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

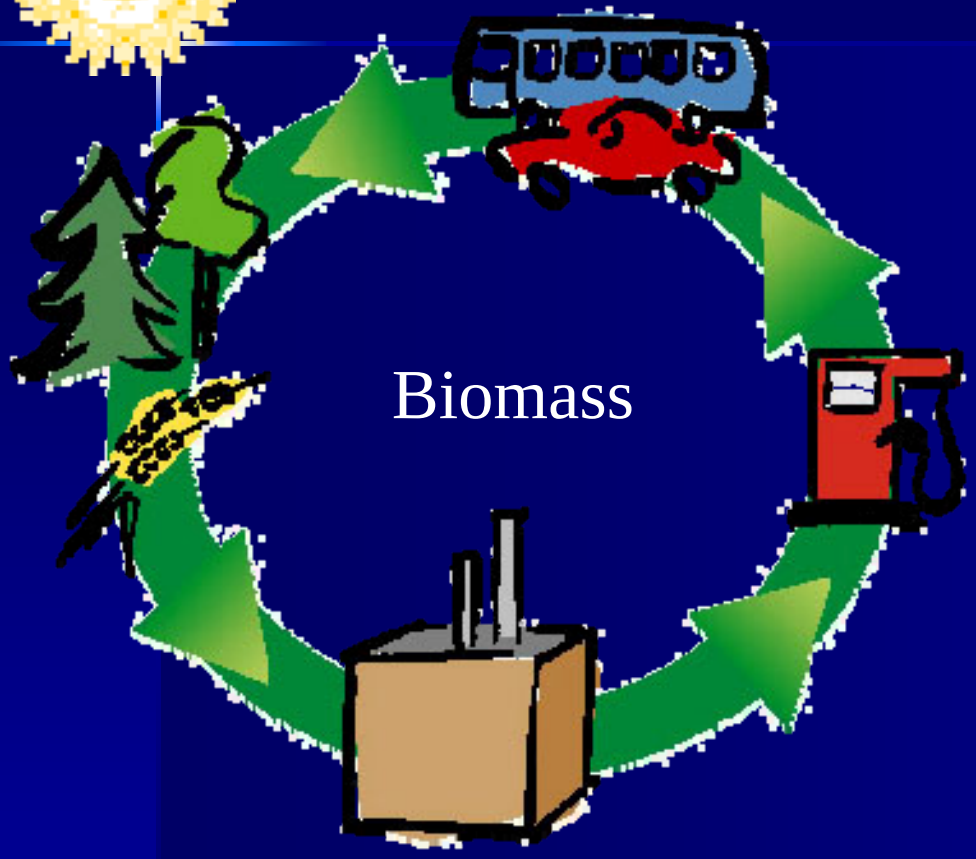
Ranked # 8 among public universities in the nation

Ranked in the top 5 for most engineering disciplines

Outline

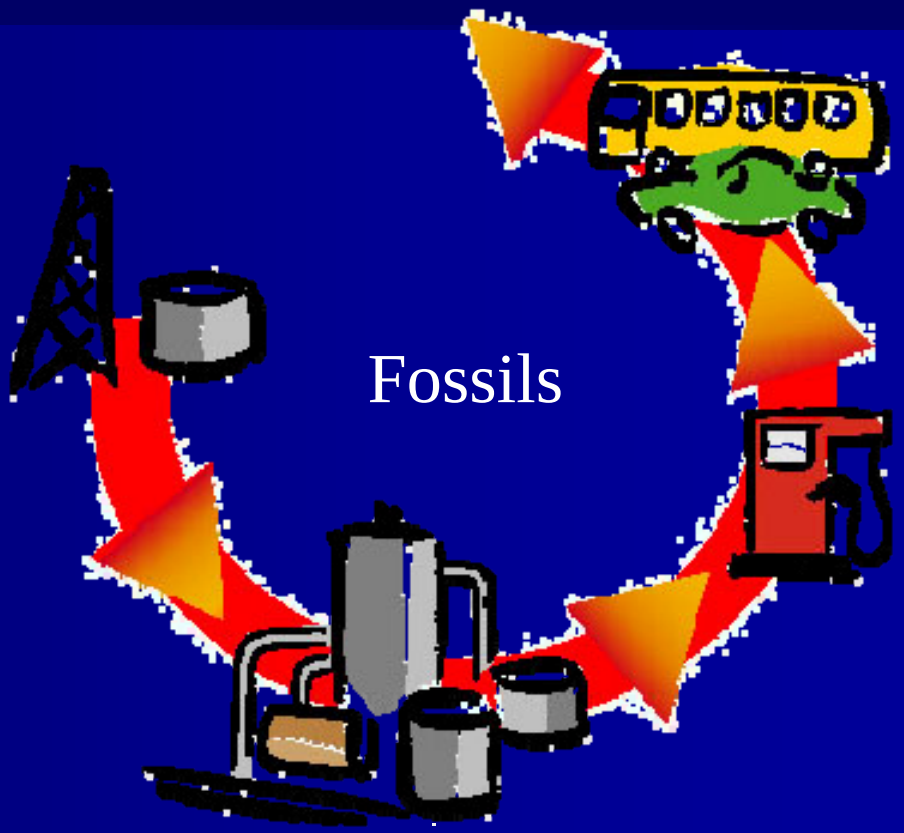
- Fossil fuels vs. Biofuels
- Current biodiesel analytical methods
- Developing a new analytical tool
  - Chemical approach
  - Phosphitylating agent
  - ^{31}P-NMR chemical shift library
- Process sample analysis
  - Method optimization
  - Rapid sample analysis

