



Esterification of Phenolic Oil for Use as Diesel Engine Fuel

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Challenges with Bio-Oil

- Properties are incompatible with use as fuel:
 - Poor stability
 - High acidity
 - High viscosity
 - Poor storage capability
 - Not miscible with diesel fuel
- Hydrotreatment is technically feasible but capital intensive
- FCC upgrading has low carbon yield



Overall Goal

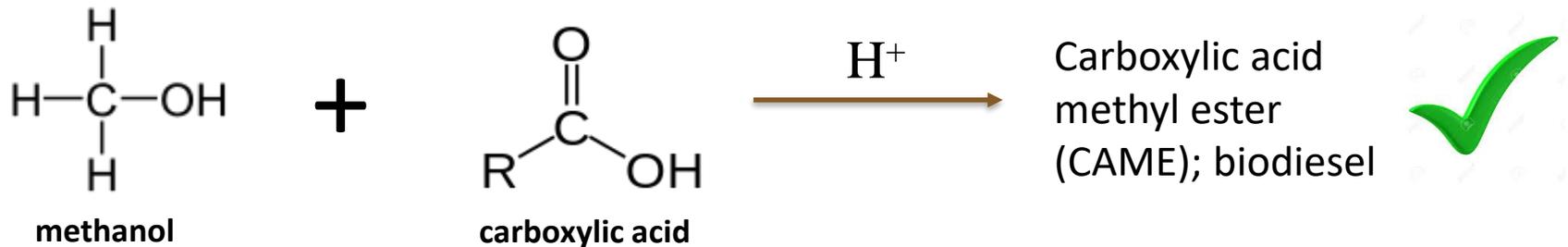
Develop stable liquid fuel from phenolic oil fraction of bio-oil

Specific Objectives

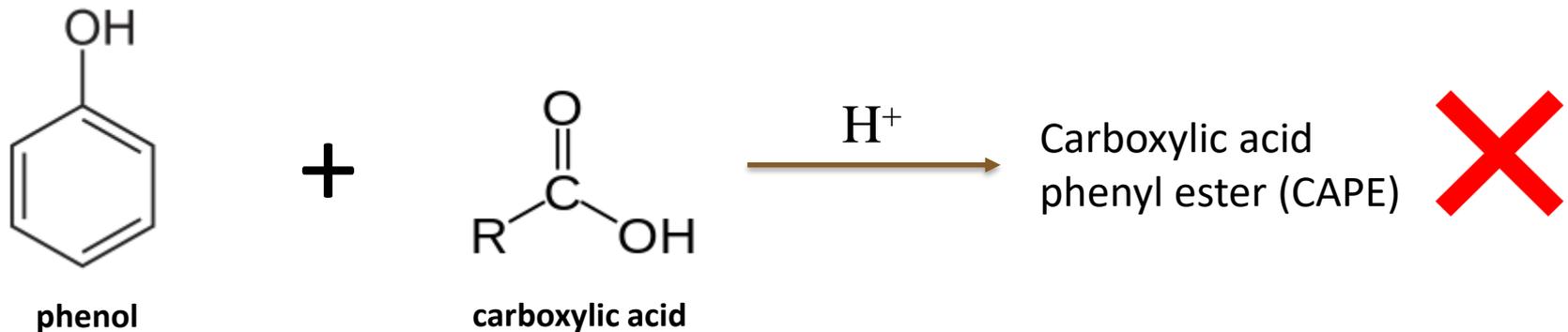
- Use acid-catalyzed direct esterification to produce *phenyl esters* from phenolic oil (PO) and long chain carboxylic acids
- Attain fuel properties comparable to bio-diesel
 - Viscosity
 - Cetane number
 - Lubricity

But Can We Use Phenolics to Esterify Fatty Acids?

Classical esterification with alcohol to make bio-diesel



Chemistry textbooks indicate use of phenol in esterification is problematic



Evidence in Support

1. Offenbauer, 1964 showed the direct esterification using *p*-cresol and hexanoic acid (1:1 mole:mole)

- Toluene used as solvent
- Acid catalyst: concentrated H_2SO_4
- Dean Stark Distillation time: 22 h
- Nearly quantitative % *p*-cresyl hexanoate yielded

