

# Hydrodeoxygenation of Acetic Acid as a Model Compound for the Aqueous Phase Catalytic Pyrolysis Oils

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## Abstract

Catalytic pyrolysis of biomass generates organic, aqueous, gaseous and solid fractions. The organic fraction can be easily hydrotreated to produce hydrocarbons, but the aqueous phase that contains between 10 to 25% soluble organics can pose challenges in wastewater treatment. The aqueous fraction from the catalytic pyrolysis of Pinyon Juniper wood was characterized for its organic content. The fraction contained about 15 wt% organic compounds determined from Karl Fischer analysis. The organic fractions were further characterized using gas chromatography and mass selective detection (GC/MS) and HPLC. The analysis showed that the dissolved organics were composed of acetic acid, ketones, aldehydes, and phenolic compounds. In this study we investigated the hydrodeoxygenation (HDO) of 15 wt.% acetic acid solution to represent aqueous phase Pinyon Juniper catalytic pyrolysis oil (APPJCPO). HDO experiments were carried out at different temperatures (150, 250, 350, and 450 °C) using Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst in a high pressure Parr reactor. HDO of acetic acid produced acetaldehyde, ethanol, ethyl acetate, carbon dioxide, methane, ethane, and coke at different concentrations depending on the reaction temperature. Reaction pathways of acetic acid HDO were proposed based on analysis of the products. The final products of acetic acid HDO were methane, water at reaction temperature of 450 °C. HDO of APPJCPO was carried out at 450 °C. During HDO the pH of APPJCPO increased from 2.97 to 6.93. The final products of HDO of APPJCPO were water and methane. After HDO experiments, the catalyst was partially deactivated due to coke formation. This study provided insight in the

reaction network of acetic acid HDO and suggests that HDO is a promising technique to overcome toxicity and corrosion of aqueous phase pyrolysis oil.

**Keywords:** Bioenergy, Biofuels, Biological Engineering



## Hydrodeoxygenation of Acetic Acid as a Model Compound for Aqueous Phase Catalytic Pyrolysis Oil

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## 1. Introduction

Utilization of lignocellulosic biomass for production of sustainable energy has received a lot of attention due to the diminishing fossil fuel resources and environmental concerns [1–7].

Lignocellulosic biomass can be thermochemically converted into transportation fuels by three major pathways: syngas production by gasification, bio-oils production by pyrolysis or

liquefaction, and hydrolysis of biomass to produce sugar monomer units [4]. Pyrolysis

is a thermal decomposition process of organic compounds in the absence of oxidizing agents.

This process produces char, syngas, and liquid products [5]. The liquid products contain aqueous and organic phases. The organic phase can be upgraded to transportation fuel through various

processes including catalytic cracking, hydrodeoxygenation (HDO), emulsification, esterification under supercritical ethanol, and steam reforming followed by Fischer Tropsch synthesis [6]. The

aqueous phase pyrolysis oil contains about 10~30% soluble organics such as aldehydes, ketones, acids, and methoxy phenols [7-10]. Overcoming corrosion and toxicity of water-soluble bio-oil

compounds such as carboxylic acids, phenolic compounds, furans, and aldehydes, is a major challenge that can increase the cost of wastewater treatment.

HDO can improve pyrolysis oil quality through improving oil stability and higher energy density [9]. HDO of the bio-oil involves four major classes of reaction (1) hydrogenation of C–O, C=O,

and C=C bonds, (2) dehydration of C–OH groups, (3) C–C bond cleavage by retro-aldol

condensation and decarbonylation, and (4) hydrogenolysis of C–O–C bonds [4, 10-19]. Several

parameters including temperature, hydrogen pressure, residence time, and catalyst loading have significant effect on HDO product distribution [12]. Typical process conditions for HDO include

temperatures between 250 and 400 °C and hydrogen pressure between 3 to 30 MPa. However the high H<sub>2</sub> consumption and capital costs and low product selectivity are some challenges

associated with this method [13, 18]. Increasing the HDO reaction temperature and time results in increased hydrocracking of organic compounds and increased gas product yield while application of suitable amount of catalyst inhibits unfavorable reactions such as cracking and condensation reactions [18-24].