The Carbon-cycle



Biomass

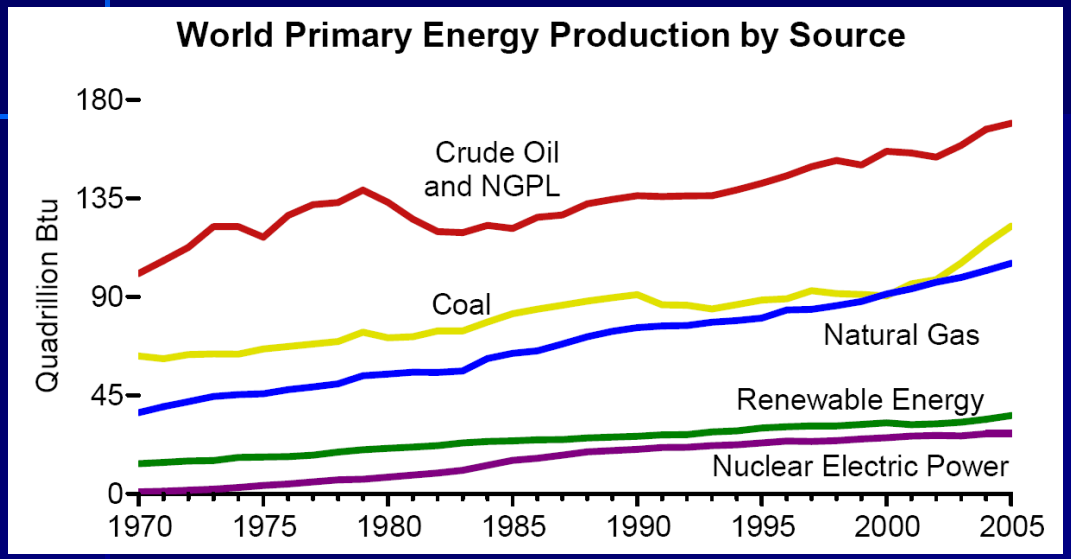
Closed cycle

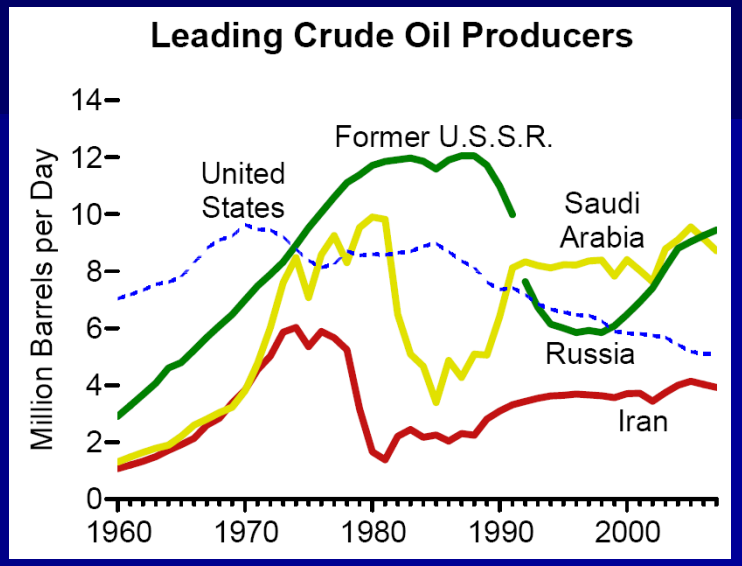


Fossils

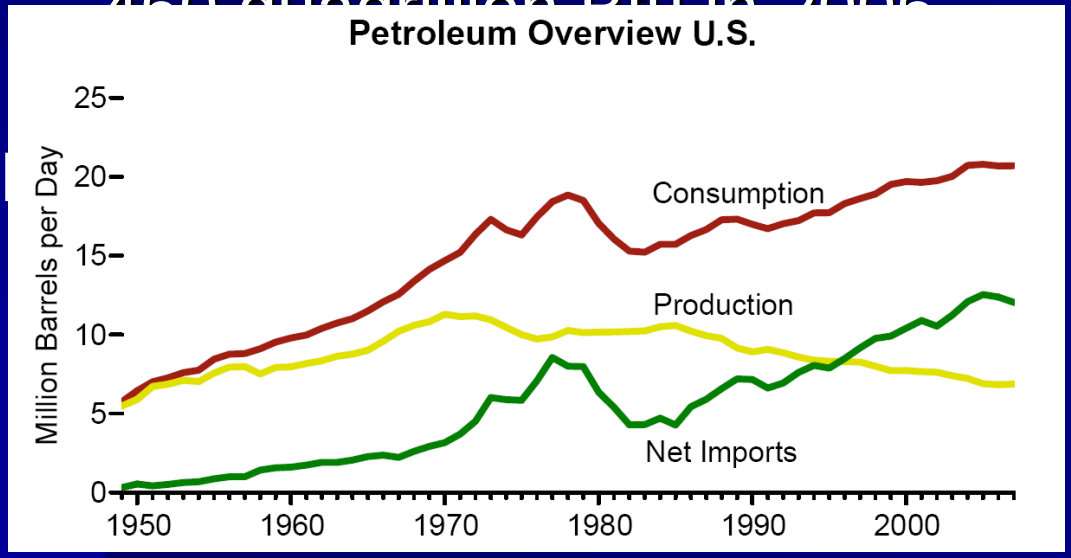
Broken cycle

International Energy Overview





460 quadrillion Btu in 2006



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

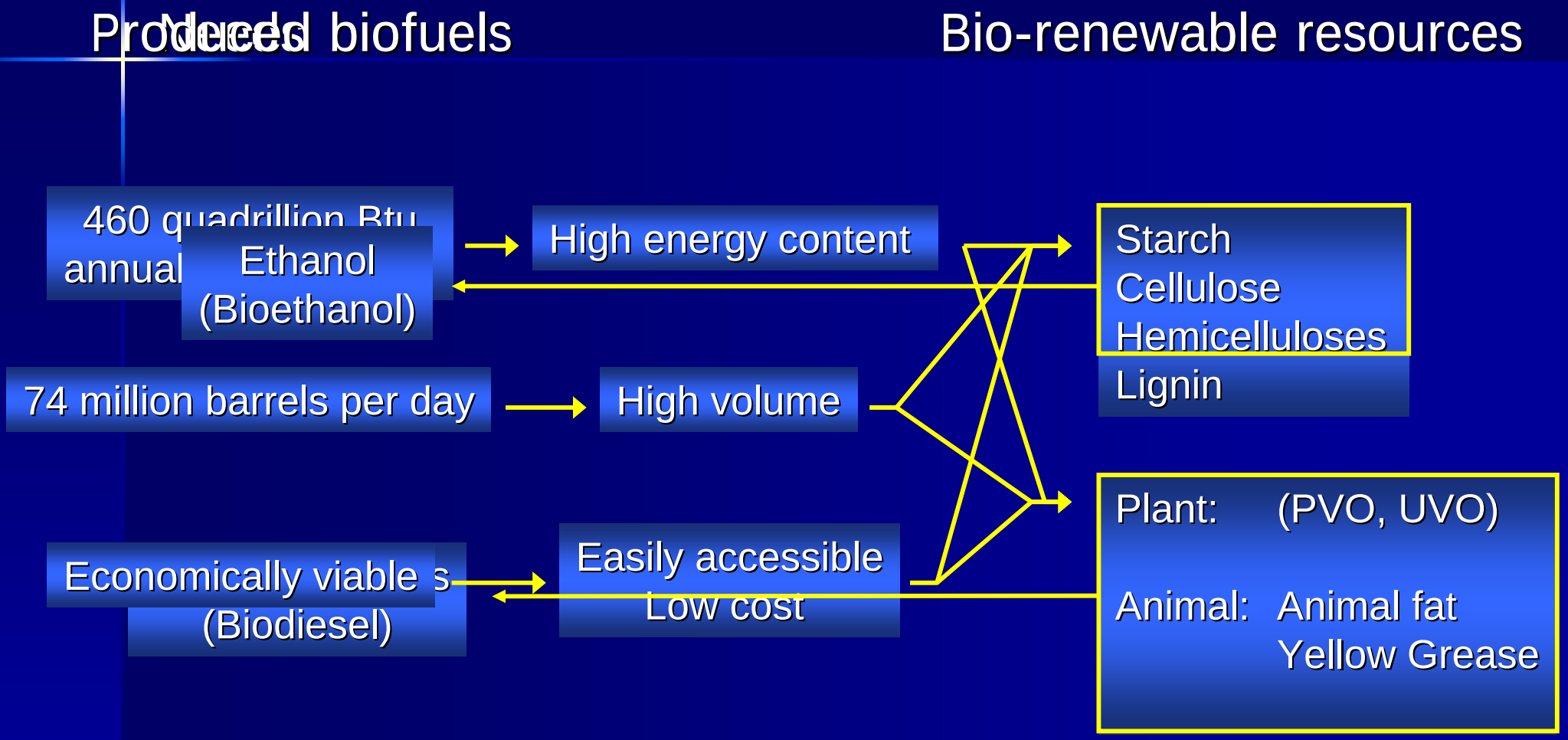
Need for Renewable Biofuels:

Energy security (Local)

Carbon neutral/climate change

Sustainability

Potential Biofuel Precursors



Potential Biofuel Precursors

Produced biofuels	Bio-renewable resources
Ethanol (Bioethanol)	Starch Cellulose Hemicelluloses Lignin
Alkali fatty esters (Biodiesel)	Plant: (PVO, UVO) Animal: Animal fat Yellow Grease

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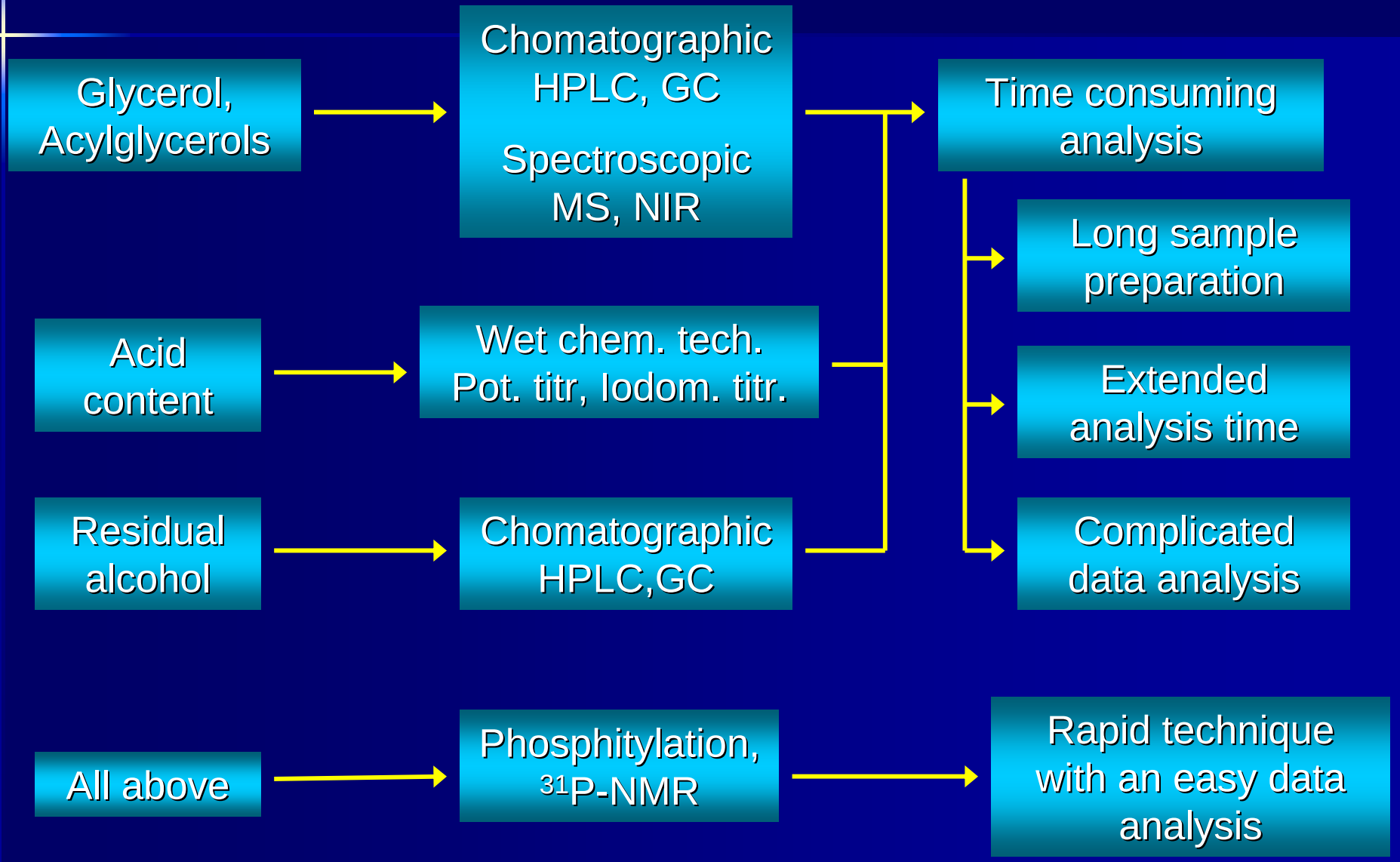
Current Biodiesel Analytical Methods



Gerpen J.V, et. al. Biodiesel analytical methods, (2004) NREL/SR-510-36240

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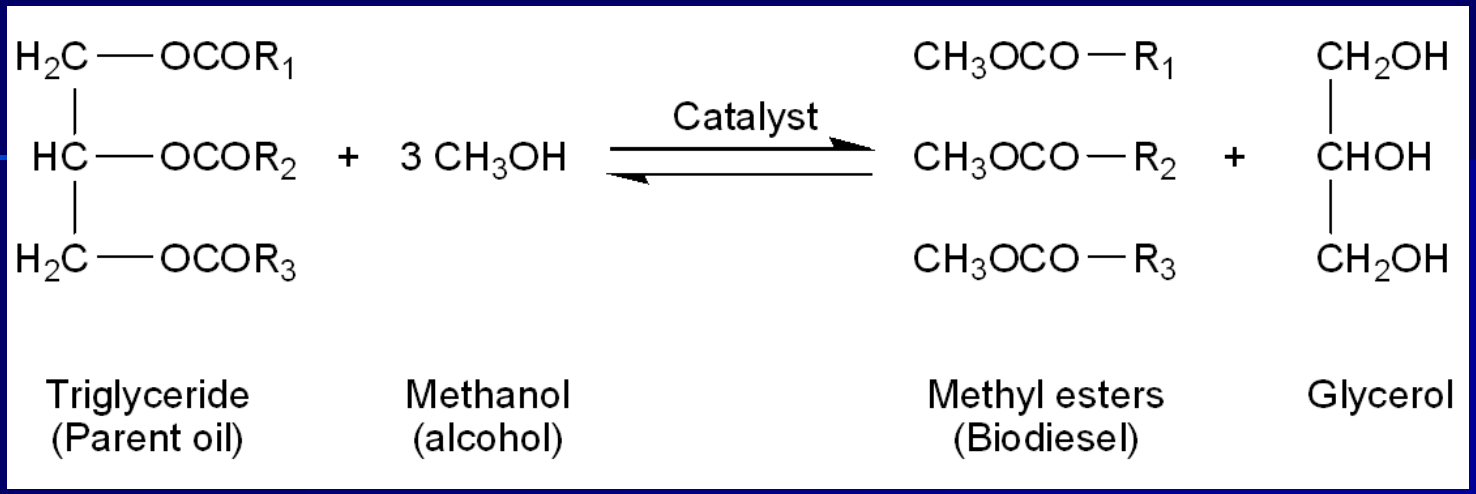
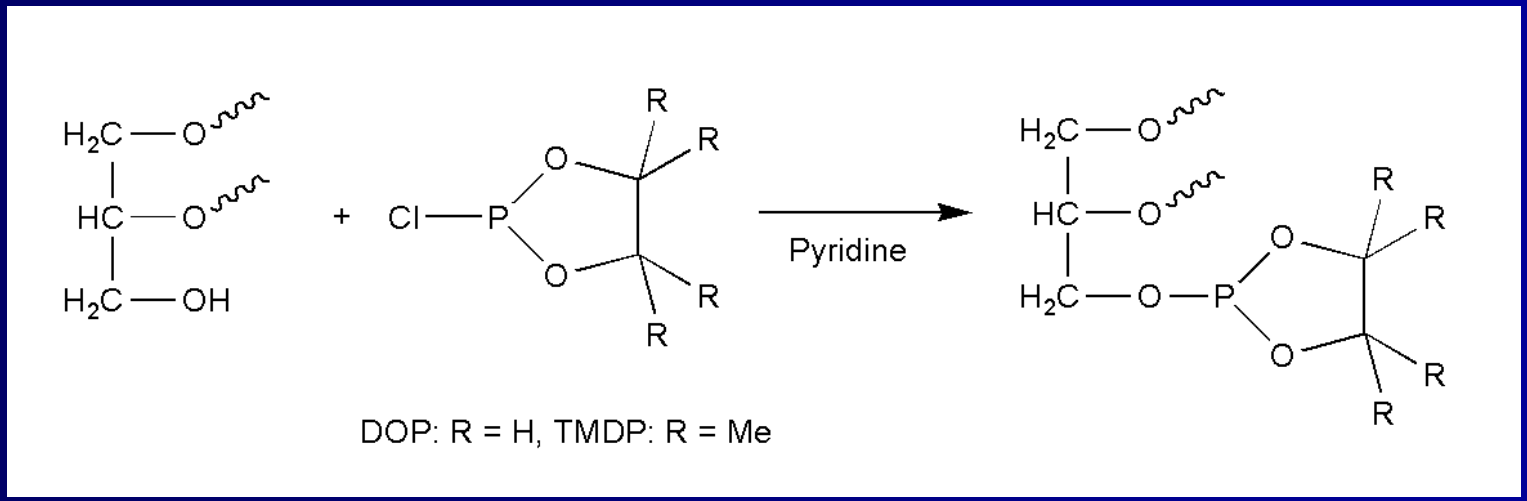
Chemical Approach



Transesterification reaction for biodiesel production, $R_{1\text{-}3}$ are hydrocarbon groups



Phosphitylation of partially substituted glycerols with DOP or with TMDP

Máté Nagy, et. al. Journal of Biobased Material and Bioenergy, (2009), 3(1), 1-4.

