Drivers of Thermal Instability of Catalytic Pyrolysis Oils During Hydrotreating and Co-processing to Sustainable Fuels

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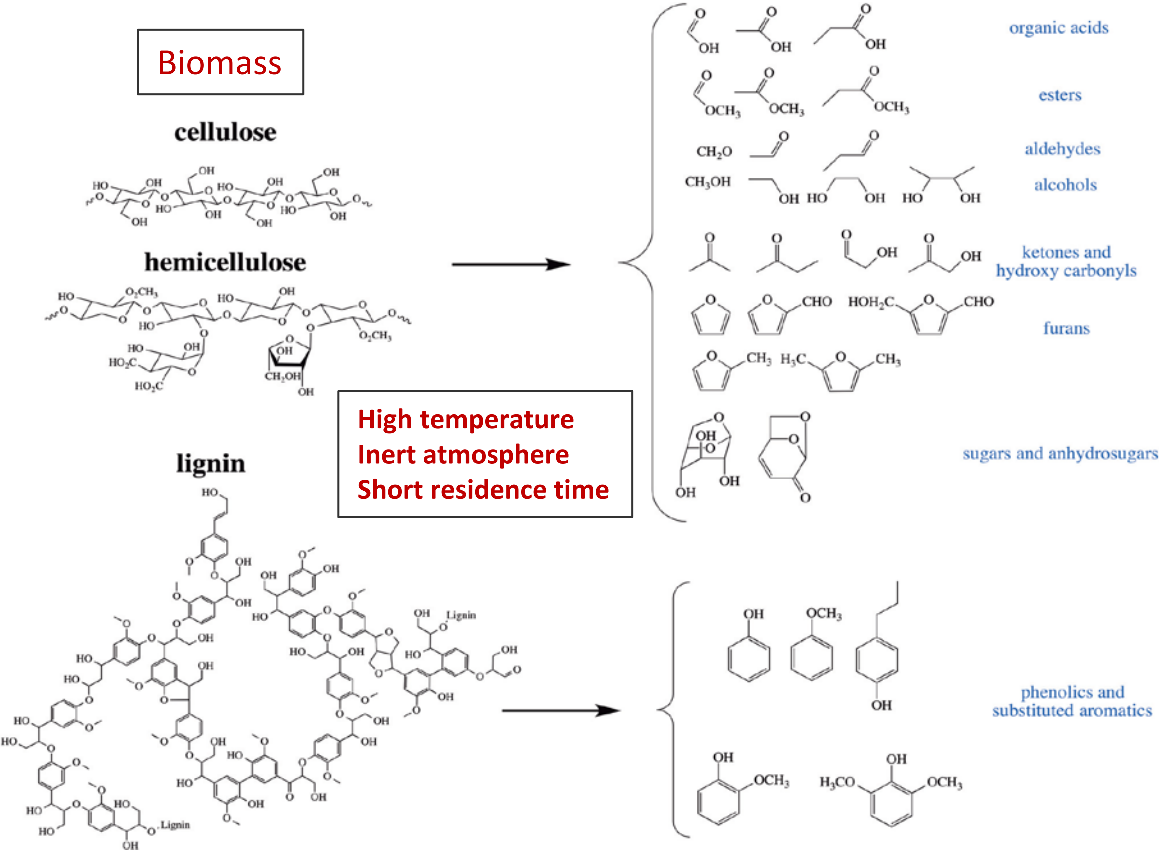
Fast Pyrolysis Bio-Oils (FP)



Bio-oil

Example Oil

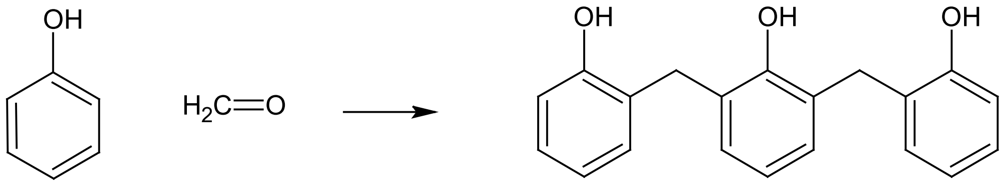
Carbon, wt%	57
Hydrogen, wt%	7
Oxygen, wt%	36
Water, wt%	20
Viscosity, cP	68
Acid Number, mg KOH/g	64

