Continuous Catalytic Ketonization and Esterification of Fast Pyrolysis Oils Using Metal Oxides

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Auburn, Al

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3 Oak Ridge National Lab, DOE
Concept/Rational

• Produce an inexpensive solid catalyst from red mud
• Esterify, ketonize, and condense (aldol condensation) the acids in fast pyrolysis oil
• Recover carbon and reduce acidity
• Inexpensive catalyst that does not require H\textsubscript{2} to stabilize the bio-oil would improve the economics
• Produce a value added product from spent catalyst
Past Work/Rational

- Ce-ZrOx – Ketonization of acetic acid/acetol (Hakim et al., Applied Catalysis B: Environmental 142–143, 2013)
  - Defined transfer hydrogenation pathway for acetol via pyruvaldehyde & propylene glycol
  - Furfural inhibits ketonization, Did not study levoglucosan (caused plugging)

- Fe, Ce, Al Mixed Metal Oxide - Ketonization of model bio-oil containing acetic, hydroxyacetone, furfural, phenolics (Jackson, Energy and Fuels. 27, 3936, 2013)
  - Furfural, guaiacol, eugenol, inhibits ketonization
  - Acetol transformed to primarily acetone, 2-butanone, 3-pentanone

- Fe$_3$O$_4$ (magnetite) in red mud – Batch ketonization of carboxylic acids, decomposition of formic acid (Karimi et al., Energy & Fuels, 24, 2747-2757, 2010; Catalysis Today, 190, 73-88, 2012; App Cat B:Env, 145, 2014)
  - Magnetite probable active metal oxide, formic acid converted to H$_2$
  - Catalytic ketonization of carboxylic acids to ketones
  - All batch kinetic studies (4-8 h)
  - Little information on reaction rates, yields, and selectivity under continuous conditions
  - Little information on how catalyst changes after reaction
Fe$_2$O$_3$ $\rightarrow$ Fe$_3$O$_4$

**Products – Linear/Cyclic Ketones**

- Aqueous Phase Acids, Ketones, Sugars
- Oil Phase Phenolics, Lignin Oligomers

**Catalytic Packed Bed Reactor**

- Space Time Yield, g/L-cat/h
- % Selectivity

- Total + Diones + Cyclic Ketones
- Acetone
- 2-Butanone
- Butyrolactone
- STY
Reactor including a biomass hopper (A), sand bed reactor (B), nitrogen sweep gas (C), hot gas filter (D), condenser inlet (E), and char collector (F).
## Compositional Analysis of Water Extracted Bio-oil

<table>
<thead>
<tr>
<th></th>
<th>Levoglucosan (g/L)</th>
<th>Acetol (g/L)</th>
<th>Formate (g/L)</th>
<th>Acetate (g/L)</th>
<th>5-HMF (g/L)</th>
<th>Furfural (g/L)</th>
<th>Water (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ILC (aq)</td>
<td>75-90</td>
<td>3.2</td>
<td>50-65</td>
<td>30-37</td>
<td>1.5-1.7</td>
<td>0.8-1.0</td>
<td>Spray</td>
</tr>
<tr>
<td>FP (aq)</td>
<td>74</td>
<td>5.0</td>
<td>57</td>
<td>37</td>
<td>2.25</td>
<td>1.5</td>
<td>50</td>
</tr>
<tr>
<td>FP (oil)</td>
<td>130</td>
<td>15-17</td>
<td>80</td>
<td>72</td>
<td>3.0</td>
<td>2.5</td>
<td>20</td>
</tr>
<tr>
<td>ENSYN (aq)</td>
<td>51</td>
<td>10.3</td>
<td>34</td>
<td>50</td>
<td>1.0</td>
<td>2.4</td>
<td>50</td>
</tr>
<tr>
<td>ENSYN (oil)</td>
<td>57</td>
<td>36</td>
<td>NP</td>
<td>58</td>
<td>1.1</td>
<td>6.4</td>
<td>20</td>
</tr>
</tbody>
</table>