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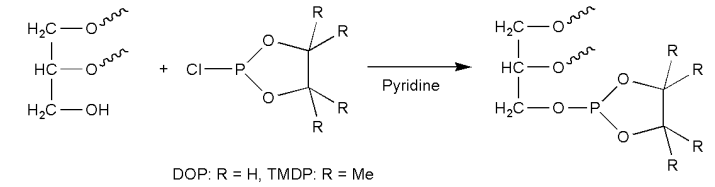
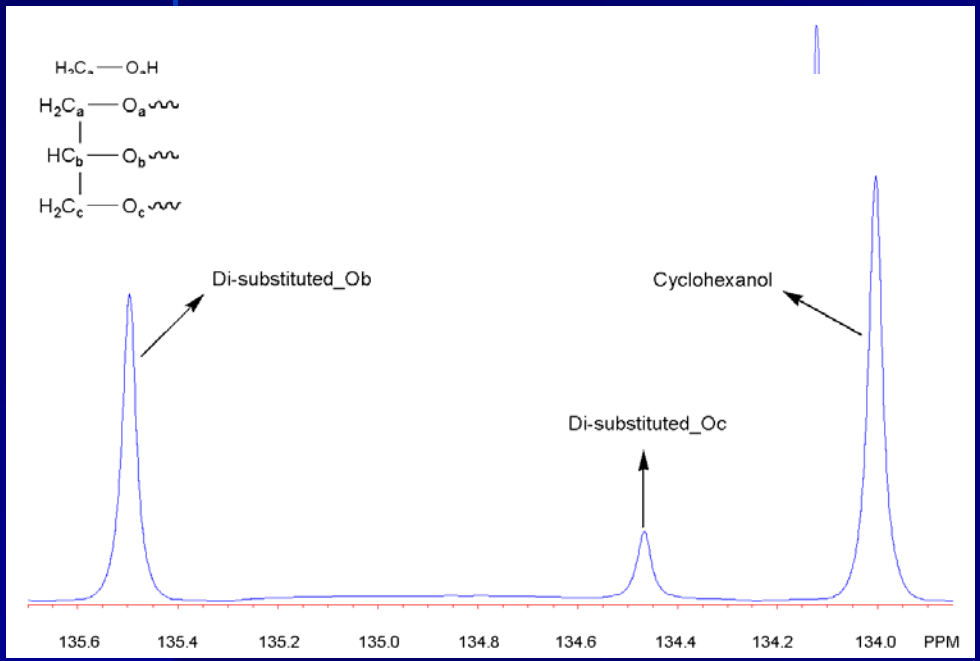
Phosphitylating Agent

DOP vs. TMDP

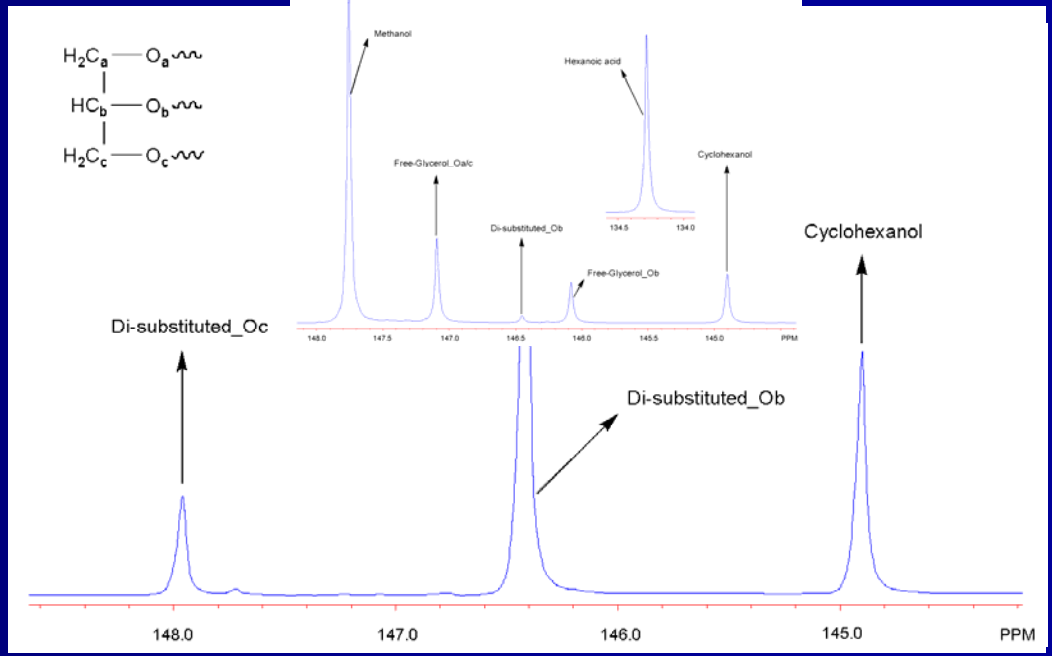


~85% 1,3-Dioleoylglycerol and ~15% 1,2-Dioleoylglycerol mixture

DOP



TMDP



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

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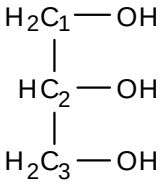
Biodiesel Analysis

^{31}P-NMR chemical shift library

	δ31P Signal (ppm)	Phosphityl. position
Biodiesel production by-products		
Free glycerol	147.1	O-a/c
	146.1	O-b
Methanol	147.8	
Ethanol	146.3	
Isopropanol	146.4	
Analysis by-products		
TMDP	174.7	
TMDP hydrolyzate	132.0	
Cyclohexanol (internal standard)	144.9	



	Glycerol derivatives					Fatty acid
	Mono-substituted		Di-substituted		Tri *	
Substituted position	1		1,2	1,3	1,2,3	
Phosphitylated hydroxyl	O-b	O-c	O-c	O-b	N/A	
Lipid chain						
Lauric	146.2	147.5	---	146.5	No signal	134.5
Myristic	146.2	147.5	---	146.4	No signal	134.5
Palmitic	146.2	147.6	147.9	146.4	No signal	134.4
Stearic	146.2	147.4	147.9	146.4	No signal	134.4
Oleic	146.1	147.4	147.7	146.4	No signal	134.4
Linoleic	146.2	147.4	147.7	146.4	No signal	134.3
Linolenic R—OH	---	---	---	---	---	134.3
δ31P Signal (ppm)	**146.1-146.2**	**147.4-147.6**	**147.7-147.9**	**146.4-146.5**	**No signal**	**134.3-134.5**

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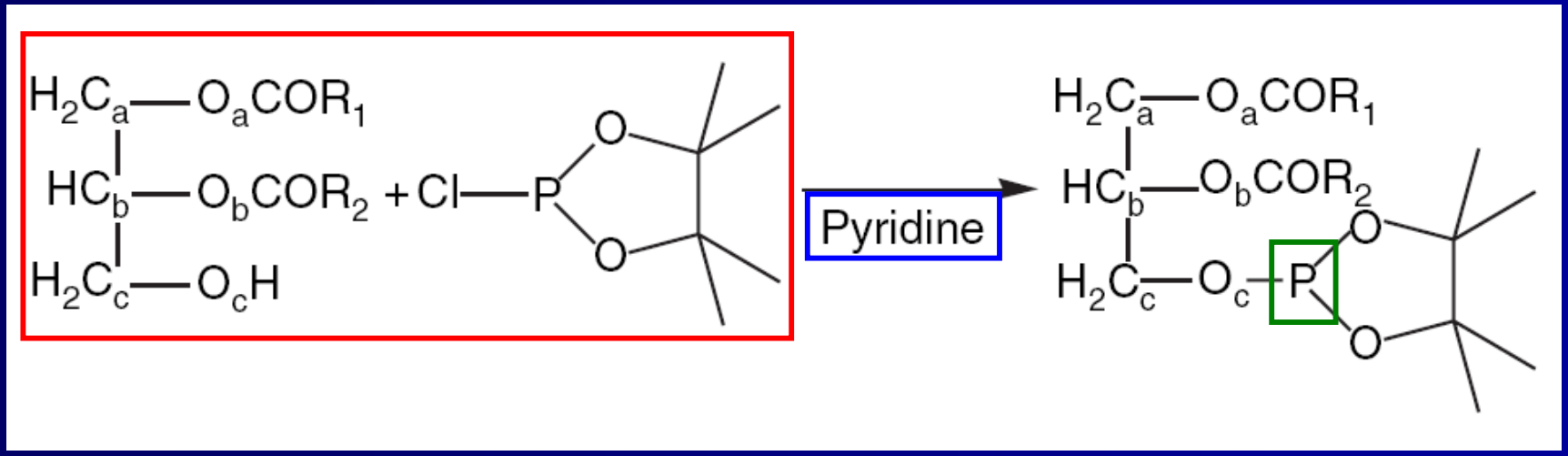
TMDP/^{31}P-NMR Method Optimization

Solvent system for biodiesel constituents



Phosphitylation of 1,2-diacylglycerol with 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane at c-position. $R_{1\text{-}2}$ are hydrocarbon groups

Solvent mixture

The process sample and the reagent mixture has to be in solution

Máté Nagy, et. al. Journal of Biobased Material and Bioenergy, (2009), 3(1), 1-4.