- **High oxygen content**
- **Low heating value**
- **High water content**
- **Acidic**
- **Immiscible with Hydrocarbons**

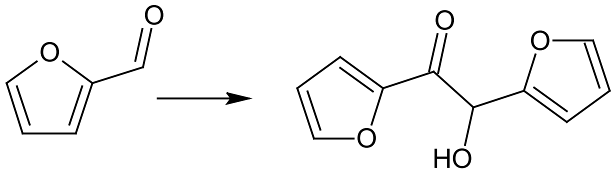
Talmadge et al., Green Chem., 2014, 16, 407

Storage and Thermal Stability

- Condensation reactions increase viscosity, water, molecular weight, density, and phase separation
- Aldehydes and phenols



- Furfurals



- Thermally unstable during distillation and upgrading
- Relative stability can be rated with reactive carbonyl concentration

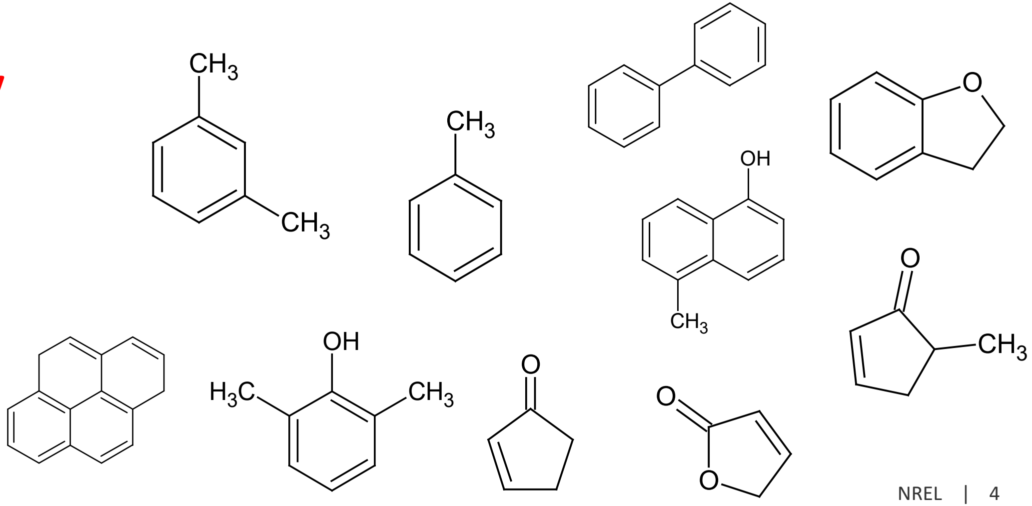
Black and Ferrell, RSC Adv., 2020, 10, 10046

Catalytic Fast Pyrolysis Bio-Oils (CFP)

- In Situ or ex situ – partial deoxygenation to improve oil properties
- Zeolite; HZSM-5 high aromatic content
- Metal-acid; e.g., Pt/TiO_2 with H_2 improved carbon yield