ILC – In-line condensation  
FP – fast pyrolysis oil  
aq – aqueous phase (all UGA generated)  
Acetol is 1-hydroxy-2-propanone  
Extraction: Room temp., 1:1 v/v water to oil, agitate, centrifuge
Approach 1 - Ketonization

A

Fast Pyrolysis → Bio-oil Vapor → Condensation → Liquid Bio-oil → Catalytic Hydrodeoxygenation and Hydroprocessing → Light Gases, Naptha, Liquid Hydrocarbons, Water

Solids/Biochar

B

Fast Pyrolysis → Bio-oil Vapor → Water/Aq. Phase → Oil (Lignin Phase) → Condensation → Liquid Bio-oil → Solvent + Catalyst + \( \text{H}_2 \) → Catalytic Hydrodeoxygenation and Hydroprocessing → Light Gases, Naptha, Liquid Hydrocarbons, Water

Reduced Red Mud + \( \text{H}_2 \) → Ketonization → Ketones → Zeolite to Gasoline

Spent Catalyst Coke for Steel Making → Bi-cyclic Ketones → Jet Fuel Precursor
Surface Area, Pore Size, TPR of Red Mud

Red Mud
- Fe$_2$O$_3$: 24.0%
- SiO$_2$: 9.0%
- Al$_2$O$_3$: 17.0%
- TiO$_2$: 5.0%
- CaO: 5.0%
- MgO: 0.3%

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Catalyst</th>
<th>Surface Area m$^2$/g</th>
<th>Average Pore Size Å</th>
<th>Average Pore Volume cm$^3$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>Granulated Red Mud</td>
<td>13.3</td>
<td>13.58</td>
<td>0.0091</td>
</tr>
<tr>
<td>None</td>
<td>H$_2$ Reduced (RRM)</td>
<td>30.7</td>
<td>15.63</td>
<td>0.024</td>
</tr>
</tbody>
</table>

H$_2$ TPR

- H$_2$ reduction of Red Mud
- Flowing 95% H$_2$, 20-30 g of red mud reduced in-situ at 100 mL/min, 300°C and held until dark grey to black
Catalyst Structure/Function Relationships

NH₃ TPD

Ammonia TPD

Temperature, °C

Signal, mV

Unreacted Red Mud
H₂-Reduced Red Mud
HZSM5
Catalyst Structure/Function Relationships

CO$_2$ TPD

A

Granulated Red Mud

B

H$_2$ Reduced Red Mud

Signal, mV vs. Temperature, °C
Continuous Packed Bed Reactor

- ENSYN and UGA oil stored at 4°C
- Catalytic PBR
  - Prep and characterize red mud
    - Granulated (1-2 mm), H\textsubscript{2} reduced (300°C, 95% H\textsubscript{2} in PBR)
  - Bio-oil and model compounds
  - W/F: 0.5-6.0 (h)
    - 5-20 g cat
    - 0.5-1 ml/min liquid feed
  - T: 350-425°C
  - P: 1 atm
  - HPLC/GC-MS/GC-FID of inlet and outlet
Catalytic Ketonization via RRM-Model Compounds

Continuous catalytic ketonization of model compounds (4 wt%) using reduced red mud at 350°C, 1 atm, 5 g catalyst, and a WHSV of 0.48 h⁻¹ (g_{reactant, fed}/g-cat/h) or W/F of 2.1 h. Note-2HP is 1-hydroxy-2-propanone or acetol and LG is levoglucosan.