The objective of this work is to study the hydrogenation and HDO of Aqueous Phase Pinyon Juniper Catalytic Pyrolysis Oil (APPJCPO) to overcome its toxicity and corrosion. In order to get a deeper insight of the process and reaction pathways, we hydrogenated a solution of 15% acetic acid in water as model compound to represent APPJCPO.

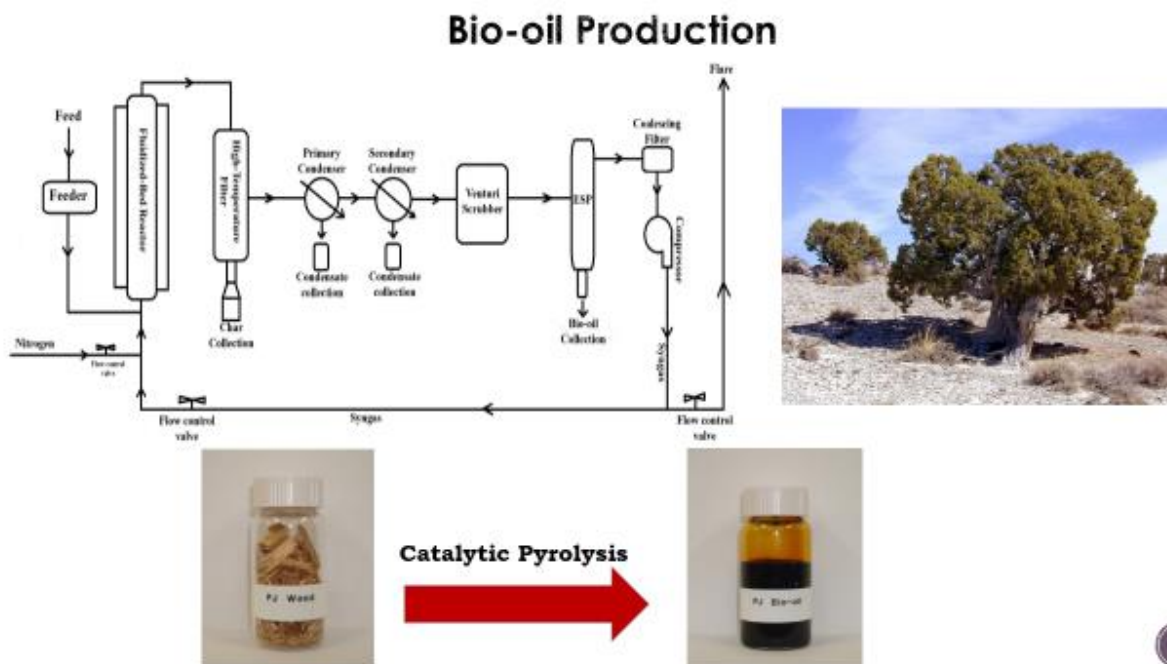
## **2. Material and methods**

Pinyon Juniper (PJ) biomass chips were supplied by the U.S. Bureau of Land Management. Red Mud was used as catalyst for fast pyrolysis of biomass. Reagent grade acetic acid was bought from EMD Millipore (Billerica, MA). For HDO experiments, nickel on silica-alumina (~65 wt % loading Ni) catalyst powder was obtained from Sigma-Aldrich (St. Louis, MO). High purity (99%) hydrogen (Airgas, PA) was used for HDO experiments.

PJ chips ground to pass a 2-mm mesh were used as feedstock for production of catalytic pyrolysis oil. The pyrolysis was carried out in a pilot plant bubbling fluidized bed reactor described in detail by Mante and Agblevor [2]. At feeding rate of 0.9 kg/h, catalytic pyrolysis oil was produced at 450 ° C using a pilot scale fluidized bed reactor system. The pyrolytic products were condensed using a series of two ethylene glycol-cooled condensers and an electrostatic precipitator (ESP) operating at 30 kV. Details of the pyrolysis pilot plant can be found elsewhere [2]. Liquid products captured by condensers were collected in centrifuge test tubes and centrifuged for 30 minutes at