↓ **Oxygen**
Water
Acidity
Reactivity

↑ **Energy density**
Processibility
Stability
Miscibility

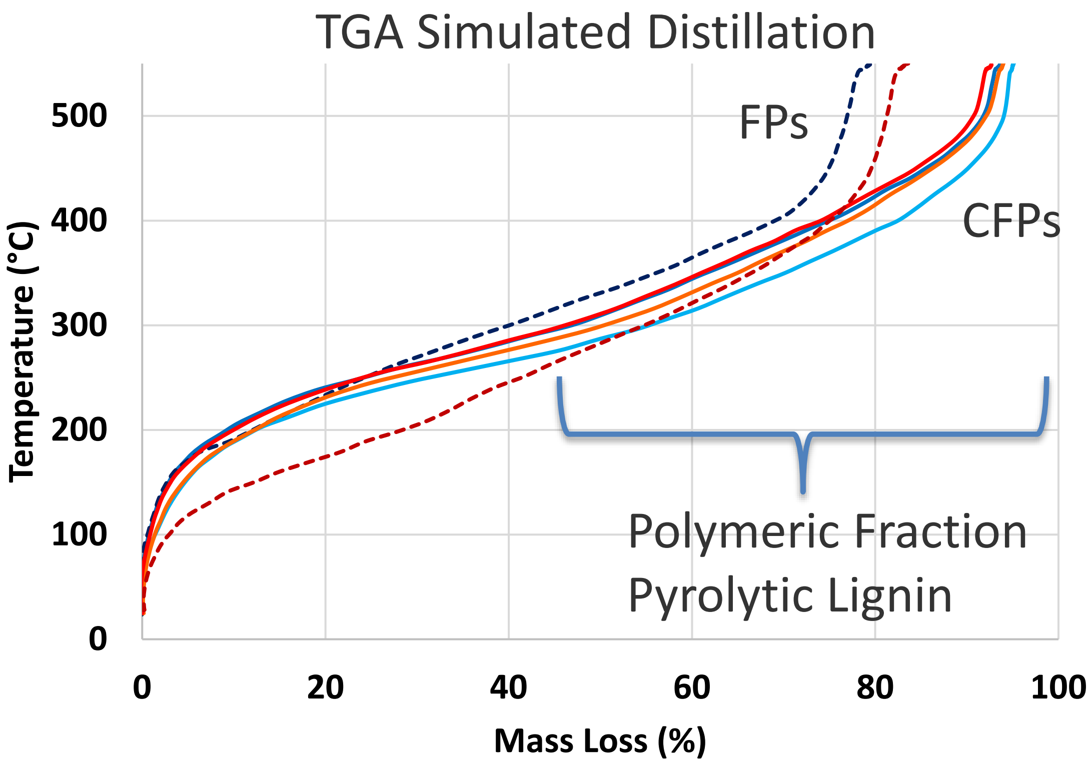


Griffin et al., Energy Environ. Sci., 2018, 11, 2904
Dutta et al., NREL/TP-5100-80291

Catalytic Fast Pyrolysis Bio-Oils (CFP)

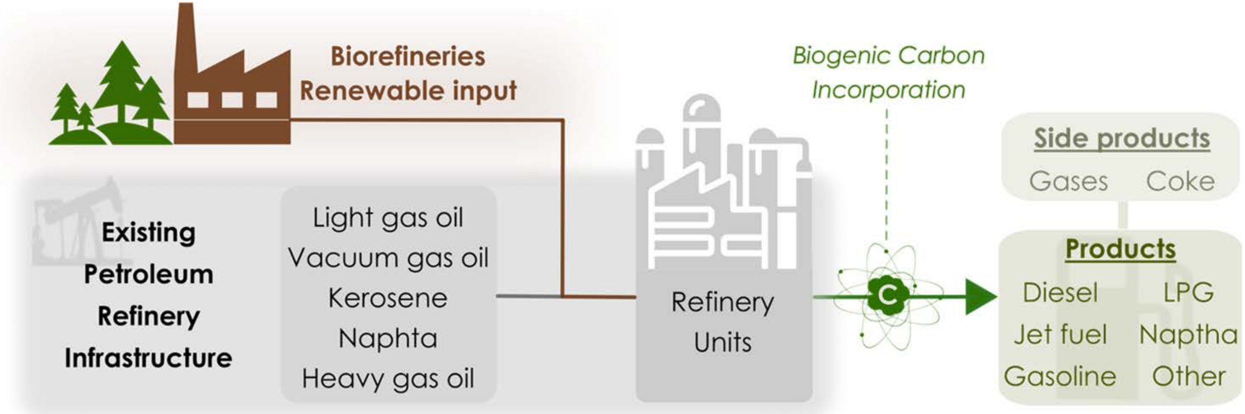
- Distillation range similar for FPs and CFPs

- FP and CFP contain hundreds of components
- Approximately 40 wt% amenable to GC analysis
- Low molecular weight monomers
- High molecular weight oligomers mostly aromatic/lignin type structure