Acetic $\rightarrow$ Acetone

2HP $\rightarrow$ Acetone, 2-Butanone

Levo $\rightarrow$ Acetic, 2HP, Acetone
Continuous catalytic ketonization of model compound mixtures (4 wt% each) using reduced red mud at 350°C, 1 atm, 5 g catalyst, and a WHSV of 0.48 h⁻¹ (g_{reactant fed}/g-cat/h) each or W/F of 0.69 h total. Note-2HP is acetol, aa is acetic, fa is formic, and 2-MP is 2-methoxyphenol at 1 wt%.
Effect of Increasing Catalyst Mass or Residence Time

Effect of lower liquid feed rate and increased catalyst mass on catalytic ketonization of mixture containing acetic, formic, and 2HP (4 wt% each) using reduced red mud at 350 and 400°C and 1 atm (5, 10, 15 and 20 g of catalyst). W/F is for all three compounds or total.

Closed Symbols: 400°C     Open Symbols: 350°C
Time On Stream

**Graph 1:**
- **% Conversion**
- **Time on Stream, h**
- **Graph showing the relationship between % Conversion and Time on Stream for Acetic, Formic, 2HP, and LG.**

**Graph 2:**
- **% Yield (mol/mol)**
- **Space Time Yield (g/Lcat/h)**
- **Time on Stream, hr**
- **Graph showing the relationship between % Yield (mol/mol) and Space Time Yield (g/Lcat/h) for Acetone, 2-Butanone, Cyclic Ketones, and Space Time Yield (STY).**
Time On Stream

Selectivity (mol A/mol product)

Concentration, g/L

Abundance (TIC)

Time on Stream, hr

Time on Stream, h

Acetone  2-Butanone  Cyclic Ketones  Cyclopentanone

Acetone  2-Butanone  Cyclopentanone  Cyclic Ketones

Time, min

TOS-1

A

B
Effect of Reaction Temperature on Bio-oil Upgrading Using Red Mud

Continuous PBR Experiments

Feed: Water Extracted UGA Oil
Conditions: 1 ml/min, 5 g cat., 1 atm, WHSV 0.72 g oil/g-cat/h, or W/F = 1.38 h
Catalyst: Reduced Red Mud (300°C, H₂)
Inlet Conditions: Acetic 47 g/L; formic 15g/L; Acetol 10 g/L; Levo 44 g/L; furfural 1.2 g/L; HMF 0.75 g/L; 2MP 1.2 g/L
Effect of Catalyst Mass on Conversion
400°C, 1 atm

Bio-oil Type: WE-water extraction

X, Conversion

W/F, h

0.00 0.20 0.40 0.60 0.80 1.00 1.20 1.40

1.39 2.77 4.16

% Selectivity (moles/moles converted)

400°C, 1 atm, Reduced Red Mud

Space Time Yield, g/L-cat/h

W/F, h

0 10 20 30 40 50 60 70 80 90

0.50 1.50 2.50 3.50 4.50

Total+diones+cyclic ketones
Acetone
2-Butanone
Butyrolactone
Cyclic ketones
STY
Effect of W/F on Products

W/F = 4.2 h
400°C, 15 g-cat

W/F = 1.4 h
400°C, 5 g-cat
Approach 2 – Long Term

• Ex-situ catalytic esterification (target rxn)
HSZM-5

The graph illustrates the relationship between temperature (°C) and the concentrations of Ethyl Acetate, Ethyl Levulinate, Glucose, and Furfural, measured in g/L. The x-axis represents temperature, while the y-axis represents the concentration of each compound.

- Ethyl Acetate shows an increasing trend until around 180 °C, after which it decreases.
- Ethyl Levulinate increases steadily with temperature.
- Glucose concentration decreases with temperature.
- Furfural concentration decreases with temperature.

The graph uses different markers to distinguish between the compounds: Ethyl Acetate is represented by diamonds, Ethyl Levulinate by squares, Glucose by triangles, and Furfural by crosses.
GC/MS Analysis: HZSM-5

A, 120°C

B, 180°C
Pathway FPO/MeOH SiAl-250°C

1 methyl propionate
2 acetic
3 Pentanoic acid, ethyl ester
4 Hexanoic acid, methyl ester
5 Pentanoic acid, 4-oxo-, methyl ester
6 Butanedioic acid, methyl-
7 Phenol, 2-methoxy-
8 Phenol, 2-methoxy-4-methyl-
9 Phenol, 4-ethyl-2-methoxy-
10 Phenol, 2-methoxy-4-propyl-
11 Octanoic acid, methyl ester
12 Nonanoic acid, methyl ester
Pathway FPO/MeOH RRM-250°C