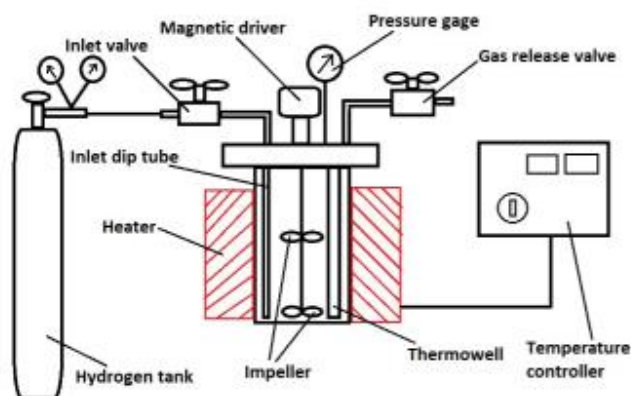
g-force of 2147 to separate the aqueous and organic phases. The aqueous phase was used for HDO experiments.

HDO reactions were carried out in a Parr Series 4571 1000 mL autoclave reactor (Parr Instruments, Moline, IL). The reactor can withstand a maximum pressure of 35 MPa at 500 ° C. A Parr 4848 controller was used to control the internal temperature and impeller speed. In a typical test, 100 g reaction mixture (APPJCPO or 15 wt. % solution of acetic acid in deionized water) and Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst (15 g) were loaded into the reactor. The reactor was flushed with hydrogen four times to purge the reactor vessel. High purity hydrogen was supplied from a reservoir tank via a pressure regulator. The reactor was then pressurized with hydrogen to 7 MPa at room temperature. A gas sample was taken from the gas sampling port for gas analysis when the reactor was at room temperature. The reactor was then heated to reaction temperature of 150, 250, 350, or 450 °C. The reaction time was recorded when the reaction temperature was reached. The reaction mixture was vigorously stirred (~500 rpm) in order to eliminate diffusion limitations.



## Experimental

Catalyst: Ni/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>



### HPLC conditions:

Column: BP-100 H+ carbohydrate

Detector: RID-10A

Oven temperature: 80 C

Mobile phase: DI water

Injection volume: 0.25 ul

Flowrate: 0.7 ml/min



## 3. Results and discussion

Characterization of APPJCPO and HDO products, and results of HDO experiments are presented in the following slides.

### Characterization of aqueous phase pyrolysis oil

Water content= 84.77 %

pH= 2.97

Aldehydes	Ketones	Acids	Other hydrocarbons
Furfural	Acetone	Acetic acid	Acetic anhydride
Acetaldehyde	1-hydroxy-2-propanone	(4.73%)	Phenol
	3-hydroxy-2-butanone		2-methoxy phenol
	2,3-butanedione		
	2,2-dimethyl-3-heptanone		
	2-methyl-2-cyclopenten-1-one		
	1-acetoxy-2-propanone		
	2-cyclopentene-1-one		



# Reactions of Acetic Acid HDO

- $\text{CH}_3\text{COOH} + \text{H}_2 = \text{CH}_3\text{CHO} + \text{H}_2\text{O}$  (production of acetaldehyde)
- $\text{CH}_3\text{CHO} + \text{H}_2 = \text{CH}_3\text{CH}_2\text{OH}$  (production of ethanol)
- $\text{CH}_3\text{CH}_2\text{OH} + \text{CH}_3\text{COOH} = \text{CH}_3\text{COOCH}_2\text{CH}_3 + \text{H}_2\text{O}$  (production of ethyl acetate)
- $\text{CH}_3\text{CH}_2\text{OH} + \text{H}_2 = \text{C}_2\text{H}_6 + \text{H}_2\text{O}$  (production of ethane)
- $2\text{CH}_3\text{COOH} = \text{CH}_3\text{COCH}_3 + \text{CO}_2 + \text{H}_2\text{O}$  (production of acetone and  $\text{CO}_2$ )
- $\text{CH}_3\text{COOH} = \text{CH}_4 + \text{CO}_2$  (production of methane and  $\text{CO}_2$ )
- $\text{CH}_3\text{COOH} + \text{H}_2 = \text{CH}_4 + \text{CO} + \text{H}_2\text{O}$  (production of CO and methane)