Oil Upgrading

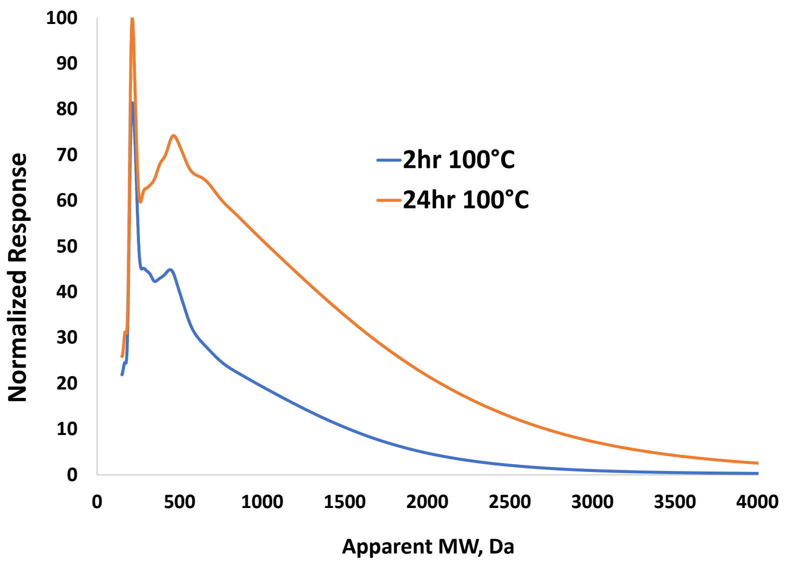
- Oxygen removal using existing refinery infrastructure; integrated biorefining
- Aromatic rich products and polycycloalkanes – potential high value for gasoline and jet fuel
- Thermal instability can cause expensive process upsets – feed plugging, catalyst fouling
- **Improving bio-oil stability enables biogenic carbon incorporation**