2. Hocking, 1980 showed the direct esterification using phenol and acetic acid (1:1 mole:mole)

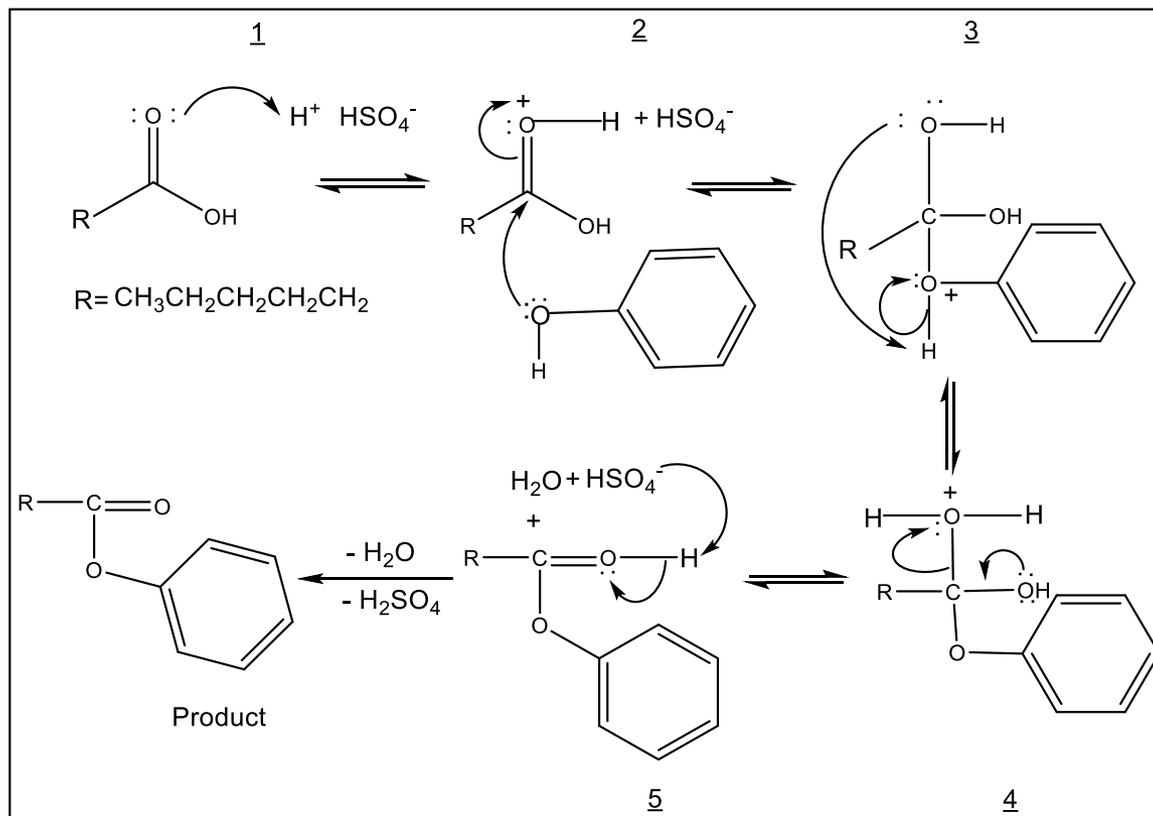
- No extra solvent used
- Acid catalyst: concentrated H_2SO_4
- Distillation time: 22 h
- 27.1 mol % phenyl acetate yielded

R.D. Offenbauer, The direct esterification of phenols, J. Chem. Educ. 41 (1964) 39.

M.B. Hocking, Phenyl acetate preparation from phenol and acetic acid: Reassessment of a common textbook misconception, J. Chem. Educ. 57 (1980) 527.

