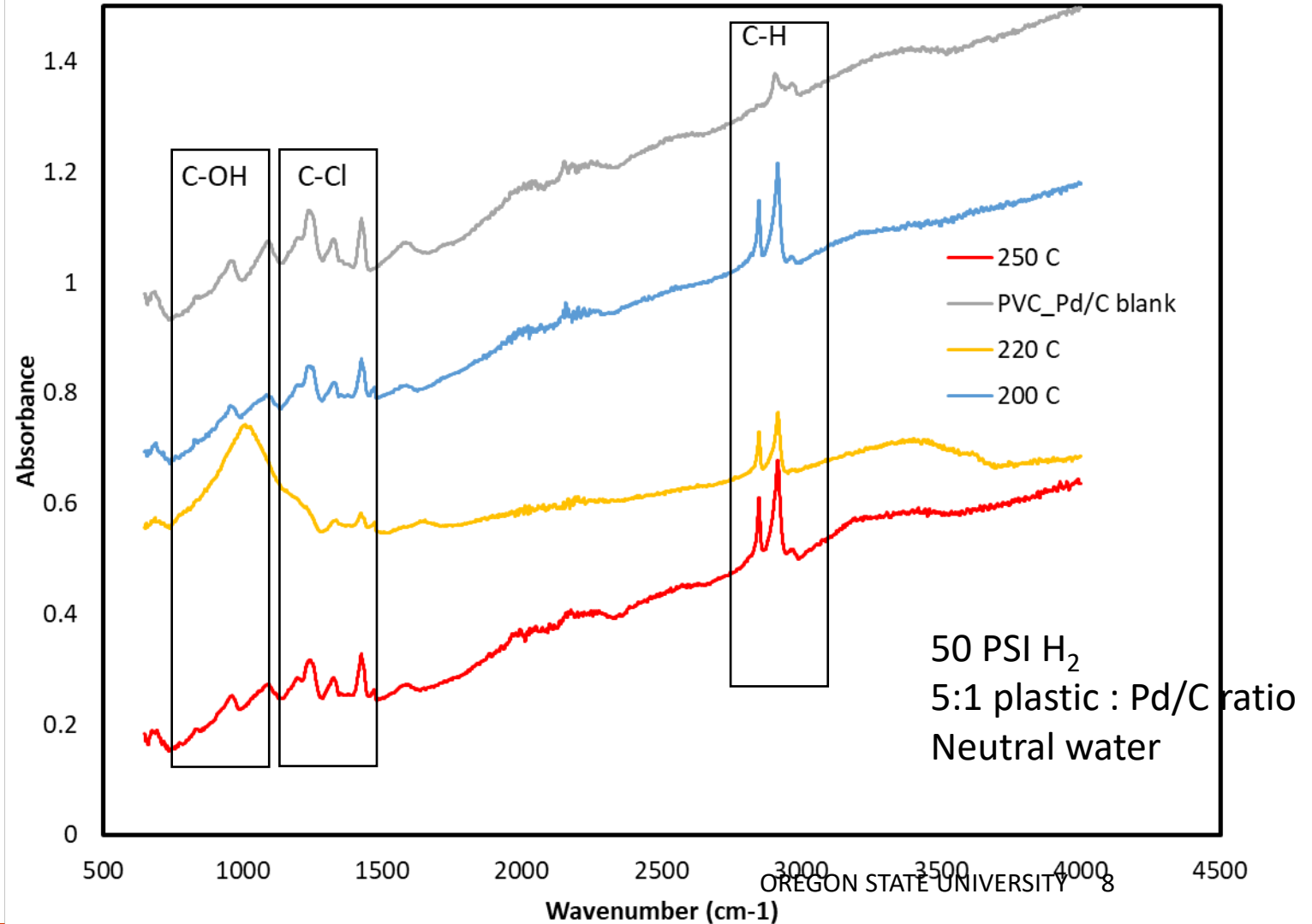
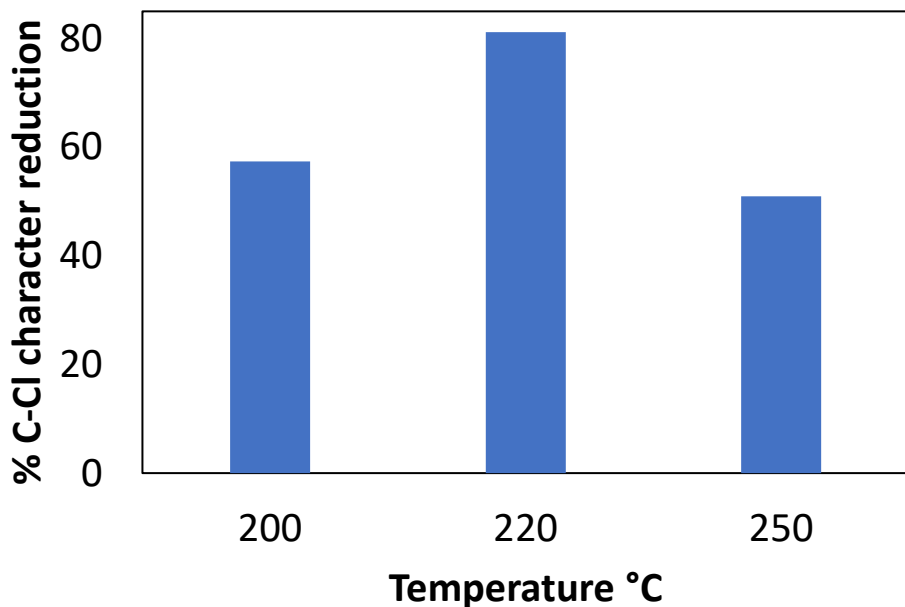
Also possible that partial dechlorination is easier in base, but full dechlorination could be easier in neutral water