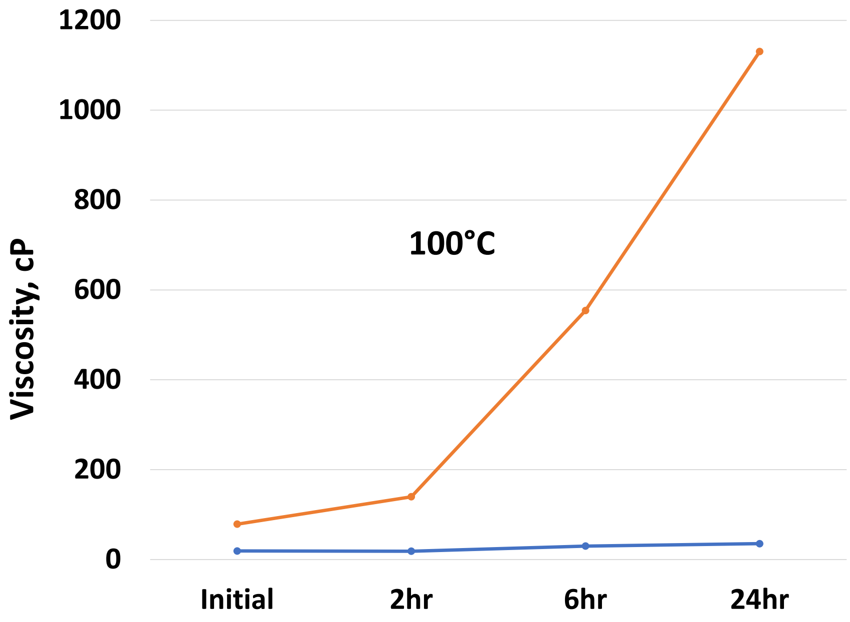


Dell'Orco et al., Anal. Chem. 2021, 93, 10, 4351–4360

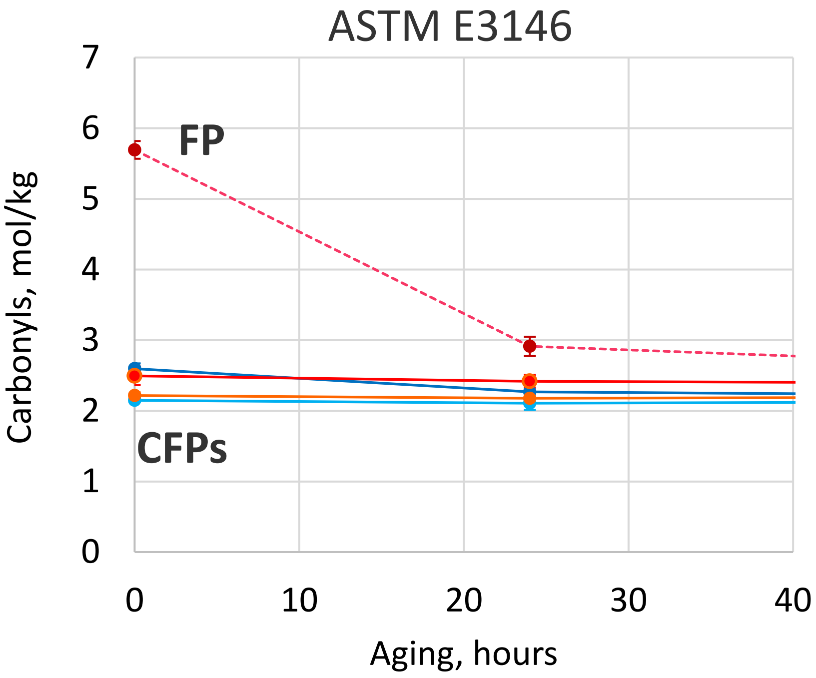
Accelerated Aging

- Assess thermal stability via changes in physicochemical properties
  - Viscosity
  - Molecular weight
  - Compound classes
  - Individual components