TMDP/^{31}P-NMR Method Optimization

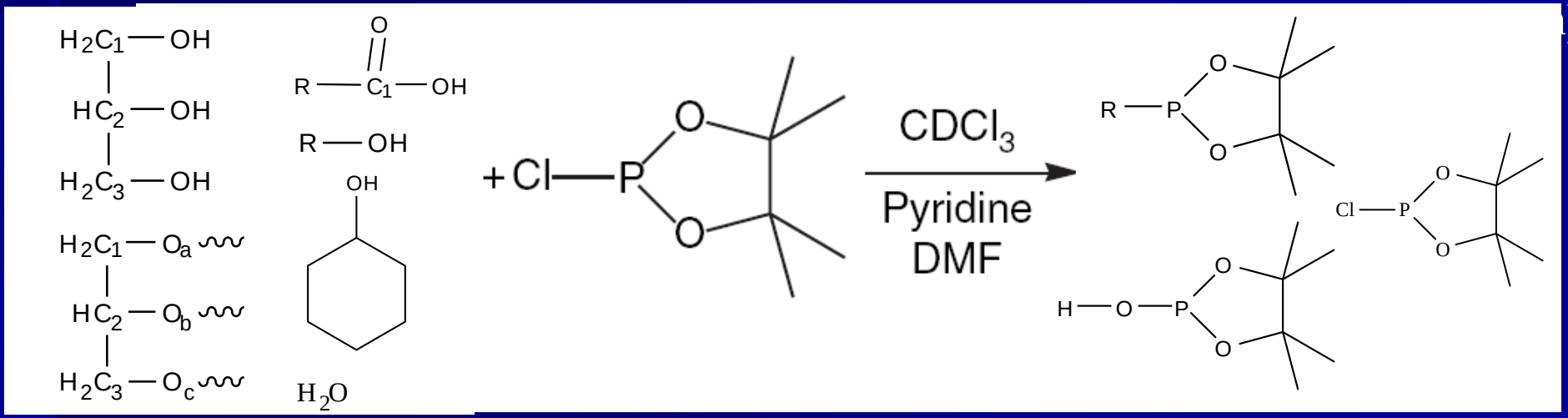
Spin-lattice relaxation time of biodiesel precursors

Rapid analytical method → Reduce analysis time to a minimum

^{31}P spin-lattice relaxation time measurement

Anhydrous pyridine/$CDCL_3$/DMF in 1:1.2:1 ratio

Chromium acetylacetonate (Cr(acac)3) as a relaxation agent (~3.60 mg/mL)
400 MHz, 25 °C, magnetic field of 9.4 T,



Máté Nagy, et. al. Fuel (2009), 88, 1793-1797.

Máté Nagy, et. al. J. Phys. Chem. A, (2009), doi: 10.1021/jp906543g

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
~3.60 mg/mL of Cr(acac)3 (*relaxation agent*)
~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 → Mix
TMDP (100 μL)

Sample preparation	→	**Under 5 min**
Analysis time	→	**56 sec**
Data analysis	→	**~30 minutes**

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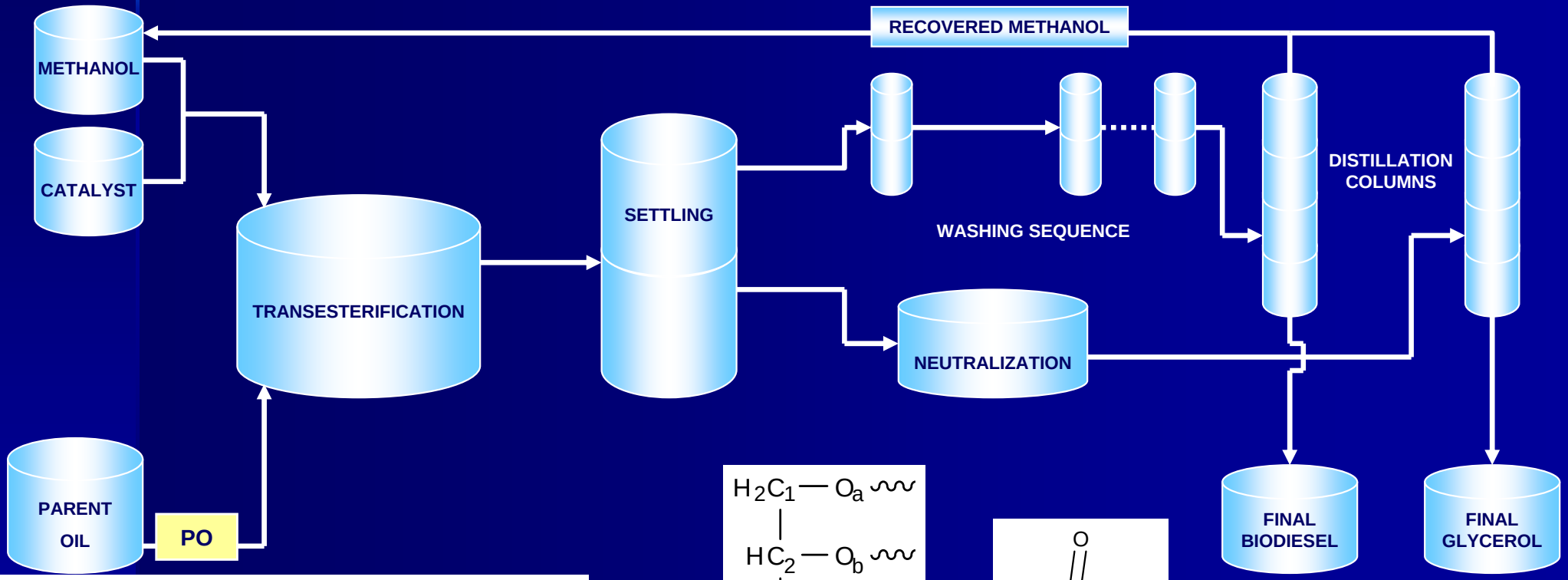
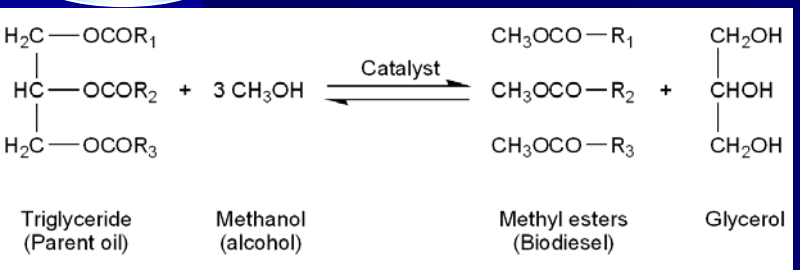
Biodiesel Analysis

Process outline and sampling



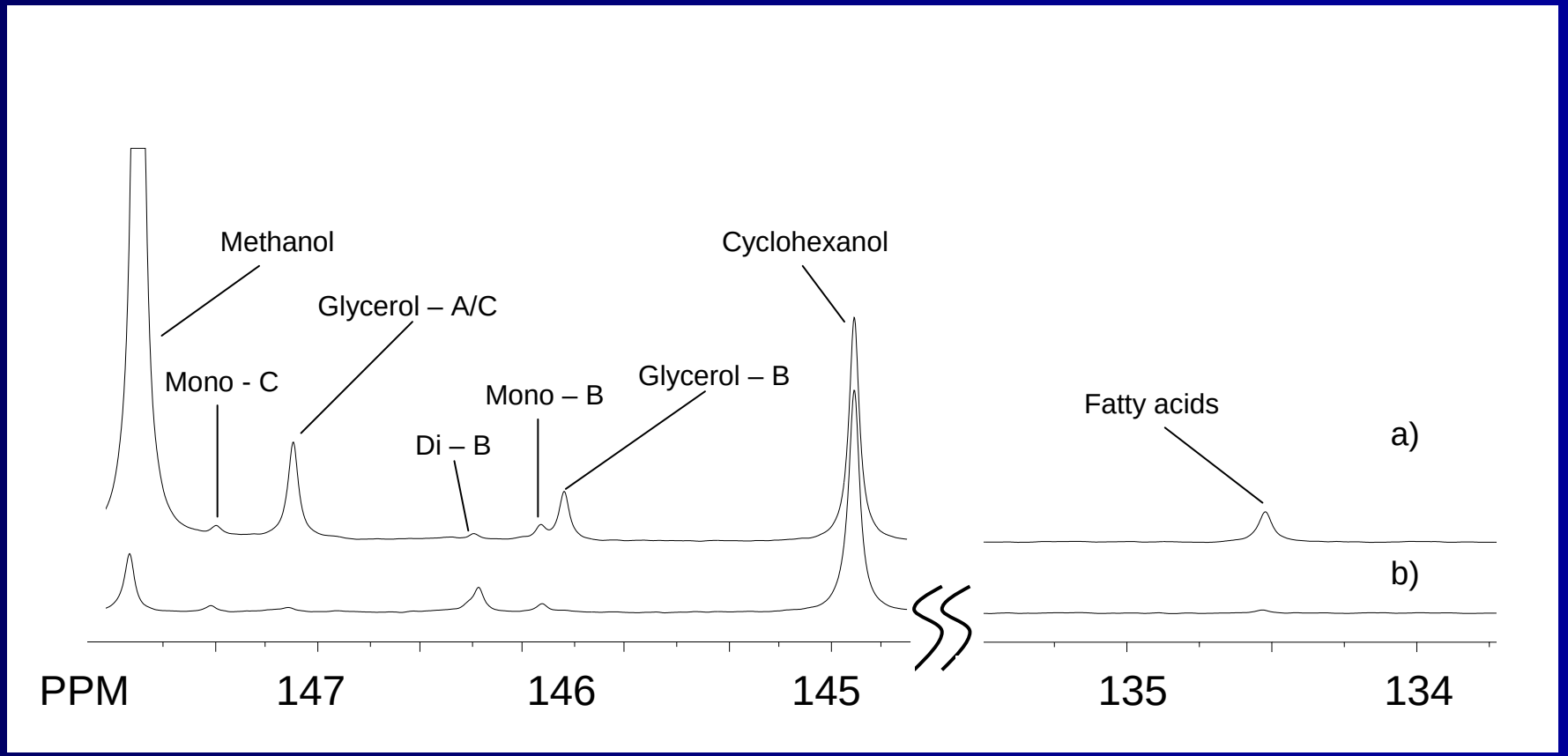


R — OH

Máté Nagy, et. al. J. Phys. Chem. A, (2009), doi: 10.1021/jp906543g

Biodiesel Analysis

The parent oil



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

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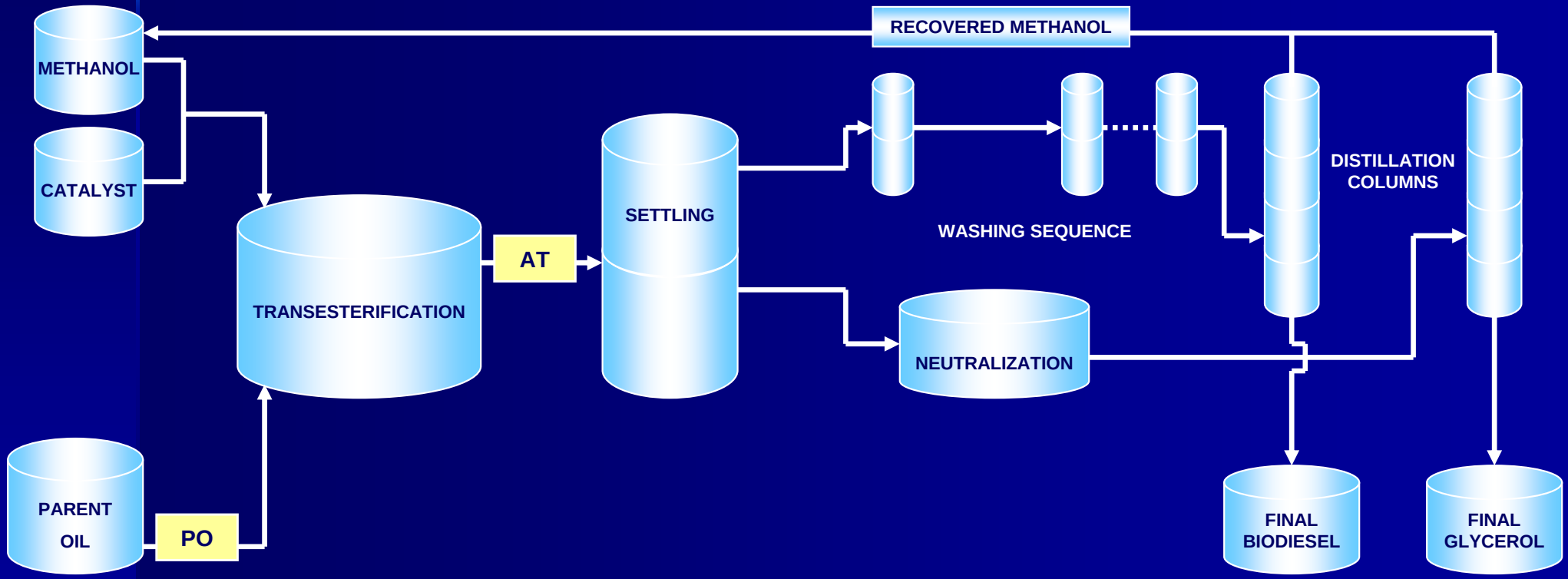
Biodiesel Analysis

