Novel Quantitative Method for Biodiesel Analysis
Georgia Institute of Technology

North Avenue Trade School opened in 1888 with 84 students

Over 17,000 students are currently enrolled

Sits on 400 acre campus

Ranked # 8 among public universities in the nation

Ranked in the top 5 for most engineering disciplines
Outline

- Fossil fuels vs. Biofuels
- Current biodiesel analytical methods
- Developing a new analytical tool
  - Chemical approach
  - Phosphitylating agent
  - $^{31}\text{P}$-NMR chemical shift library
- Process sample analysis
  - Method optimization
  - Rapid sample analysis
The Carbon-cycle

Biomass

Closed cycle

Fossils

Broken cycle
International Energy Overview

- World primary energy production by source:
  - Crude Oil and NGPL
  - Coal
  - Natural Gas
  - Renewable Energy
  - Nuclear Electric Power

- World crude oil production totaled 74 million barrels per day in 2008.

Need for Renewable Biofuels:
- Energy security (Local)
- Carbon neutral/climate change
- Sustainability

Energy Information Administration. www.eis.doe.gov
**Potential Biofuel Precursors**

- **Produced biofuels**
  - Ethanol (Bioethanol)
  - Biodiesel (Biodiesel)
- **Bio-renewable resources**
  - Starch
  - Cellulose
  - Hemicelluloses
  - Lignin
  - Yellow Grease

### Characteristics

- **High energy content**
- **High volume**
- **Easily accessible**
- **Low cost**

### Annual Consumption
- 460 quadrillion Btu
- 74 million barrels per day
Potential Biofuel Precursors

Produced biofuels
- Ethanol (Bioethanol)
- Alkali fatty esters (Biodiesel)

Bio-renewable resources
- Starch
- Cellulose
- Hemicelluloses
- Lignin
- Plant: (PVO, UVO)
- Animal: Animal fat
- Yellow Grease

Bio-renewable resources
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  Rapid sample analysis
Current Biodiesel Analytical Methods

**Glycerol, Acylglycerols**
- Chromatographic: HPLC, GC
- Spectroscopic: MS, NIR
- Time consuming analysis
- Long sample preparation
- Extended analysis time
- Complicated data analysis
- Rapid technique with an easy data analysis

**Acid content**
- Wet chem. tech.: Pot. titr, Iodom. titr.

**Residual alcohol**
- Chromatographic: HPLC, GC
- Phosphitylation: $^{31}$P-NMR
- Rapid technique with an easy data analysis

**All above**
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Chemical Approach

Transesterification reaction for biodiesel production,
R\textsubscript{1-3} are hydrocarbon groups

Phosphitylation of partially substituted glycerols with DOP or with TMDP\textsuperscript{11}

Outline

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Phosphitylating Agent

DOP vs. TMDP

~85% 1,3-Dioleoylglycerol and ~15% 1,2-Dioleoylglycerol mixture

TMDP provides greater spectral resolution of the individual hydroxyl groups of glycerol-derivatives → reagent of interest for additional studies.

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   Rapid sample analysis
### Biodiesel Analysis

**$^{31}$P-NMR chemical shift library**

<table>
<thead>
<tr>
<th>Substituted position</th>
<th>Mono-substituted</th>
<th>Di-substituted</th>
<th>Tri *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphitylated hydroxyl</td>
<td>O-b</td>
<td>O-c</td>
<td>O-c</td>
</tr>
</tbody>
</table>

**Lipid chain**

<table>
<thead>
<tr>
<th>Fatty acid</th>
<th>$\delta^{31}$P Signal (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lauric</td>
<td>146.2, 147.5, 146.5</td>
</tr>
<tr>
<td>Myristic</td>
<td>146.2, 147.5, 146.4</td>
</tr>
<tr>
<td>Palmitic</td>
<td>146.2, 147.6, 147.9, 146.4</td>
</tr>
<tr>
<td>Stearic</td>
<td>146.2, 147.4, 147.9, 146.4</td>
</tr>
<tr>
<td>Oleic</td>
<td>146.1, 147.4, 147.7, 146.4</td>
</tr>
<tr>
<td>Linoleic</td>
<td>146.2, 147.4, 147.7, 146.4</td>
</tr>
<tr>
<td>Linolenic</td>
<td>146.2, 147.4, 147.7, 146.4</td>
</tr>
</tbody>
</table>

*Tri* denotes the presence of multiple $\delta^{31}$P signals due to the substitution position.
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Phosphitylation of 1,2-diacylglycerol with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane at c-position. \( R_{1-2} \) are hydrocarbon groups.