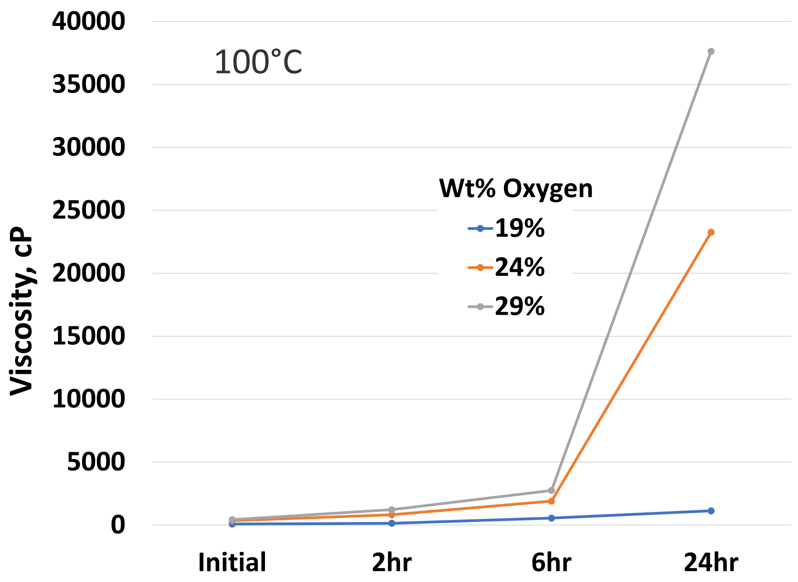
Reactive Species: FP vs CFP

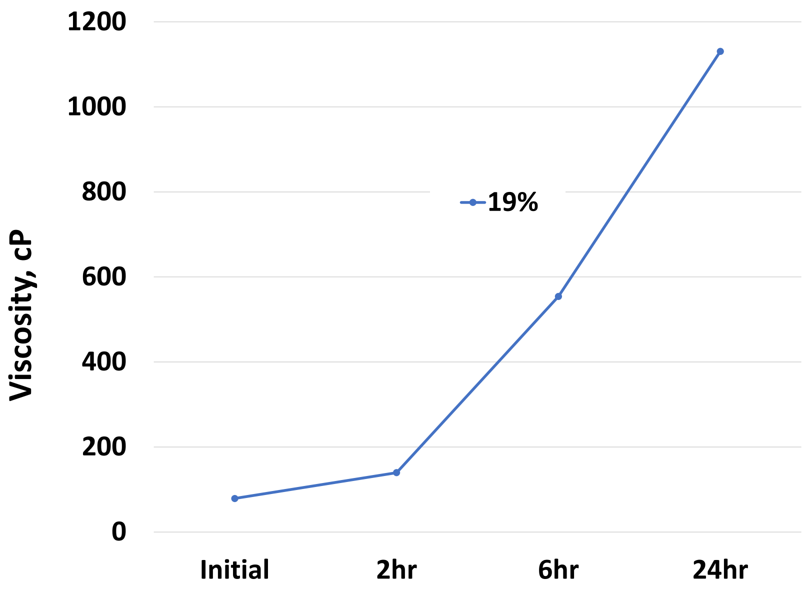


- FP oils contain reactive carbonyls linked to thermal instability/process upsets
- Pre-treatment via mild hydrotreating stabilizes feed and can be gauged from carbonyl content
- FP stability relatively understood
- CFPs instability apparently not driven by carbonyls

CFP Thermal Stability

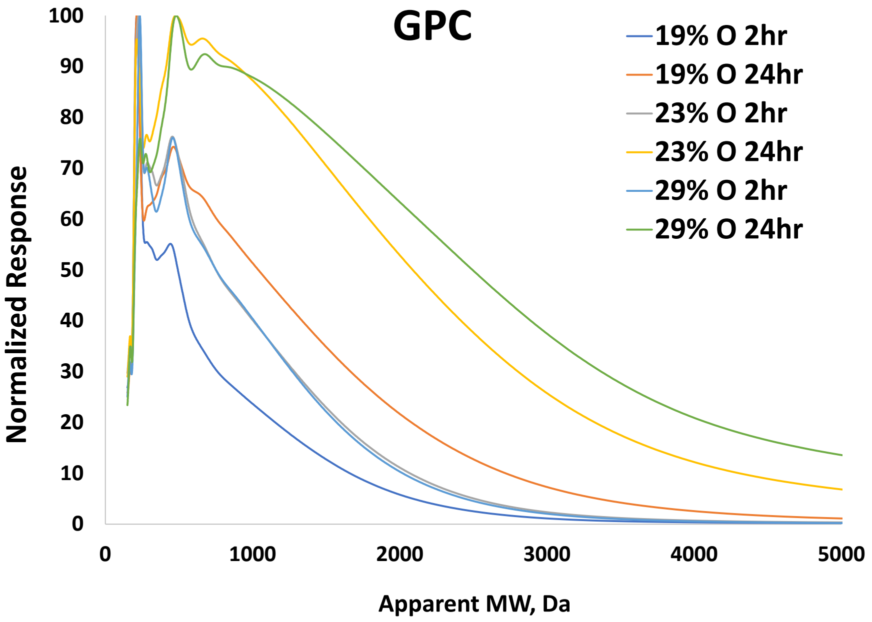
- Despite lack of reactive carbonyls viscosity increase still observed at elevated temperature
- Correlation with oxygen concentration