Process outline and sampling



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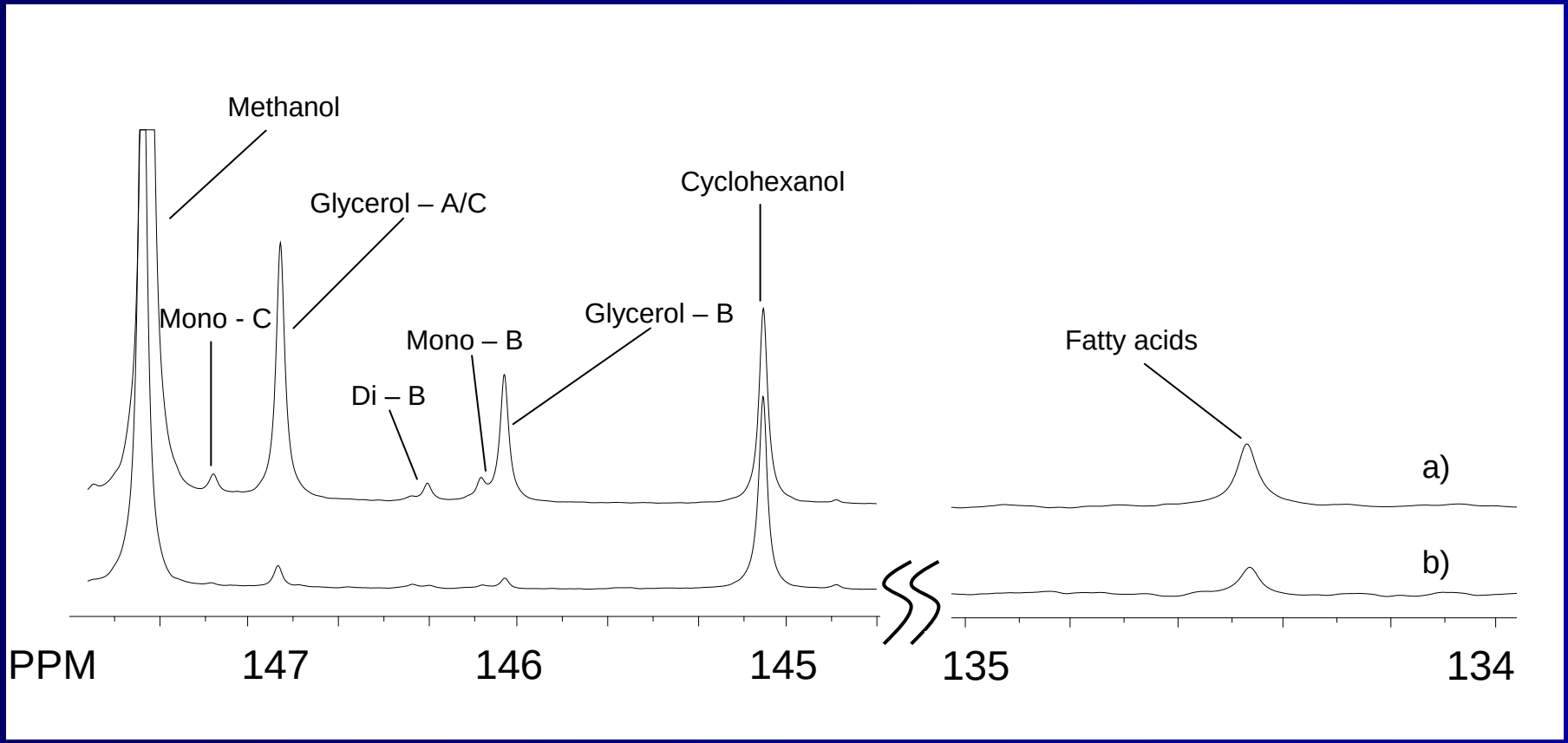
Biodiesel Analysis

The transesterification step

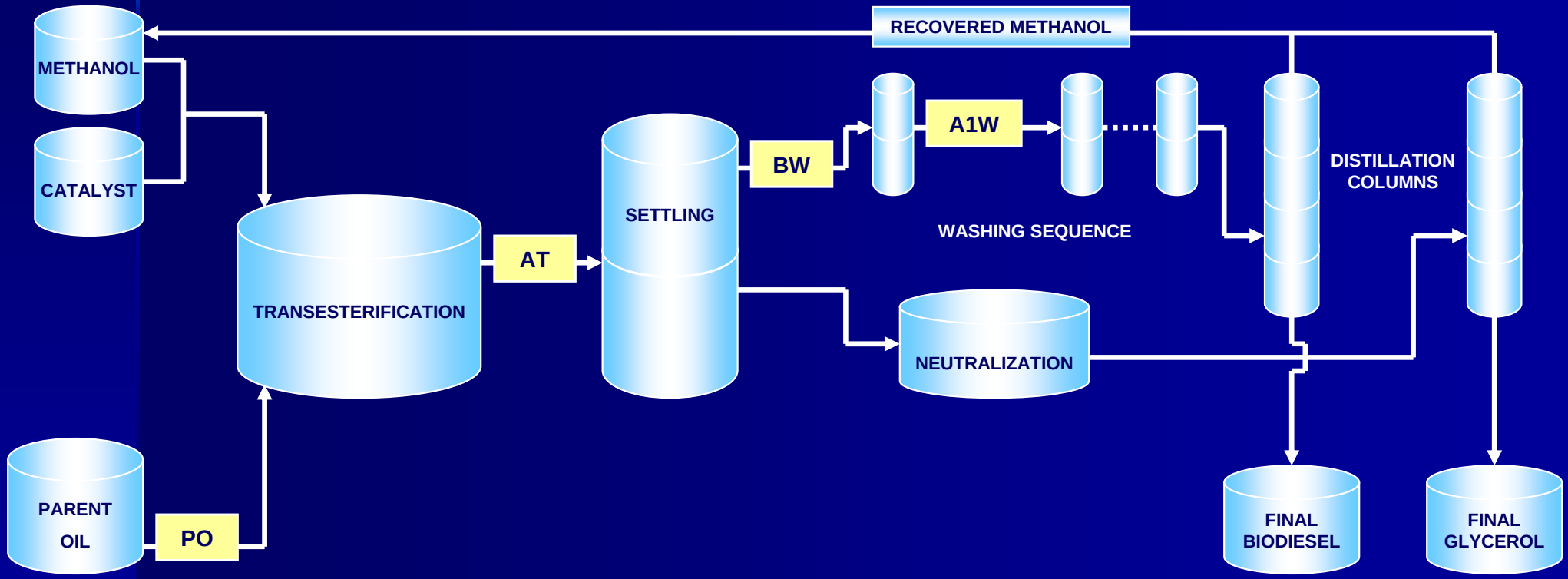


Quantitative 31P-NMR spectra of samples taken after the transesterification step utilizing different process conditions using soybean oil as feedstock