1 methyl propionate
2 acetic
3 Pentanoic acid, ethyl ester
4 Cyclopentanone, 2-methyl-
5 Hexanoic acid, methyl ester
6 trans-2-Methyl-4-hexen-3-ol
7 Heptanoic acid, methyl ester
8 Phenol, 2-methoxy-
9 Phenol, 2-methoxy-4-methyl-
10 Phenol, 4-ethyl-2-methoxy-
11 Phenol, 2-methoxy-4-propyl-
12 Octanoic acid, methyl ester
13 Nonanoic acid, methyl ester

RRM-300C
W/F = 0.46 h
250°C, 5 g-cat
FPO-MeOH Catalytic Upgrading

Bio-oil Type: FPO:MeOH (1:1 v/v), W/F=0.44 h, 250°C

- Acetic Acid
- Formic Acid
- 2HP
- Levo

- Methyl Acetate
- Acetone
- Methyl Levulinate
- Cyclic Ketones
- Total

Bar charts showing conversion and yield for different catalysts SiAlNoH2, RRMNoH2, SiAlH2, and RRMH2.
FPO-MeOH Catalytic Upgrading

Space Time Yield, (g/L-cat/h)

BBio-oil Type: FPO:MeOH (1:1 v/v), W/F=0.44 h, 250°C

- Methyl Acetate
- Acetone
- Methyl Levulinate
- Cyclic Ketones
- Total
Conclusions and Future Work

• Continuous catalytic ketonization/esterification using red mud is feasible
• Acetone/ketone selectivity increases with catalyst mass and temperature
• Bio-oil acidity significantly reduced
• Simultaneous ketonization/esterification/HDO might be possible
• Reaction pathways and kinetics unclear
  – Formic acid decomposition pathway and role in HDO?
  – Levoglucosan pathway?
  – HDO pathways?
• Longer TOS studies needed
• Catalyst Structure/Function Studies Needed
  – Modulate iron oxide valance in red mud
The End

Thanks,

Questions
Possible pathways for formation of alkyl levulinates from glucose and fructose (Démolis et al., ACS Sustainable Chem. Eng., Just Accepted Manuscript Publication Date (Web): 28 Apr 2014). Red is the proposed predominate pathway for fructose and green is for glucose.
Products/Intermediates

1. 

2. 

7. 

19. 

Primary:

Intermediate/Trace:

Same as with acetic, acetol
# Catalyst Consistency

<table>
<thead>
<tr>
<th>Date</th>
<th>6/6/2013(^a) / 08/04/14(^b)</th>
<th>6/6/2013(^a) / 08/04/14(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W/F (g-cat/g*h)</td>
<td>1.38 ± 0.33</td>
<td>2.75 ± 0.65</td>
</tr>
<tr>
<td>T, °C</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td><strong>Fractional Conversion</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>0.80 ± 0.12</td>
<td>1.00 ± 0.01</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>0.98 ± 0.05</td>
<td>1.00 ± 0.00</td>
</tr>
<tr>
<td>Acetol</td>
<td>0.80 ± 0.02</td>
<td>1.00 ± 0.00</td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>0.97</td>
<td>1.00</td>
</tr>
<tr>
<td><strong>Yield (mol/mol)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>7.29 ± 2.95</td>
<td>7.72 ± 2.73</td>
</tr>
<tr>
<td>2-Butanone</td>
<td>1.10 ± 1.00</td>
<td>2.10 ± 0.25</td>
</tr>
<tr>
<td><strong>Reaction Rate (mmol/g-cat/h)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>2.89 ± 0.54</td>
<td>1.79 ± 0.09</td>
</tr>
<tr>
<td>Formic Acid</td>
<td>4.81 ± 0.15</td>
<td>2.46 ± 0.19</td>
</tr>
<tr>
<td>Acetol</td>
<td>2.02 ± 0.10</td>
<td>1.26 ± 0.10</td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>1.28</td>
<td>0.66</td>
</tr>
</tbody>
</table>