Proposed Mechanism

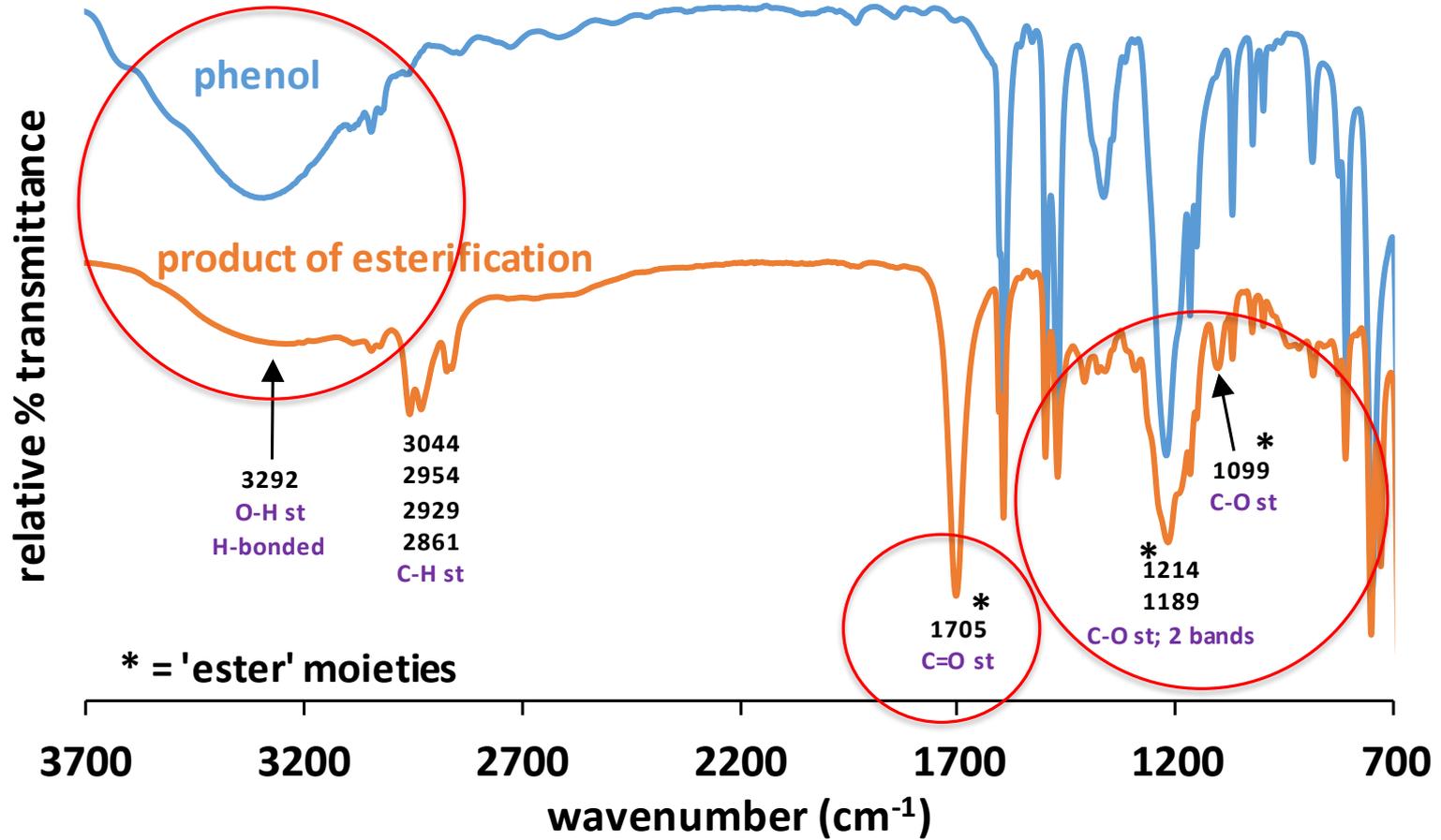
Follows standard acid catalyzed esterification reaction*



Methodology for Model Compound

- Pure phenol + hexanoic acid (1:1 molar ratio)
- Toluene used as solvent
- Acid catalyst: concentrated H_2SO_4
- Dean Stark trap to collect water
- Refluxed for 26 h under 24-26 °C vapor temperature
- Rotary evaporator to remove excess toluene
- Ester formation monitored with FTIR