**Solvent mixture**

The process sample and the reagent mixture has to be in solution.
The document discusses the optimization of NMR methods for the spin-lattice relaxation time of biodiesel precursors. The rapid analytical method aims to reduce analysis time to a minimum. The specific method involves using anhydrous pyridine/CDCl₃/DMF in a 1:1.2:1 ratio and adding Chromium acetylacetonate (Cr(acac)₃) as a relaxation agent (~3.60 mg/mL). The measurements are conducted at 400 MHz, 25 °C, with a magnetic field of 9.4 T, using a standard inversion recovery pulse sequence with a 20 s recycle delay, 8 scans.

The chemical structures show the precursors made of hydroxyl groups and phosphorus, reacting with pyridine and DMF to form the biodiesel precursors.

References:
TMDP/$^{31}$P-NMR Method Optimization

Optimized TMDP/$^{31}$P-NMR analysis protocol

**Solvent mixture**

Anhydrous pyridine/CDCl$_3$/DMF in 1:1.2:1 ratio

$\sim 3.60$ mg/mL of Cr(acac)$_3$ (*relaxation agent*)

$\sim 4.00$ mg/mL of cyclohexanol (*internal standard*)

**Optimized NMR pulse program (400 MHz, at 25 °C)**

5 sec pulse delay, inverse-gated decoupling (Waltz-16), 90° pulse angle, a time domain of 32 K with one degree of zero filling, 4.0 Hz line broadening, and 16 acquisition transients.

**Phosphitylation**

Biodiesel process sample (150 μL) or Glycerol process sample (10 μL)

Solvent mixture 500 μL $\rightarrow$ Mix

TMDP (100 μL)

<table>
<thead>
<tr>
<th>Sample preparation</th>
<th>Under 5 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis time</td>
<td>56 sec</td>
</tr>
<tr>
<td>Data analysis</td>
<td>$\sim 30$ minutes</td>
</tr>
</tbody>
</table>
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Biodiesel Analysis
Process outline and sampling

CATALYST

METHANOL

PARENT OIL

TRANSESTERIFICATION

SETTLING

WASHING SEQUENCE

COLUMNS

DISTILLATION COLUMNS

FINAL BIODIESEL

FINAL GLYCEROL

RECOVERED METHANOL

H₂C₁ — Oₐ
H₂C₂ — Oₐ
H₂C₃ — Oₐ

H₂C₁ — Oₐ
H₂C₂ — Oₐ
H₂C₃ — Oₐ

H₂C₁ — Oₐ
H₂C₂ — Oₐ
H₂C₃ — Oₐ

Biodiesel Analysis
The parent oil

Quantitative $^{31}$P-NMR spectra of parent oil samples of waste vegetable oil (a) and soybean oil (b)

Biodiesel Analysis
Process outline and sampling

Biodiesel Analysis
The transesterification step

Quantitative 31P-NMR spectra of samples taken after the transesterification step utilizing different process conditions using soybean oil as feedstock

Biodiesel Analysis
Process outline and sampling

Biodiesel Analysis
The washing phase

Quantitative 31P-NMR spectra showing the washing efficiency of a soybean oil based commercial process on samples taken before wash (a) and after the first washing cycle (b)

Biodiesel Analysis
Process outline and sampling

Biodiesel Analysis

The final biodiesel

Quantitative 31P-NMR spectra of final biodiesel samples of soybean oil (a) and waste vegetable oil (b)