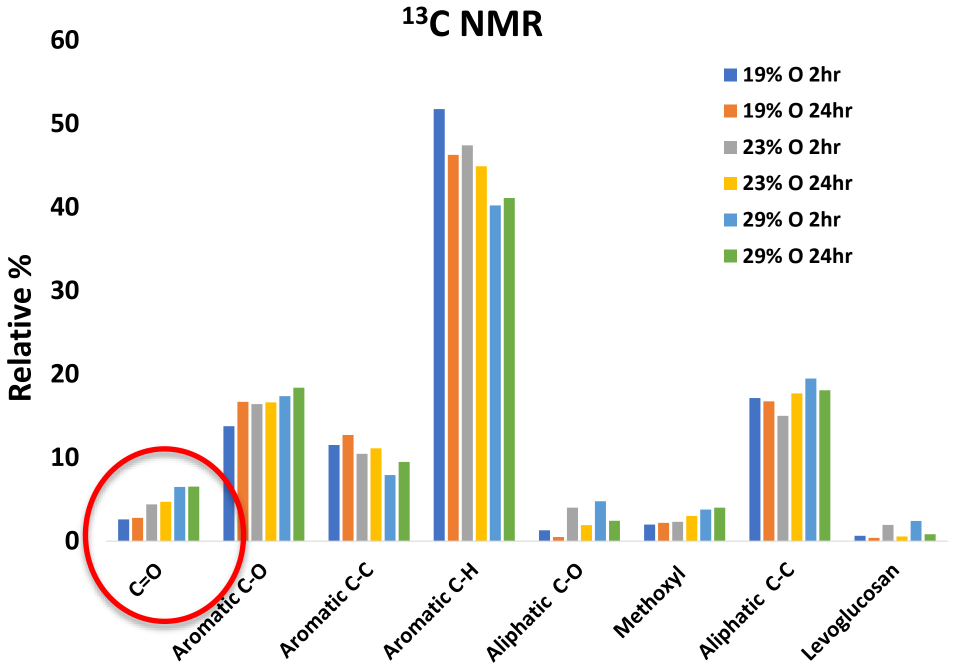




CFP Thermal Stability

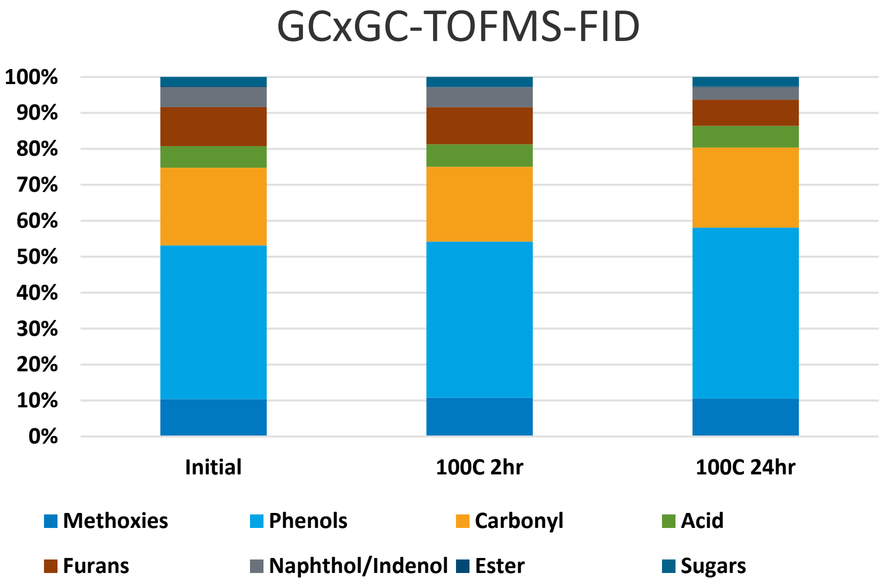
- Oxygenate polymerization results in viscosity increase – reactor feed plugging