\(^a\) The runs on 6/6/13 contained 4% acetic, formic, and acetol

\(^b\) The runs on 8/4/14 contained 4% acetic, formic, acetol, and levoglucosan

Error based on range of duplicate experiments and analysis
Change in Catalyst Structure

% Change in Tar/Coke, Surface Area, Pore Volume

- Coke/Tar
- Surface Area
- Pore Vol

- Acetic Acid
- Formic Acid
- Acetol
- Acetic, Formic
- Acetic, Formic, Acetol
- Acetic and 2-MP
- Levoglucosan
- Commercial Oil/Aq. Phase
- UGA FPO Aq. Phase
TGA Analysis of Reacted Catalysts

**Reduced Red Mud**

**Commercial Oil/Water Extracted**

**Water Extracted Oil UGA_RRM_350C**

**AA-FA-2HP_RRM_350C**
No Change in Catalyst Structure
Change in Catalyst Structure

![Graph 1: RRM, Acetol, LG](image1)

![Graph 2: RRM, Acetic Acid, Formic Acid](image2)

![Graph 3: RRM, AA, FA, 2HP, AA, 2MP](image3)

![Graph 4: RRM, UGA Oil, CO](image4)
Potential Pathways

- Acetol
- Pyruvaldehyde
- Acetic
- 3-methyl cyclopent-2-en3-one (1I)
- 2-Butanone (2D)
- Propanal
- Formic (1C)

S.H. Hakim et al. / Applied Catalysis B: Environmental 142–143 (2013) 368–376
Acetic Acid/Formic - Potential Pathways

1-formic acid
2-acetic acid
3-acetaldehyde
4-acetone
5-3-penten-2-one
6-2-pentanone

Red indicates a compound that has been identified via GC/MS, except if a reactant/substrate
Acetol-Potential Pathways

7-1-hydroxy-2-propanone (acetol)
8-pyruvaldehyde
9-2,3-hexanedione
10-2-methyl-2-Cyclopenten-1-one

Red indicates a compound that has been identified via GC/MS, except if a reactant/substrate.
Acetol-Potential Pathways

Red indicates a compound that has been identified via GC/MS, except if a reactant/substrate.

- 11-propanal
- 12-propanoic acid
- 13-3-pentanone
- 14-1,2-propylene glycol
- 15-propanal
- 16-2-butanone
- 17-2,3-butanedione
- 18-1-buten-3-one
Levoglucosan-Potential Pathways

19: Levoglucosan
20: Levoglucosenone

Red indicates a compound that has been identified via GC/MS, except if a reactant/substrate
Possible Catalytic Pathways
### Carbon Balance

<table>
<thead>
<tr>
<th>W/F (h)</th>
<th>T °C</th>
<th>% C Recovered In Liq</th>
<th>% C Lost in Gas Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.61</td>
<td>350</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.21</td>
<td>350</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.21</td>
<td>375</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>1.21</td>
<td>400</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>1.21</td>
<td>425</td>
<td>400</td>
<td></td>
</tr>
<tr>
<td>2.43</td>
<td>400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.64</td>
<td>400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.86</td>
<td>400</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Note:**
- W/F: Weight Feed
- h: Hours
- °C: Celsius
- % C Recovered In Liq: Percentage of carbon recovered in liquid phase
- % C Lost in Gas Phase: Percentage of carbon lost in gas phase
Why Ethyl Levulinate?