Comparison of alkaline to neutral water: new vision of process without base



Temperature screens show transition from PVA to PE product in FTIR analysis

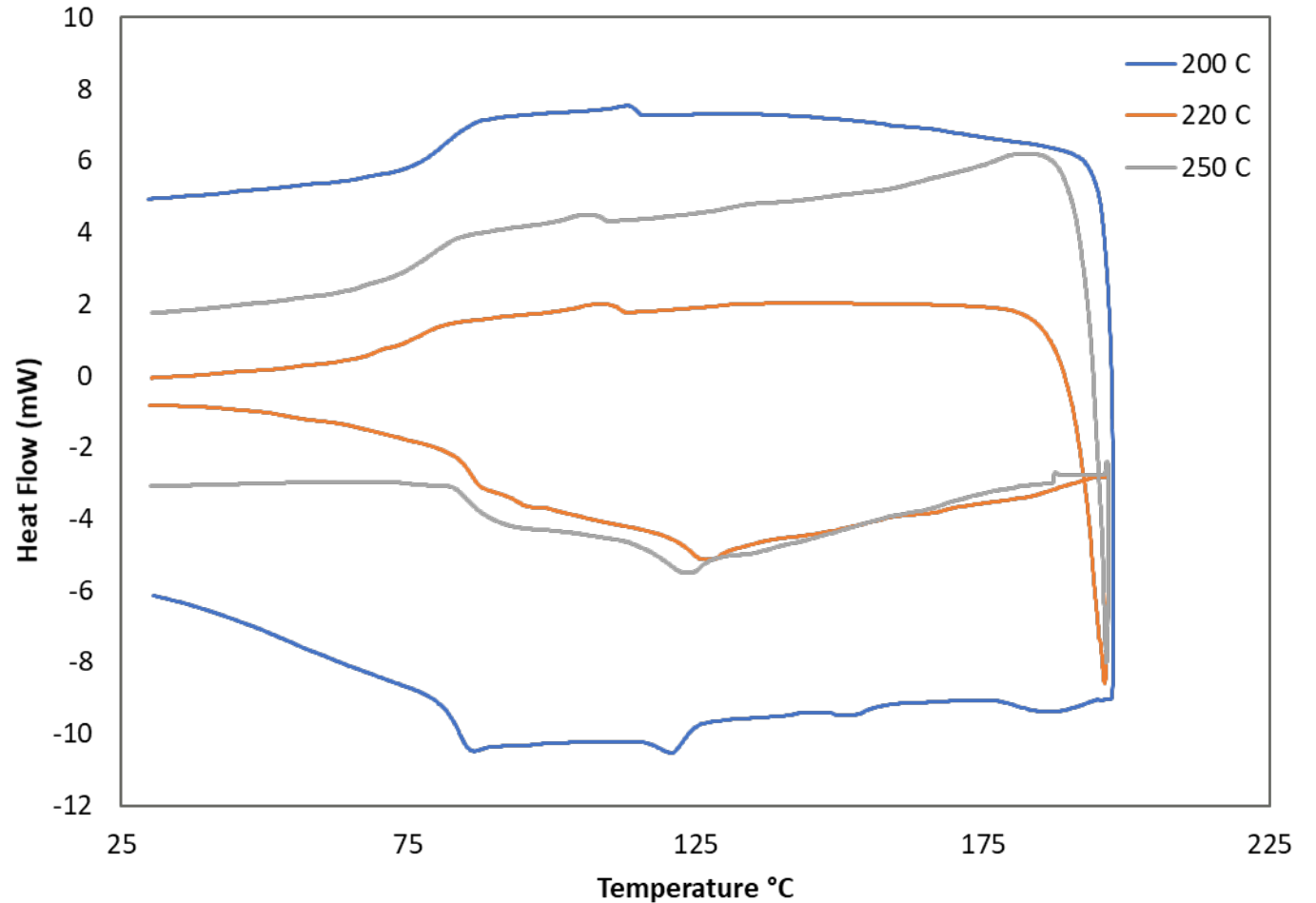
- Increase in C-H bond character in treated PVC
- Formation of OH, C-H groups while C-Cl character is reduced