FTIR Spectra

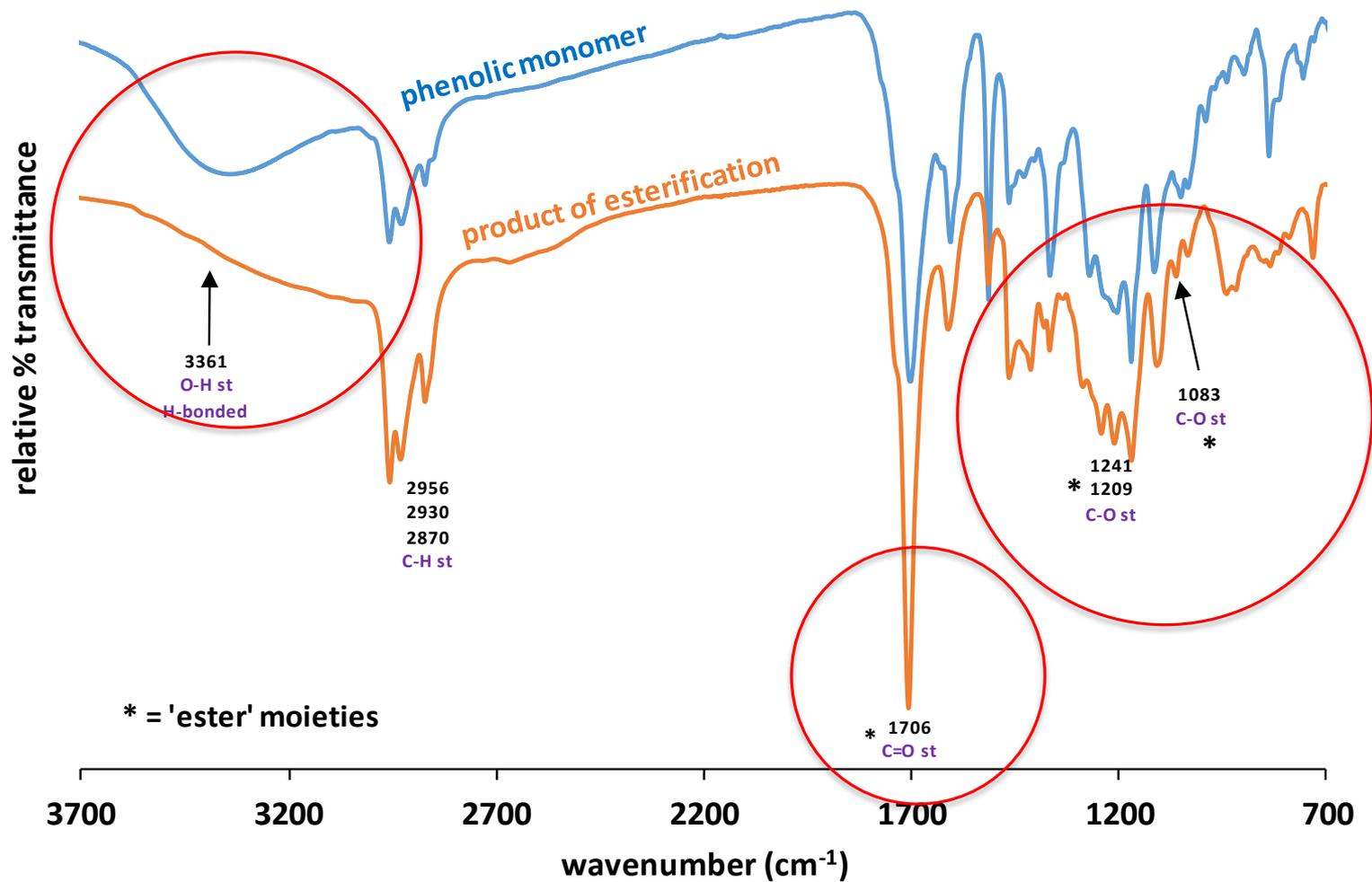


Methodology for Phenolic Oil

- Phenolic oil + hexanoic acid (1:1 molar ratio)
- Solvent used: Methyl isobutyl ketone (MIBK)
- Acid catalyst: H_2SO_4
- Dean Stark distillation for 6-48 h at 26-45 °C vapor temperature
- Rotary evaporation to remove excess MIBK
- Ester formation monitored with FTIR