Máté Nagy, et. al. J. Phys. Chem. A, (2009), doi: 10.1021/jp906543g

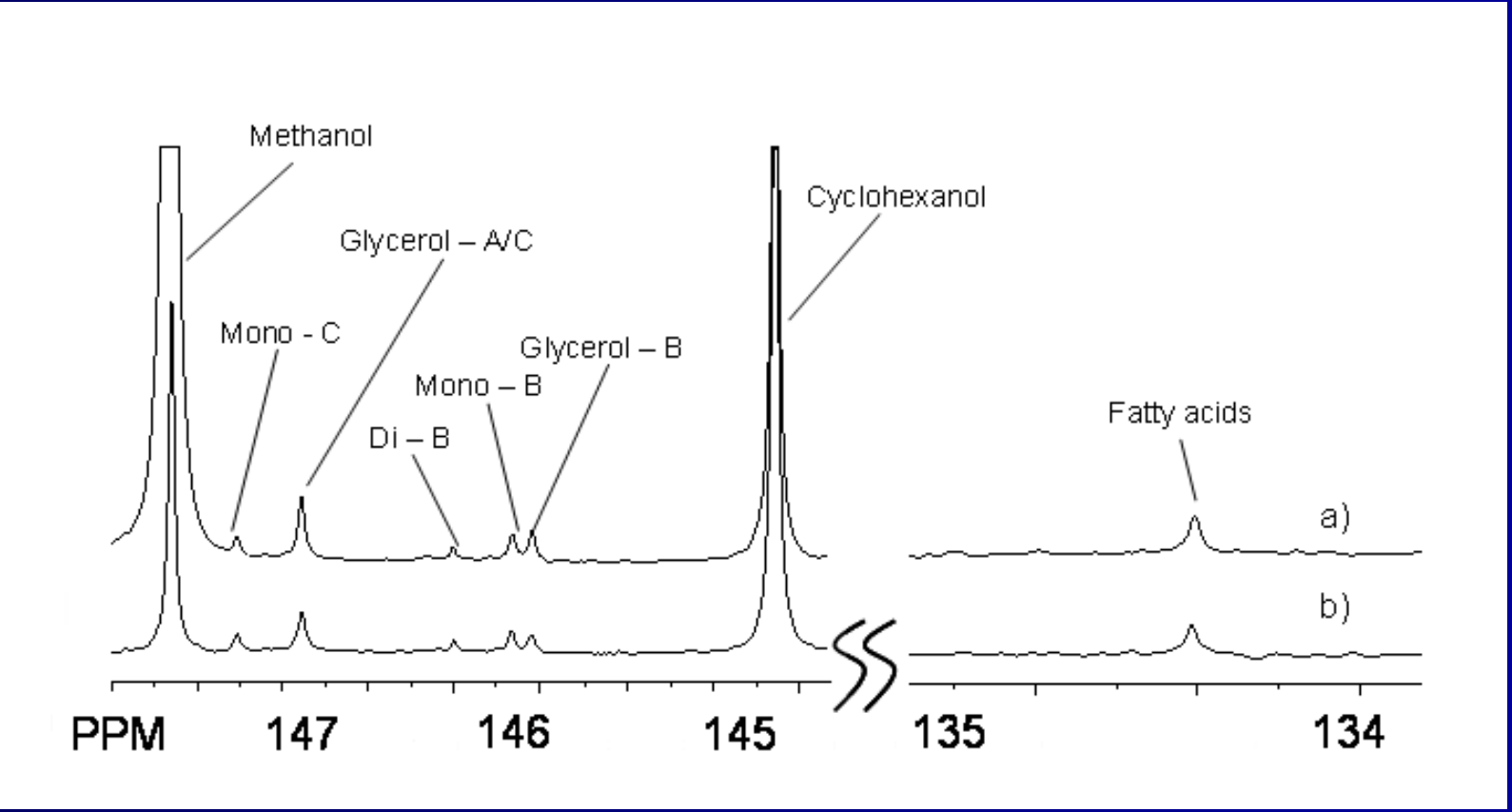
Biodiesel Analysis

Process outline and sampling



Máté Nagy, et. al. J. Phys. Chem. A, (2009), doi: 10.1021/jp906543g

Biodiesel Analysis
The washing phase

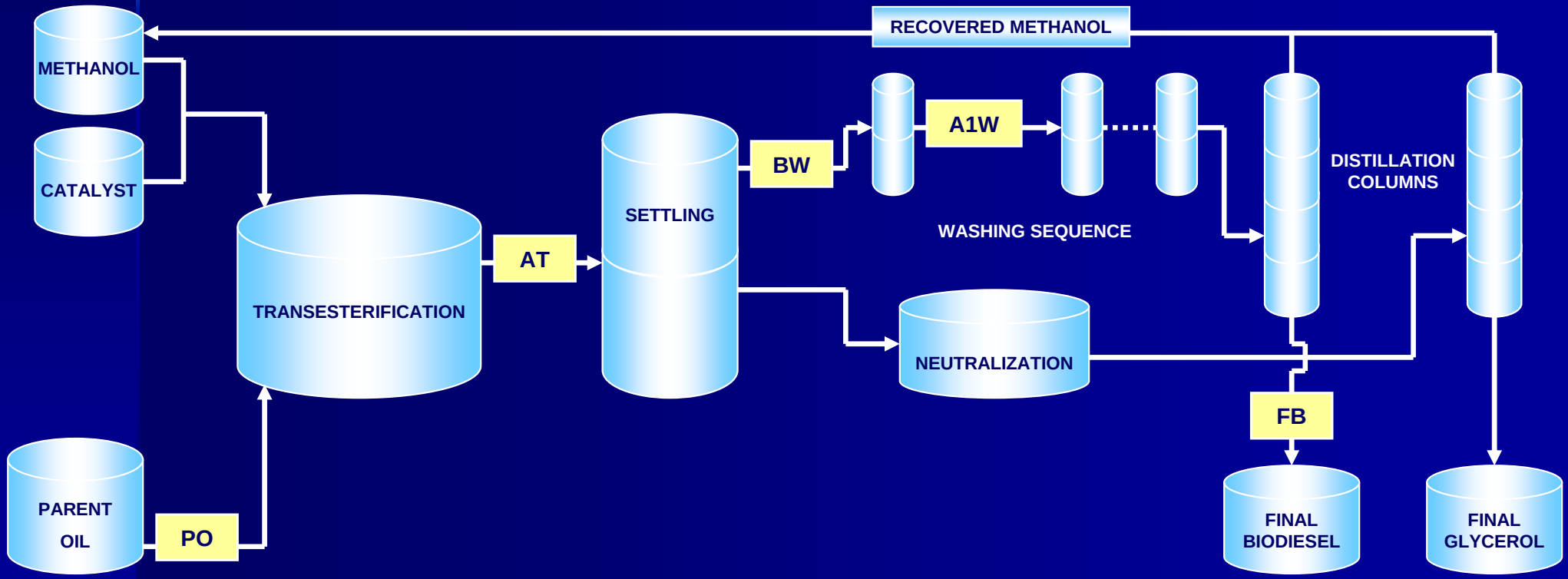


Quantitative 31P-NMR spectra showing the washing efficiency of a soybean oil based commercial process on samples taken before wash (a) and after the first washing cycle (b)

Máté Nagy, et. al. J. Phys. Chem. A, (2009), doi: 10.1021/jp906543g

Biodiesel Analysis

Process outline and sampling



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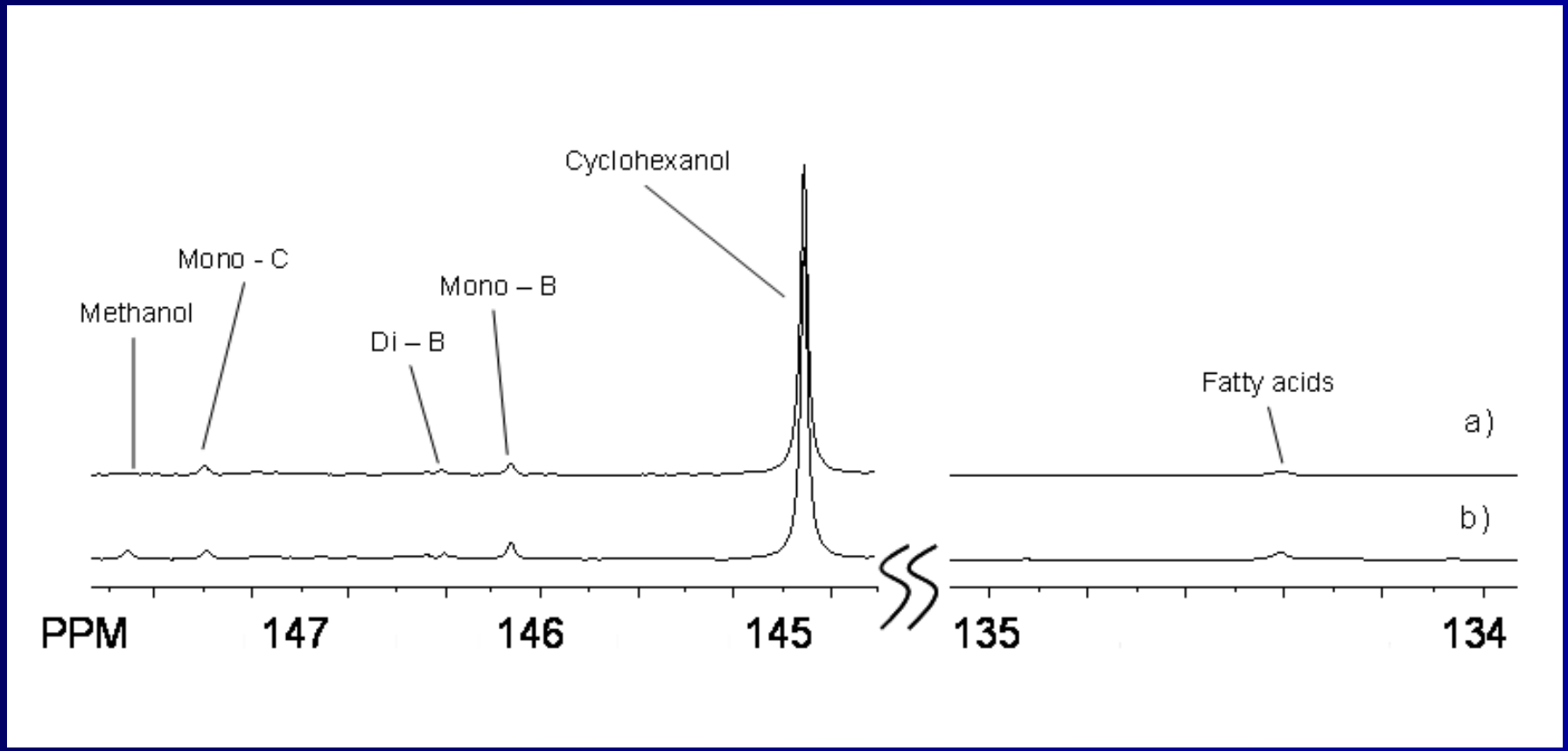
Biodiesel Analysis

The final biodiesel



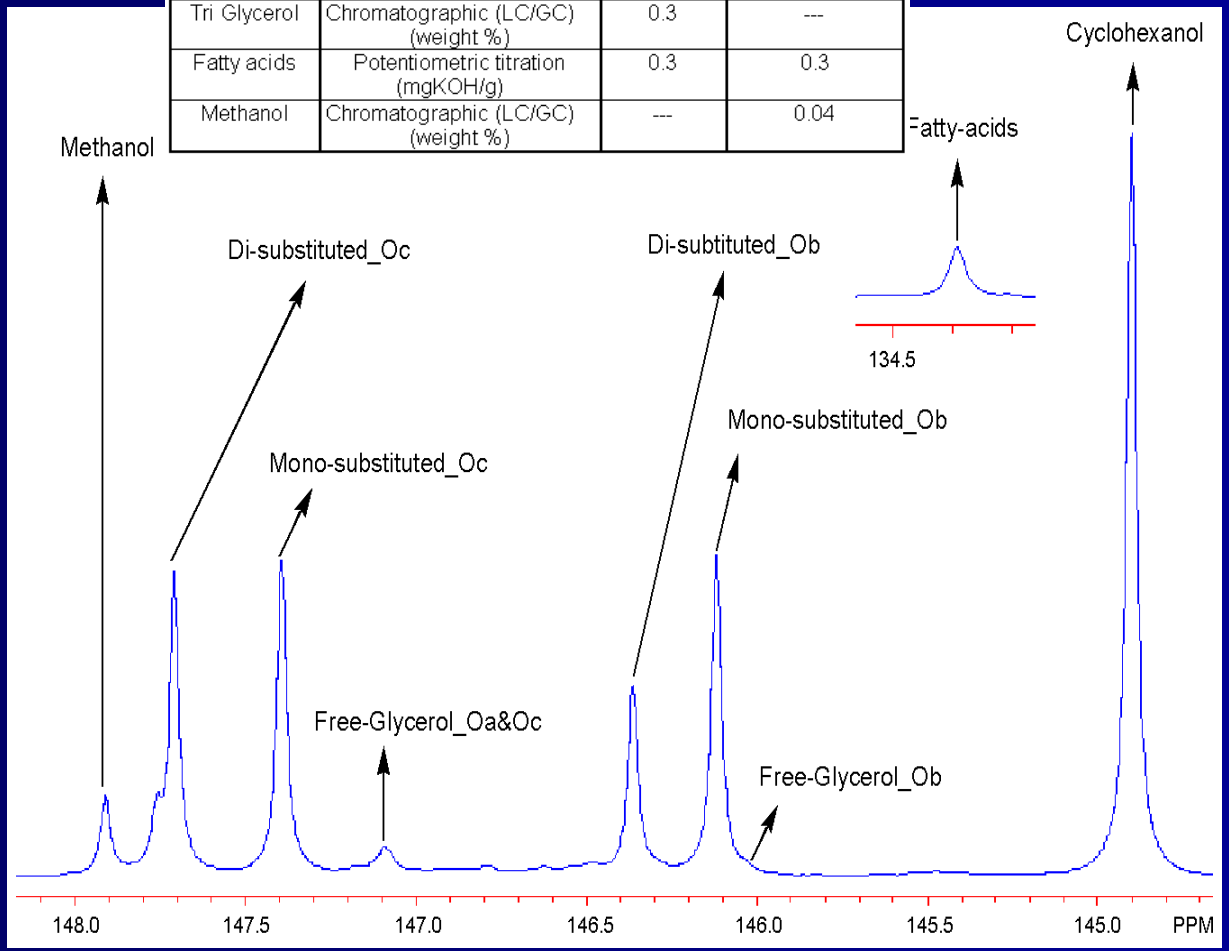
Quantitative 31P-NMR spectra of final biodiesel samples of soybean oil (a) and waste vegetable oil (b)