• Gasoline blending agent
  – Alternative to ethanol (higher heating value, reduced water absorption, higher lubricity)

• Diesel blending agent
  – Improves combustion efficiency and reduces emissions

• Potential biodiesel alternative
  – Reduces cold flow properties and gum formation

• Used as a food additive and color and fragrance agent in perfumes and candles
Continuous Packed Bed Reactor

- **Reactants**
  - LG (≈90 g/L) and AA (≈45 g/L) in an ethanol-water mixture (80% EtOH:20% water, v/v)
  - FPO and MeOH (1:1 v/v)

- **Catalytic PBR**
  - HZSM-5, Ru-HZSM-5 (5% Ru)
    - W/F: 0.11 (h)
      - 5 g cat, 0.5-1 ml/min liquid feed
    - T: 120-230°C
  - SiO$_2$/Al$_2$O$_3$, RRM
    - W/F: 0.44 (h)
      - 5 g cat, 1 ml/min liquid feed
      - 100 ml/min N$_2$
    - T: 250°C
  - P: 600 psig, HPLC/GC-MS/GC-FID of inlet and outlet
Catalyst Characterization

<table>
<thead>
<tr>
<th>Properties</th>
<th>Catalyst</th>
<th>HZSM-5</th>
<th>Ru-HZSM-5</th>
<th>SiO$_2$Al$_2$O$_3$</th>
<th>RRM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface Area (m$^2$/g)</td>
<td></td>
<td>316</td>
<td>313</td>
<td>405</td>
<td>30.7</td>
</tr>
<tr>
<td>Pore Volume (cm$^3$/g)</td>
<td></td>
<td>0.17</td>
<td>0.17</td>
<td>0.42</td>
<td>0.024</td>
</tr>
<tr>
<td>Average Pore Size (radius Å)</td>
<td></td>
<td>11</td>
<td>11</td>
<td>12.1</td>
<td>15.6</td>
</tr>
</tbody>
</table>

Ammonia TPD

- Blue line: SiO$_2$-Al$_2$O$_3$
- Red line: RRM

Temperature, °C vs. Signal, mv
XRD Analysis

H$_2$ Reduced Red Mud

Granulated Red
TGA Analysis of Reacted Catalysts

![Graphs showing TGA analysis of different samples](image-url)
Corrosion Effects
Compositional Analysis of Water Extracted Bio-oil

<table>
<thead>
<tr>
<th>Oil</th>
<th>Levoglucosan (g/L)</th>
<th>Acetol (g/L)</th>
<th>Formate (g/L)</th>
<th>Acetate (g/L)</th>
<th>5-HMF (g/L)</th>
<th>Furfural (g/L)</th>
<th>Water (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FP (oil)</td>
<td>130</td>
<td>15-17</td>
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<td>6.4</td>
<td>20</td>
</tr>
</tbody>
</table>

ILC – In-line condensation
FP – fast pyrolysis oil
aq – aqueous phase (all UGA generated)
Acetol is 1-hydroxy-2-propanone
Extraction: Room temp., 1:1 v/v water to oil, agitate, centrifuge
Corrosion Rates for Bio-oil

<table>
<thead>
<tr>
<th>Metal Type</th>
<th>Carbon Steel</th>
<th>2¼Cr-1Mo</th>
<th>409 Stainless</th>
<th>304L Stainless b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>UGA</td>
<td>ENSYN</td>
<td>UGA</td>
<td>ENSYN</td>
</tr>
<tr>
<td>Sample</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
</tr>
<tr>
<td>Method</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Suspended</td>
<td>0.61/0.26</td>
<td>1.35/1.72</td>
<td>1.05/0.27</td>
<td>1.63/1.97</td>
</tr>
<tr>
<td>Immersed</td>
<td>0.56/0.45</td>
<td>1.56/1.53</td>
<td>1.35/1.12</td>
<td>1.54/1.55</td>
</tr>
</tbody>
</table>

- a, mm/year, 1000 h exposure, 50°C, average for coupon and U-bend
- b, 316L Stainless - <0.01/<0.01 for all samples

FPO – fast pyrolysis oil
UGA – FPO from Southern Pine
Suspended – Suspended above oil