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Effect of reaction temperature on HDO of acetic acid

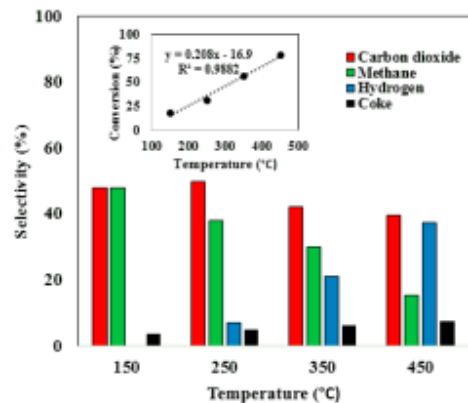
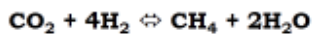
## Effect of Temperature on HDO of Acetic Acid

- Catalytic treatment and HDO of 15% acetic acid solution

$$\text{Conversion \%} = \frac{\text{Moles of acetic acid reacted}}{\text{Moles acetic acid fed}} \times 100$$

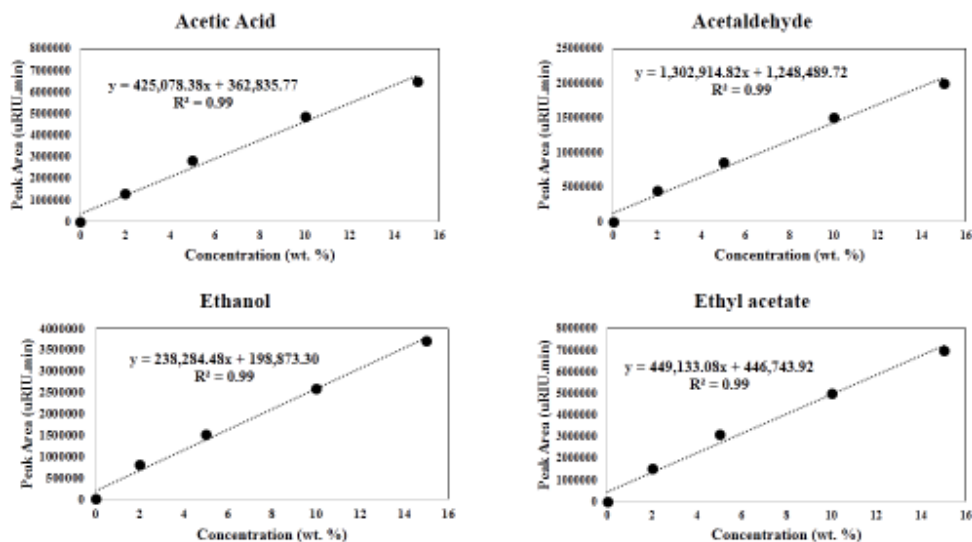
$$C_p \text{ Selectivity \%} = \frac{\text{moles } C_p}{\sum \text{moles } C_p} \times 100$$

**Sabatier reaction:**



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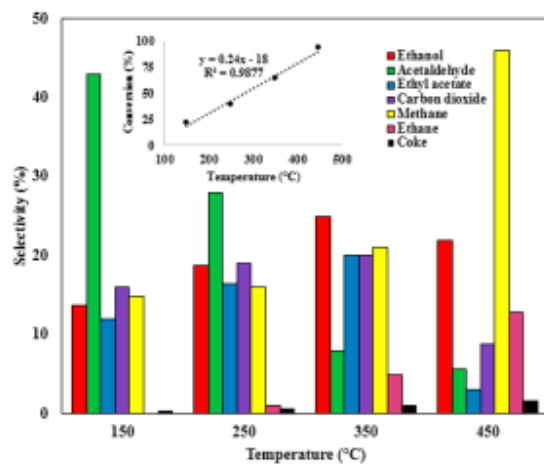
## Calibration Curves



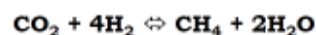
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## Effect of Temperature on HDO of Acetic Acid