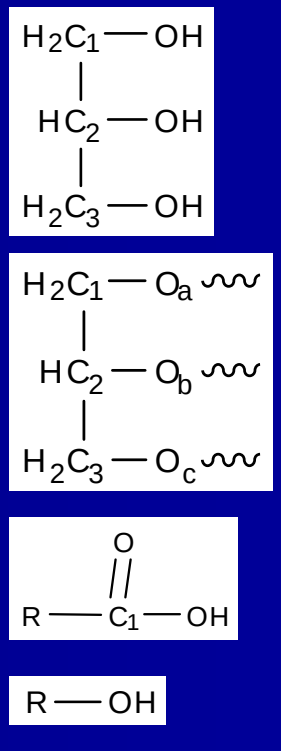
Máté Nagy, et. al. J. Phys. Chem. A, (2009), doi: 10.1021/jp906543g

Biodiesel Analysis

Quantitative analysis on final biodiesel sample

Component	Conventional technique used	Data Measured	Phosphitylation with ^{31}P-NMR
Free Glycerol	Chromatographic (LC/GC) (weight %)	0.01	0.03
Mono Glycerol	Chromatographic (LC/GC) (weight %)	1.4	1.8
Di Glycerol	Chromatographic (LC/GC) (weight %)	1.7	1.9
Tri Glycerol	Chromatographic (LC/GC) (weight %)	0.3	---
Fatty acids	Potentiometric titration (mgKOH/g)	0.3	0.3
Methanol	Chromatographic (LC/GC) (weight %)	---	0.04

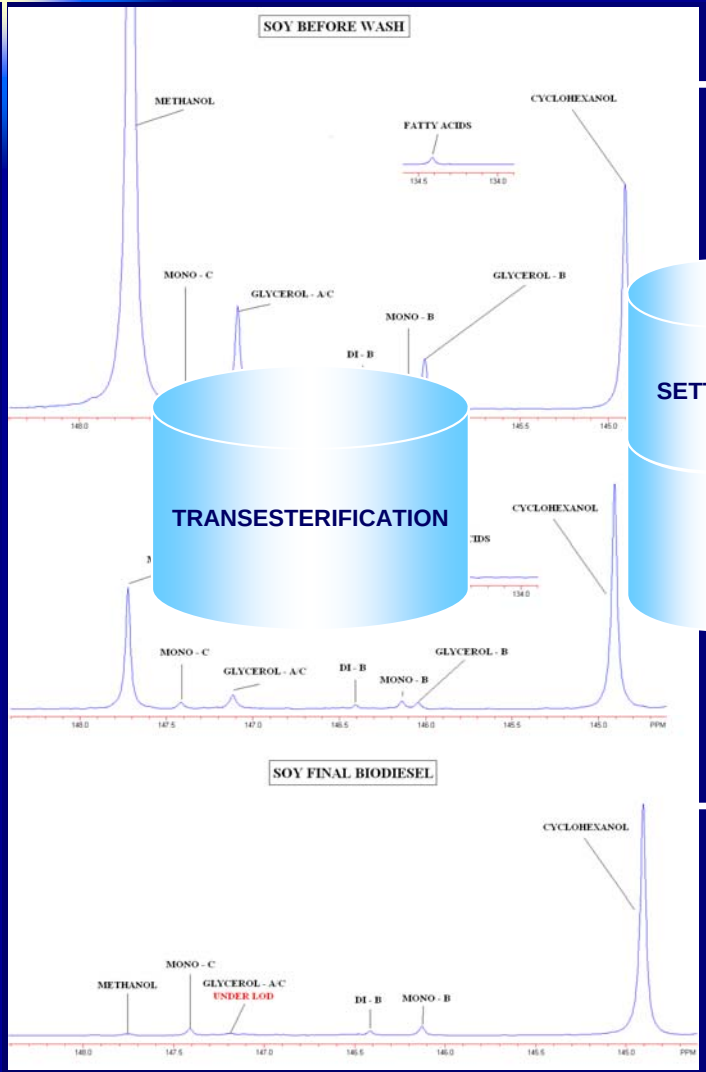


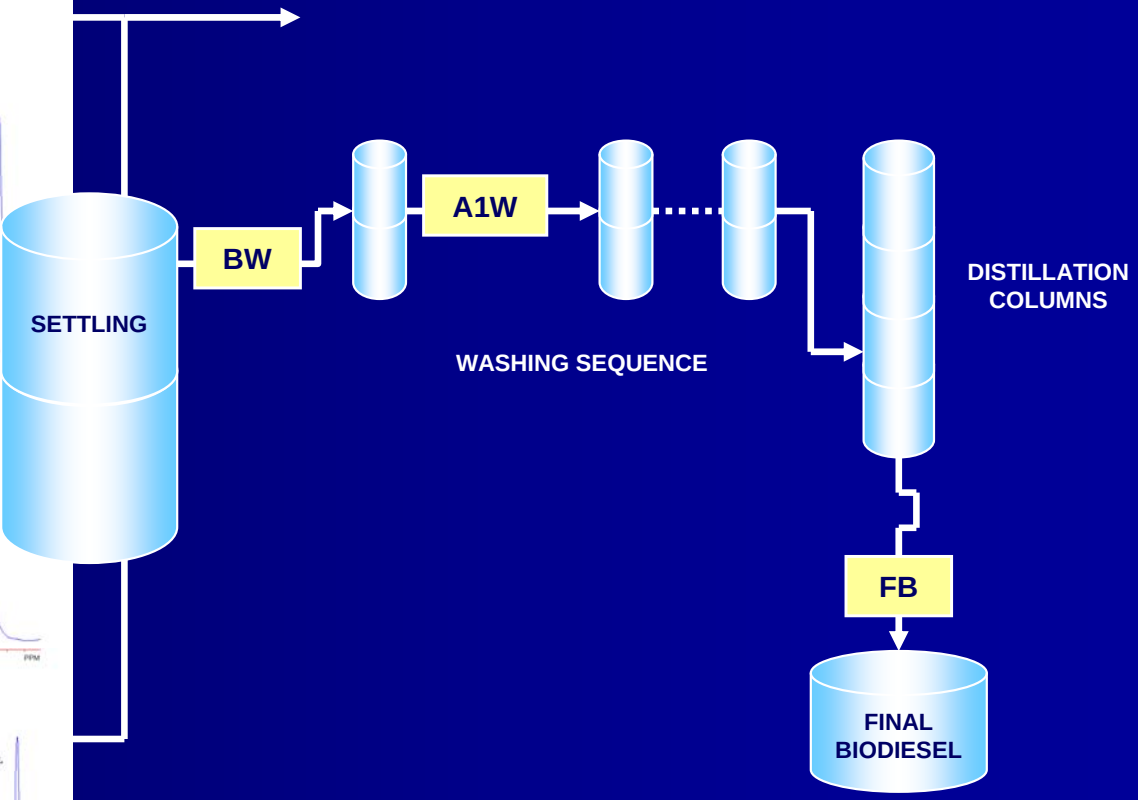


Quantitative ^{31}P-NMR spectra of biodiesel samples from commercial biodiesel operations based on soy oil

Biodiesel Analysis

Monitoring the biodiesel process stream





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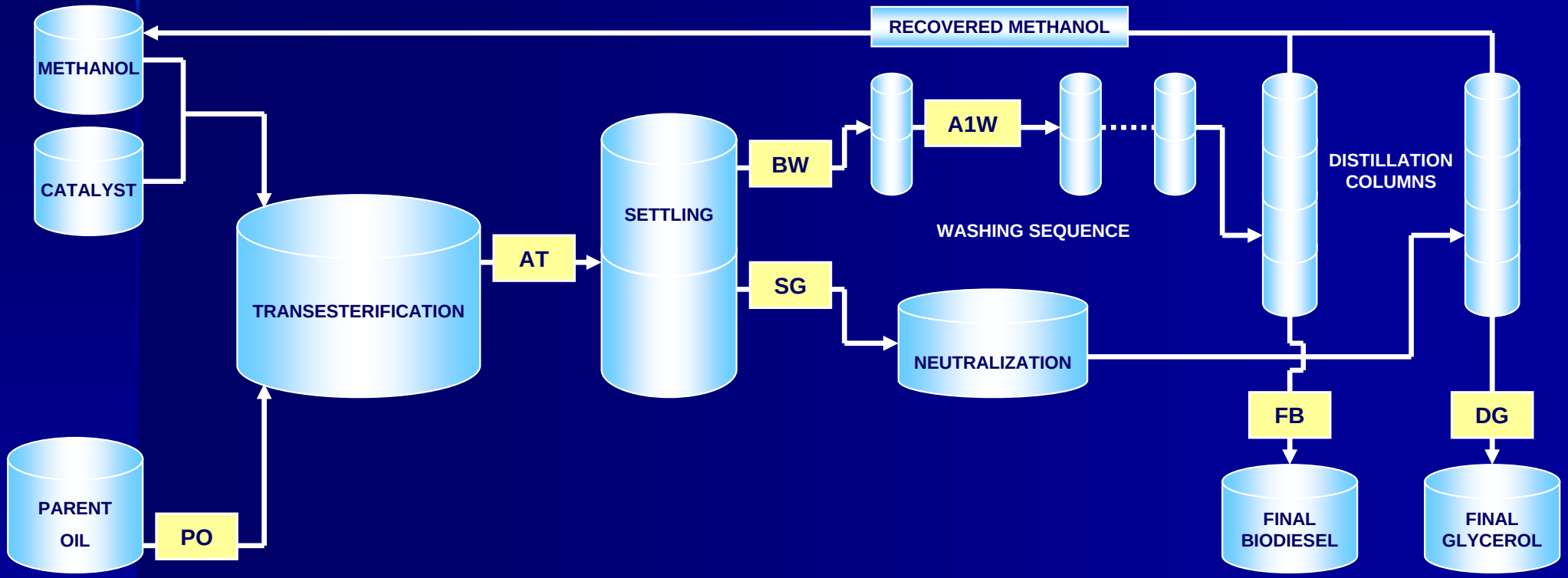
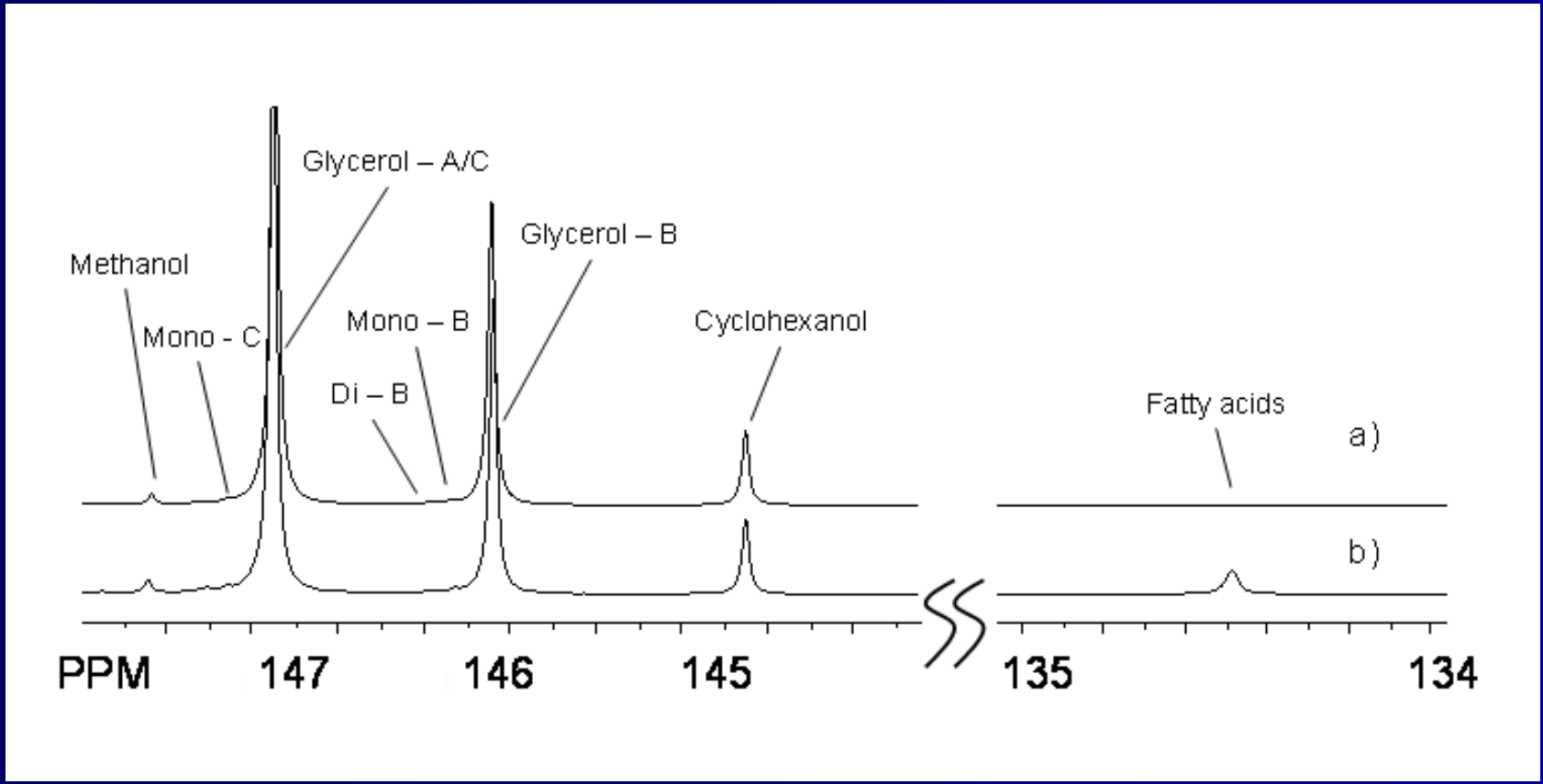
Biodiesel Analysis