Biodiesel Analysis
Quantitative analysis on final biodiesel sample

<table>
<thead>
<tr>
<th>Component</th>
<th>Conventional technique used</th>
<th>Data Measured</th>
<th>Phosphitylation with $^{31}$P-NMR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Glycerol</td>
<td>Chromatographic (LC/GC)</td>
<td>0.01</td>
<td>0.03</td>
</tr>
<tr>
<td>Mono Glycerol</td>
<td>Chromatographic (LC/GC)</td>
<td>1.4</td>
<td>1.8</td>
</tr>
<tr>
<td>Di Glycerol</td>
<td>Chromatographic (LC/GC)</td>
<td>1.7</td>
<td>1.9</td>
</tr>
<tr>
<td>Tri Glycerol</td>
<td>Chromatographic (LC/GC)</td>
<td>0.3</td>
<td>---</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>Potentiometric titration</td>
<td>0.3</td>
<td>0.3</td>
</tr>
<tr>
<td>Methanol</td>
<td>Chromatographic (LC/GC)</td>
<td>---</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Quantitative $^{31}$P-NMR spectra of biodiesel samples from commercial biodiesel operations based on soy oil.
Biodiesel Analysis
Monitoring the biodiesel process stream

Máté Nagy, et. al. Fuel (2009), 88, 1793-1797
Biodiesel Analysis
Process outline and sampling

CATALYST
METHANOL
PARENT OIL

TRANSESTERIFICATION
SETTLING
WASHING SEQUENCE
DISTILLATION COLUMNS

RECOVERED METHANOL

AT
BW
A1W
SG

NEUTRALIZATION
FINAL BIODIESEL
FINAL GLYCEROL

PO

RECOVERED METHANOL

FB
DG
Biodiesel Analysis
The glycerol process stream

Quantitative 31P-NMR spectra on glycerol samples from soybean oil based commercial process of the separated glycerol before neutralization (a) and of the final demethylated glycerol (b)

Quantitative analysis on final glycerol samples from commercial biodiesel operations based on soy oil, poultry fat & tallow

<table>
<thead>
<tr>
<th>Component</th>
<th>Conventional (weight %)</th>
<th>TMDP / (^{31})P-NMR (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free glycerol</td>
<td>---</td>
<td>75.9</td>
</tr>
<tr>
<td>Mono substituted glycerol</td>
<td>---</td>
<td>7.7</td>
</tr>
<tr>
<td>Total glycerol</td>
<td>81.0</td>
<td>83.6</td>
</tr>
<tr>
<td>Fatty acids</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

\[ \text{C}_1 \text{OH} \]
\[ \text{H}_2\text{C}_1 \rightarrow \text{OH} \]
\[ \text{HC}_2 \rightarrow \text{OH} \]
\[ \text{H}_2\text{C}_3 \rightarrow \text{OH} \]
\[ \text{H}_2\text{C}_1 \rightarrow \text{O}_a \]
\[ \text{HC}_2 \rightarrow \text{O}_b \]
\[ \text{H}_2\text{C}_3 \rightarrow \text{O}_c \]
\[ \text{R} \rightarrow \text{C}_1 \rightarrow \text{OH} \]
\[ \text{R} \rightarrow \text{OH} \]
Biodiesel Analysis
Process outline and sampling

Conclusions

- **Current methods vs. TMDP/ $^{31}$P-NMR method**
  - Fast sample preparation (under 5 min)
  - Rapid analysis and data acquisition (56 sec)
  - Accurate quantitative method (Accuracy: +95%)
  - Easy data analysis (Good separation, spectroscopic information related to the structure)
  - Sensitive novel research tool ($1.9 \, \mu\text{mol/mL LOD, } \pm1.1\% \text{ error margin}$)

- **Additional benefits**
  - Independent from feedstock
  - Direct measurement for the intermediate products through the whole production line $\rightarrow$ Process step optimization
  - Direct measurements for contamination in the final products $\rightarrow$ Quality control
Acknowledgments

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Rachel Burton

_Piedmont Biofuels_
Thank You!

Máté Nagy

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