- Catalytic treatment and HDO of 15% acetic acid solution



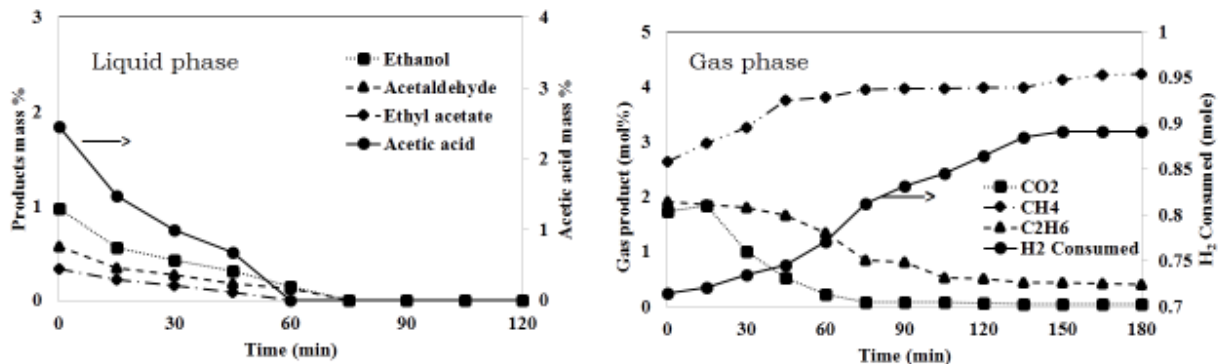
**Sabatier reaction:**



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## HDO products changes over time and mass balance

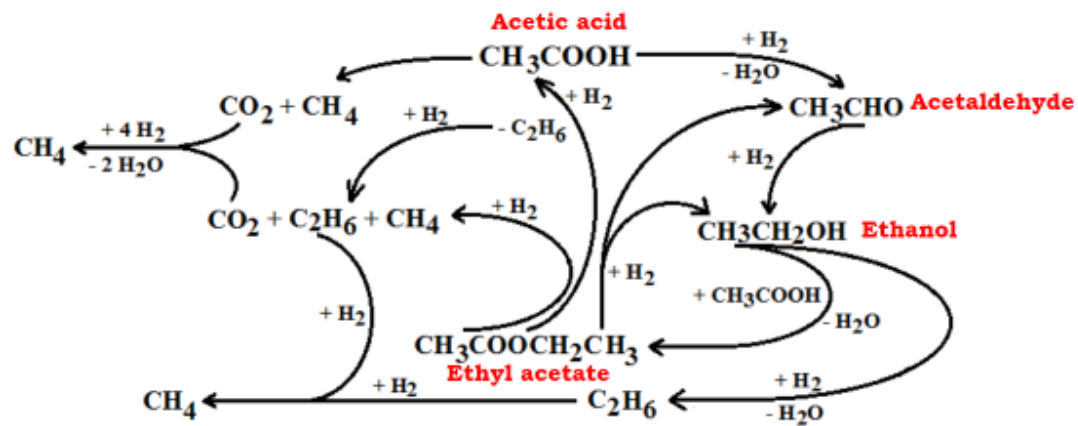


Temperature (°C)	Total mass balance (wt. %)					Carbon mass balance (wt. %)				
	Organic phase	Aqueous phase	Gas	Coke	SUM	Organic phase	Aqueous phase	Gas	Coke	SUM
150	9.3	86.6	1.7	0.4	98	35.4	5.4	55.6	2.1	98.5
250	7.5	87.4	2.3	0.7	97.9	22.8	3.7	67.2	3.6	97.3
350	2.8	89.2	4.4	1.1	97.5	12.3	2.5	77.5	5.7	98
450	0	90.3	6.7	1.7	98.7	0	0	89.6	8.8	98.4

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Reaction pathways of acetic acid HDO process was proposed based on analysis of the products and literature review.