Process outline and sampling



Biodiesel Analysis

The glycerol process stream



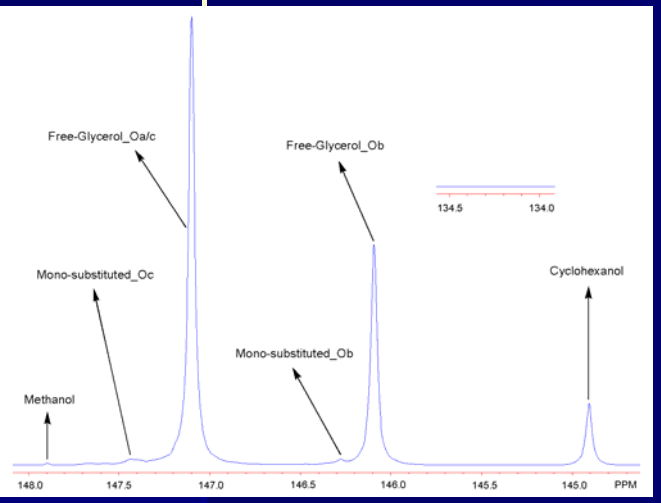
Quantitative 31P-NMR spectra on glycerol samples from soybean oil based commercial process of the separated glycerol before neutralization (a) and of the final demethylated glycerol (b)

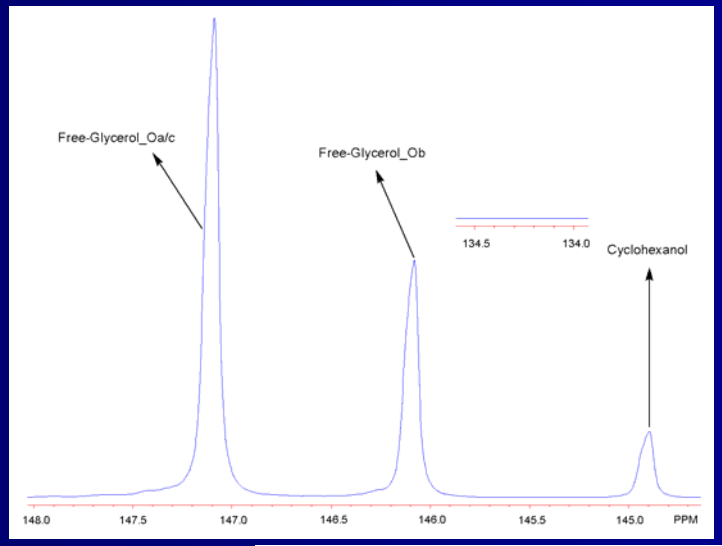
Máté Nagy, et. al. Fuel (2009), doi:10.1016/j.fuel.2009.01.020

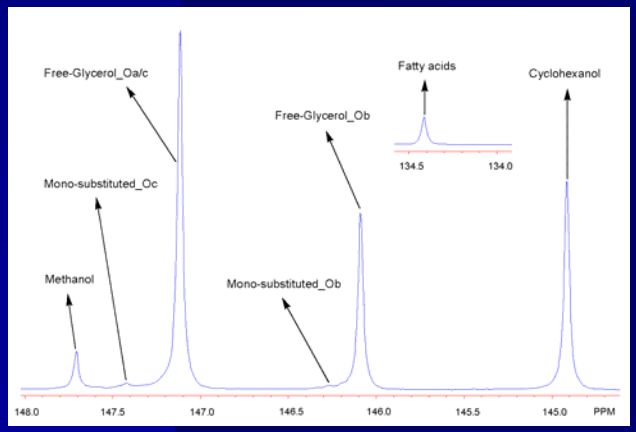
Biodiesel Analysis

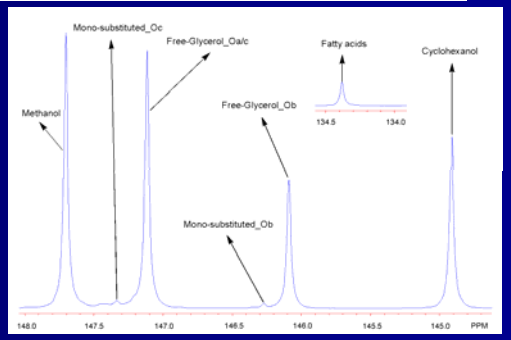
Quantitative analysis on final glycerol samples

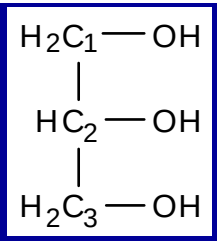
Component	Technique used	
	Conventional (weight %)	TMDP / ^{31}P-NMR (weight %)
Free glycerol	---	75.9
Mono substituted glycerol	---	7.7
Total glycerol	81.9	83.6
Fatty acids	0.0	0.0
Methanol	0.1	0.1

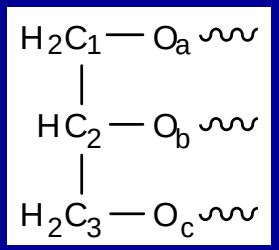


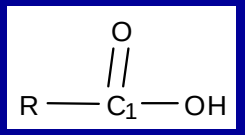


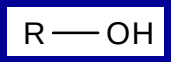








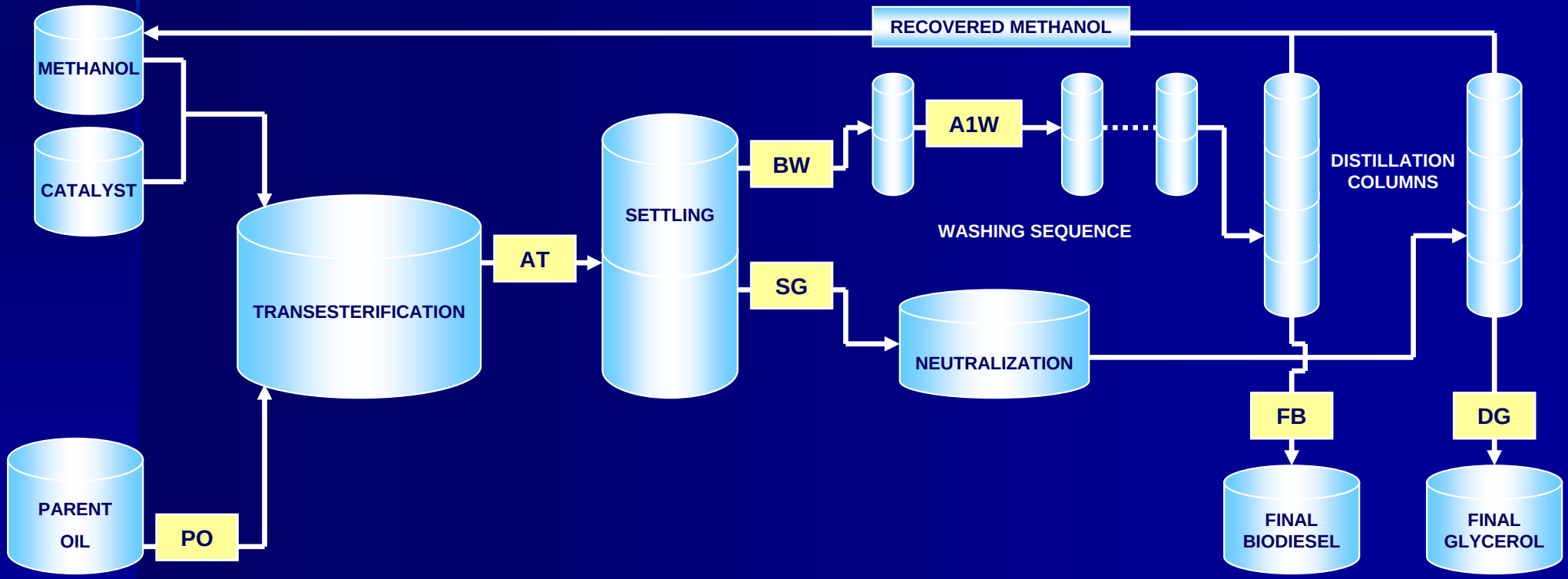




Quantitative ^{31}P-NMR spectra of glycerol samples from commercial biodiesel operations based on soy oil, poultry fat & tallow

Biodiesel Analysis

Process outline and sampling



Máté Nagy, et. al. J. Phys. Chem. A, (2009), doi: 10.1021/jp906543g

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 µmol/mL LOD, ±1.1% error margin)*
- **Additional benefits**
  - *Independent from feedstock*
  - *Direct measurement for the intermediate products through the whole production line → Process step optimization*
  - *Direct measurements for contamination in the final products → Quality control*

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Thank You!

Máté Nagy

E-mail: Mate.Nagy@ipst.gatech.edu Phone: (678)-549-6316