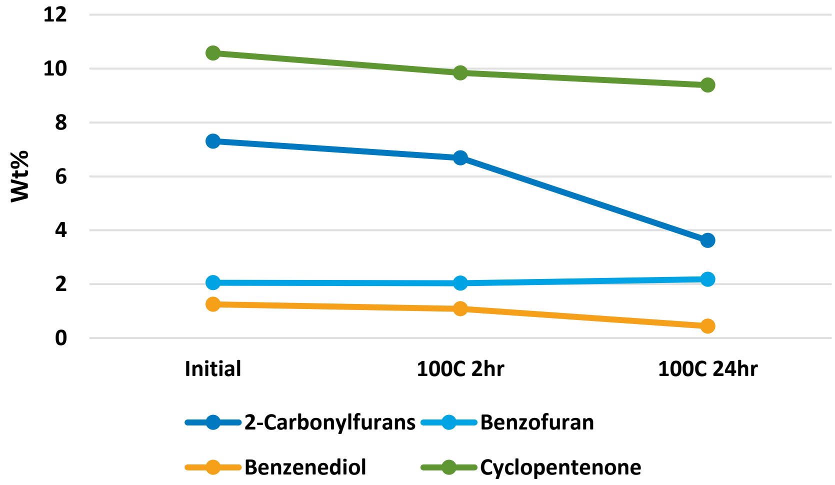




CFP Thermal Stability

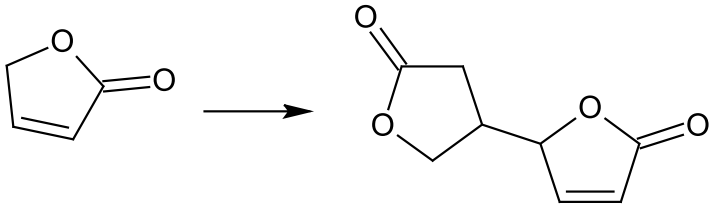
- Volatile compounds amendable to GCxGC analysis show changes in classes of monomers
- Furanones and benzenediols appear to be most impacted

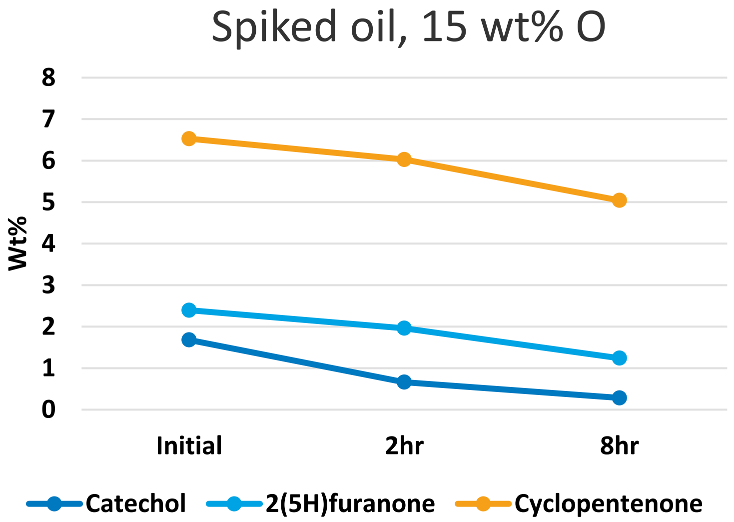


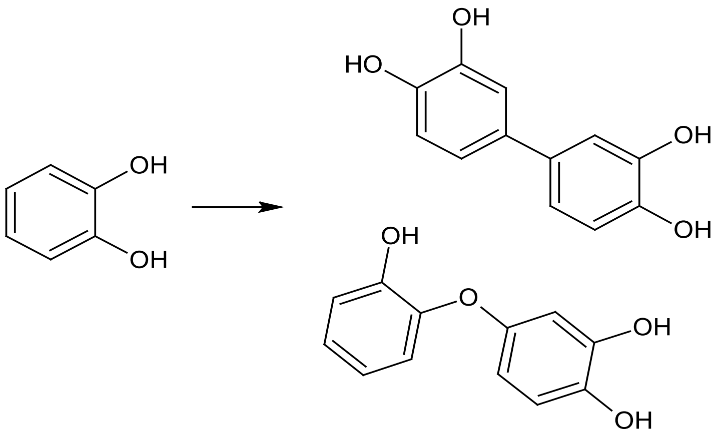


Drivers of Instability

- Furanones self polymerize while maintaining carbonyl functionality
- Benzenediols form lignin-type structures upon oligomerization







Badovskaya et al., Russian Journal of Gen Chem 2021, 91, 133
Golabi et al., Journal of Electroanalytical Chem 420, 1997 127

Conclusions

- Polymerization observed in CFPs driven by thermally labile oxygenates
- Lower oxygen oils have improved stability – a few percent decrease in oxygen greatly improves stability
- Further improvements could be realized via targeted catalytic development – further reduction in reactive species
- High stability CFP will help enable refinery integration of biogenic carbon

Questions?

Please contact Earl Christensen

Earl.Christensen@nrel.gov

Standard Bio-Oil Analytical Procedures

http://www.nrel.gov/bioenergy/bio-oil-analysis.html

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