Thermal behavior: prominent melt curves are evidence of PE behavior

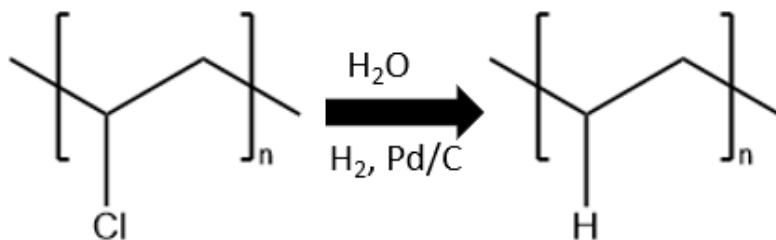
- T_g identifies unreacted PVC while T_{melt} is in range of HDPE
- Melt curve integrations increase slightly in size with increase in temperature

50 PSI H_2
5:1 plastic : Pd/C ratio
Neutral water

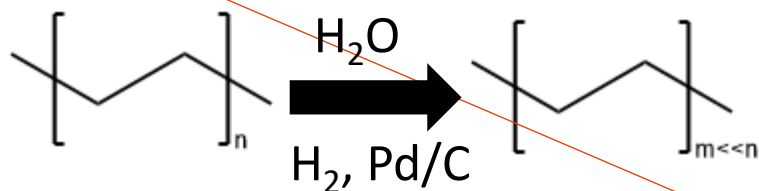


Future work: Parr reactor system for high pressure hydrogenation 100-750 psi (7 – 50 bar)

We posit high pressures will address challenge of pushing equilibrium in favor of dechlorination/hydrogenation over char



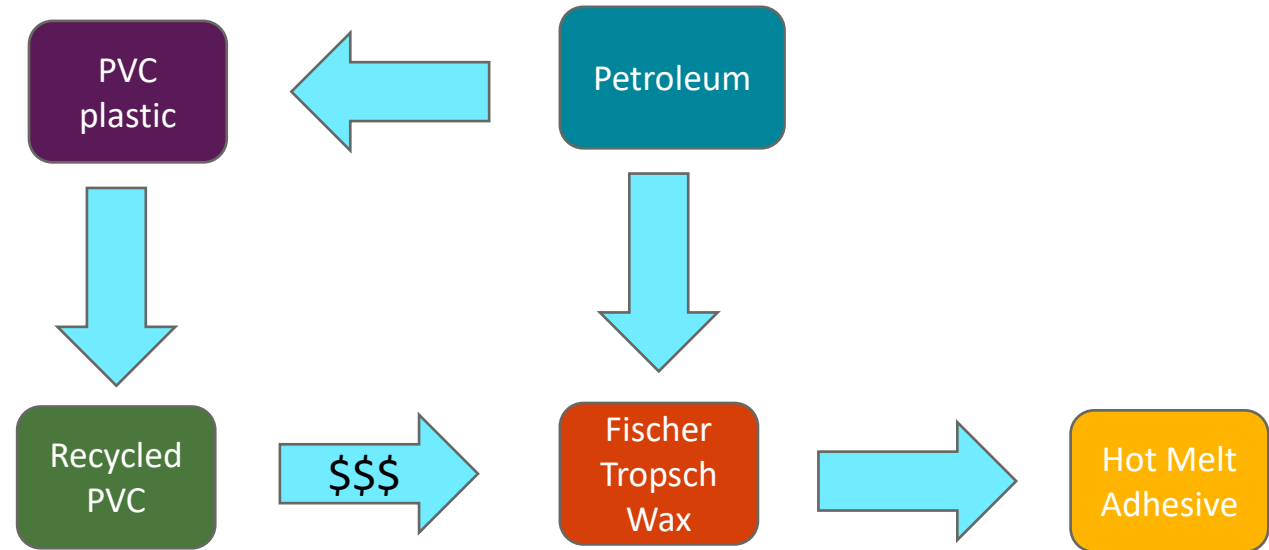
- Undesirable hydrogenolysis must be avoided



Future Work: Seeking Partners

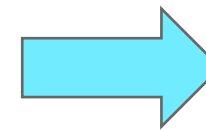
- Commercialization

- Technoeconomic analysis
- Product scale up to kilogram scale
- Product performance analysis
- Real waste treatment



- Optimization

- Maximizing yield and selectivity to HDPE
- Process safety optimization
- Vinyl flooring experiments



Acknowledgments

Vinyl Institute: Seed funding

Skip Rochefort and polymer characterization lab: DSC instrument

CQ: FTIR instrument

Thank you!

References