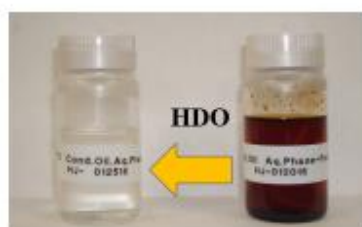
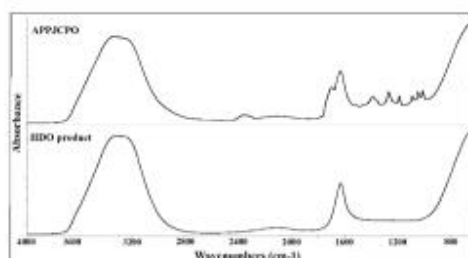
## Reaction Pathways of Acetic Acid HDO



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## Hydrotreatment of Aqueous Phase Pyrolysis Oil

T (°C)	Water content (wt. %)	pH	Gas analysis						Coke (wt.%)
			CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>8</sub>	C <sub>4</sub> H <sub>10</sub>	C <sub>2</sub> H <sub>12</sub>	
<b>Hydrodeoxygenation</b>									
150	84.77	2.97	52.12	47.88	0	0	0	0	0.7
250	88.43	4.19	52.23	45.02	1.25	0.93	0.35	0.22	1.1
350	90.37	6.45	27.15	41.62	14.81	8.14	7.11	1.17	1.5
450	94.13	6.87	10.12	75.31	7.05	4.12	2.14	1.26	1.9
450-75 min	99.52	6.93	3.12	89.14	2.17	3.64	1.34	0.59	2.2



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Total mass balance and carbon mass balance of HDO experiments were within 3% error.

## Mass balance of HDO process

Temperature (°C)	Total mass balance (wt. %)					Carbon mass balance (wt. %)				
	Organic phase	Aqueous phase	Gas	Coke	SUM	Organic phase	Aqueous phase	Gas	Coke	SUM
150	10.1	86.3	0.8	0.7	97.9	14.6	4.3	75.6	3.9	98.4
250	6.4	87.5	2.2	1.1	97.2	8.8	3.2	79.4	6.1	97.5
350	2.2	90.7	3.9	1.5	98.3	4.5	1.1	83.1	8.4	97.1
450	0.6	91.4	4.5	1.9	98.4	1.3	0.8	85.7	10.6	98.4
450-75 min	0	91.6	4.8	2.2	98.6	0	0	86.3	12.32	98.62

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#### 4. Conclusion

Hydrodeoxygenation and catalytic cracking of acetic acid was investigated as a model compound to represent aqueous phase Pinyon Juniper catalytic pyrolysis oil. Acetaldehyde, ethanol, ethyl acetate, carbon dioxide, methane, ethane, water, and coke were produced during hydrodeoxygenation. Reaction temperature had significant effect on product distribution. The reaction pathway of acetic acid HDO was proposed according to literature review and analysis of products. Analysis of APPJCPO HDO product indicated complete conversion of soluble organics at 450 °C. The HDO final products were methane and water. Catalytic cracking of acetic acid and APPJCPO produced carbon dioxide, methane, hydrogen, water, and coke. While application of hydrogen increased the cost of HDO operation, carbon dioxide and coke formation were significantly lower than that of catalytic cracking. This study showed that HDO was a promising techniques to overcome toxicity and corrosion of aqueous phase pyrolysis oil.

### Conclusion

- Acetaldehyde, ethanol, ethyl acetate, carbon dioxide, methane, ethane, water, and coke were produced during hydrodeoxygenation.
- Reaction temperature had significant effect on product distribution. The reaction pathway of acetic acid HDO was proposed according to the analysis of products.
- Analysis of APPJCPO HDO product indicated complete conversion of soluble organics at 450 °C.
- The HDO final products were methane and water.
- While application of hydrogen increased the cost of HDO operation, carbon dioxide and coke formation were significantly lower than that of catalytic cracking.
- HDO was a promising technique to overcome toxicity and corrosion of aqueous phase pyrolysis oil.

## Acknowledgement

This research was supported by Utah Science Technology and Research (USTAR). The authors would like to acknowledge Pacific Northwest National Laboratory for GC-MS analysis of APPJCPO. We would also thank Kyle Christian and Brandon Sargent for supplying the APPJCPO.

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