FTIR Spectra



Blends



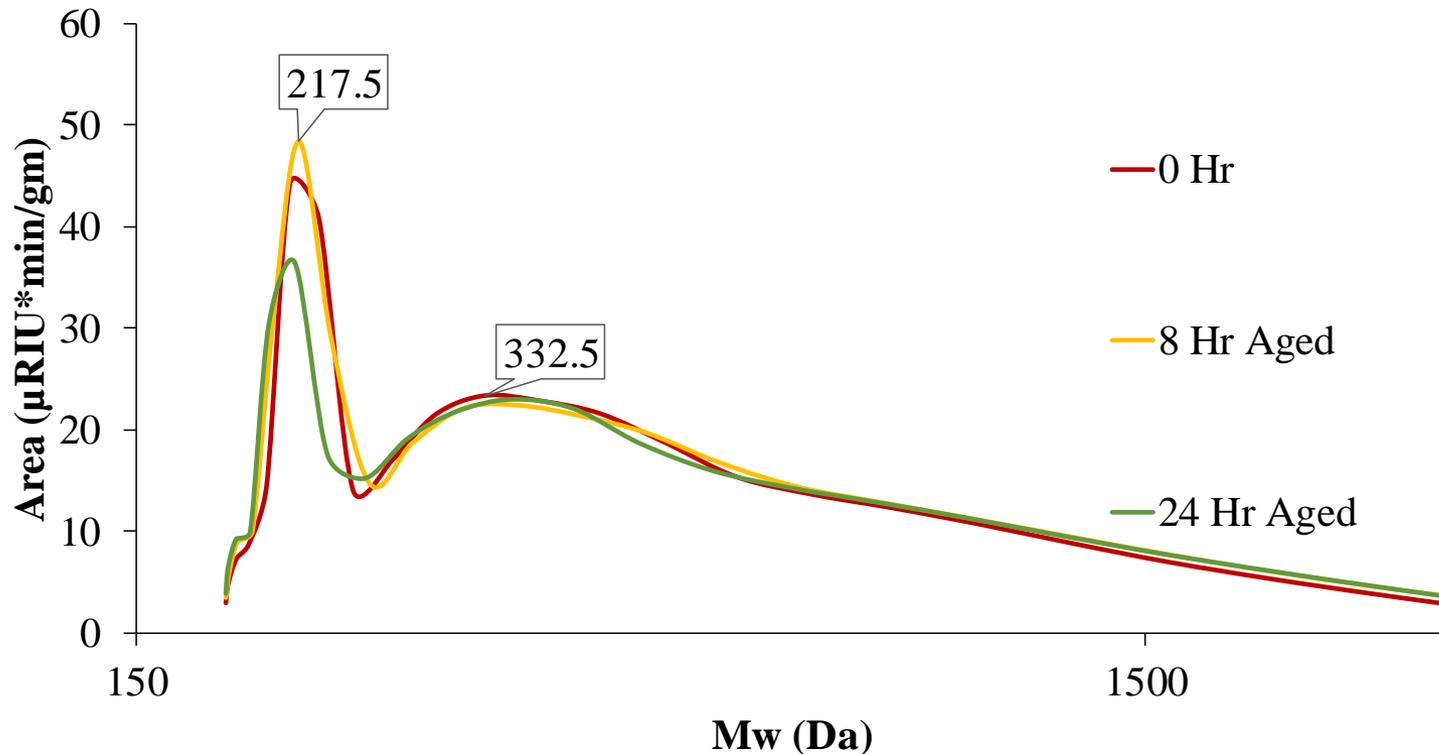
Vial Number	Blend
1	Phenolic oil and diesel fuel are immiscible
2	PH:DF = 42.8%:57.2%
3	PH:DF = 18.1%:81.9%
4	PH:DF = 7.8%:92.2%
5	PH:DF = 7.4%:92.6%
6	PS:DF = 1.3%: 98.7
7	PH:BD = 50%: 50%

PH - phenyl hexanoate; PS - phenyl stearate; DF - diesel fuel; BD – bio-diesel

Phenyl Esters Have 330-fold Lower Viscosity than Starting Phenolic oil

Sample	Temperature (°C)	Brookfield Viscosity (cP)
Diesel fuel	25	2.81
Phenolic oil	40	5184
Phenyl hexanoate	40	15.6
Phenyl hexanoate	25	28.2
Phenyl hexanoate (5%) + diesel fuel (95%)	25	2.81
Phenyl hexanoate (20%) + diesel fuel (80%)	25	3.28

Phenyl Hexanoate Showed Little Accelerated Aging



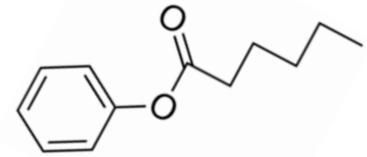
- Samples were aged in an 80 °C oven to simulate one year of storage
- Gel permeation chromatography relative Mw using refractive index

Diesel Engine Test

- 20% blending of phenyl hexanoate with diesel fuel
- Engine ran for 60 min
- Rise in heat (648 to 831 °F)
- CO (0.2 to 0.18%) decreased and CO₂ (3.63 to 4.4%) increased



Advantages of Carboxylic Acid Phenyl Esters (CAPE)



Production resembles bio-diesel production

- Waste grease and fats esterified with phenolic oil (instead of methanol)

Properties resemble bio-diesel

- High predicted cetane number
- High predicted lubricity

Improved properties compared to bio-oil

- Reduced viscosity
- Improved storage stability
- Miscible in diesel fuel



Heavy ends of bio-oil
is immiscible in
diesel fuel

Blend of 18.1%
phenyl hexanoate in
diesel fuel

Future Work with CAPE

- ASTM diesel fuel testing including flash point, kinematic viscosity, sulfur content, cetane number, cloud point, pour point and lubricity
- ^{13}C NMR study of the produced phenolic esters
- Higher blending rate with diesel fuel than the current one (30%, 50% and 100%)
- Testing on diesel engines that simulate large marine engines

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QUESTIONS