The Analysis of Biodiesels Using Supercritical Fluid Chromatography

Nathan L. Porter, Brian A. Jones, Jody Clark

Selerity Technologies USA, Inc.,
2484 W. Custer Road
Salt Lake City, UT 84104

What is Biodiesel?

- Bio-based diesel fuel is produced by a chemical reaction between methanol (or ethanol) and an oil or fat.

- 100 lb Vegetable oil + 10 lb methanol

  ➔ 100 lb biodiesel + 10 lb glycerin

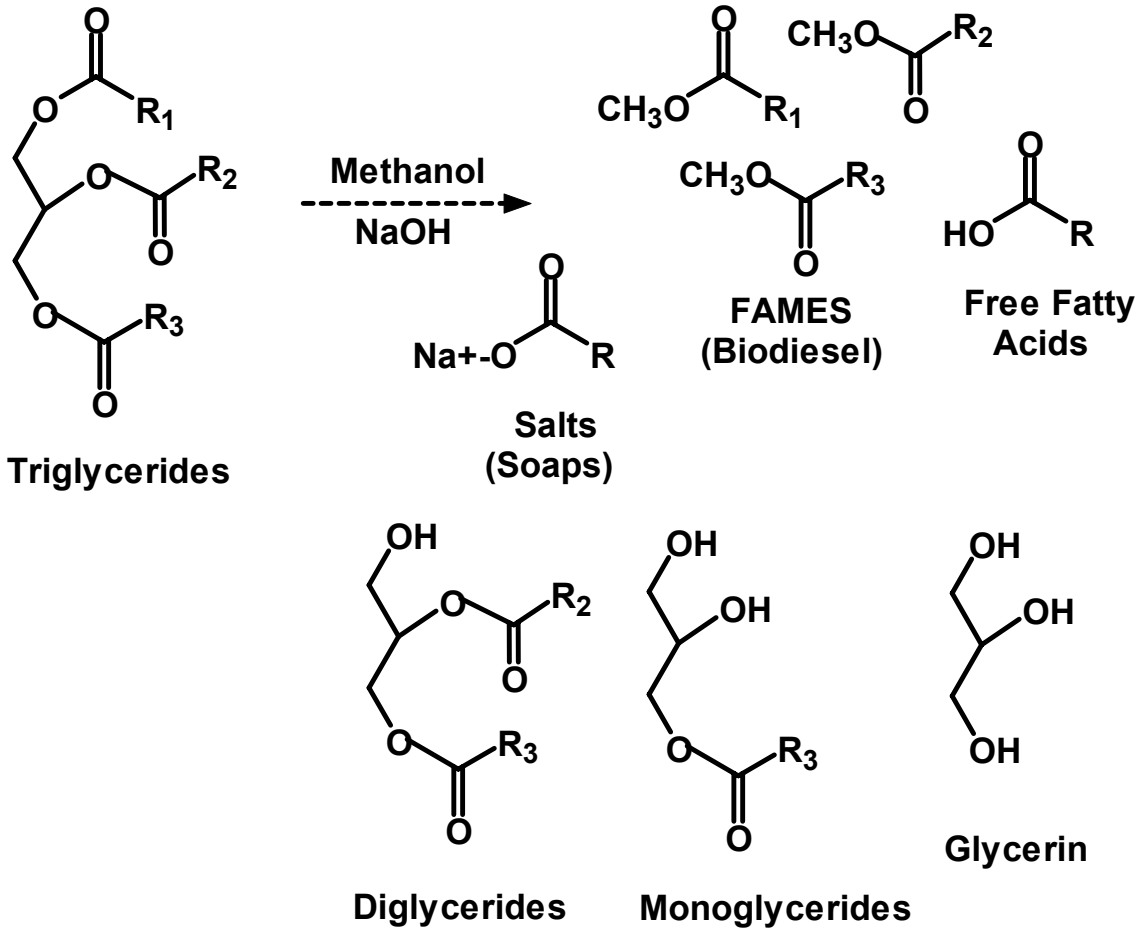
Applications of Biodiesel

- As a neat fuel (B100).
- As a medium-level blend (B5-B50). Blends can be used to meet Energy Policy Act mandates (B20 essentially = 1/5 vehicle).
- As a low-level blend (1% - 2%). Small amounts of biodiesel can restore lubricity to low-sulfur fuels.

Advantages and Disadvantages of Biodiesel

- Advantages
  - Biodegradable, nontoxic, renewable
  - Lower emissions, climate change neutral
- Disadvantages
  - Biodiesel has 8% less energy per gallon than petroleum diesel. Power and miles per gallon will be negatively affected.
  - Biodiesel is less stable than petroleum diesel fuel.

Transesterification Reaction



Why Use SFC?

- SFC has been used for years for petroleum class type separations (ASTM 5186 and 6550)
  - Method D5186 is a method for determining non-aromatics, monoaromatics and polyaromatics in diesel, kerosene, and jet fuel. It is mandated by CARB (California Air Resources Board), and State of Texas
  - Method D6550 is a method for determining olefin content in gasoline. It is also mandated by CARB.

Why Use SFC?

- Ideal mobile phase (CO_2)
  - Readily available, non toxic (green), Inert
  - CO_2 acts like a normal phase solvent
    - Makes using silica columns ideal for separating compounds of different polarity
  - CO_2 solvent properties are tunable
    - Varying the density/solvent strength allows flexibility in refining methods

Why Use SFC?

- Universal mass based detection
  - Using the FID eliminates the need for external calibration.

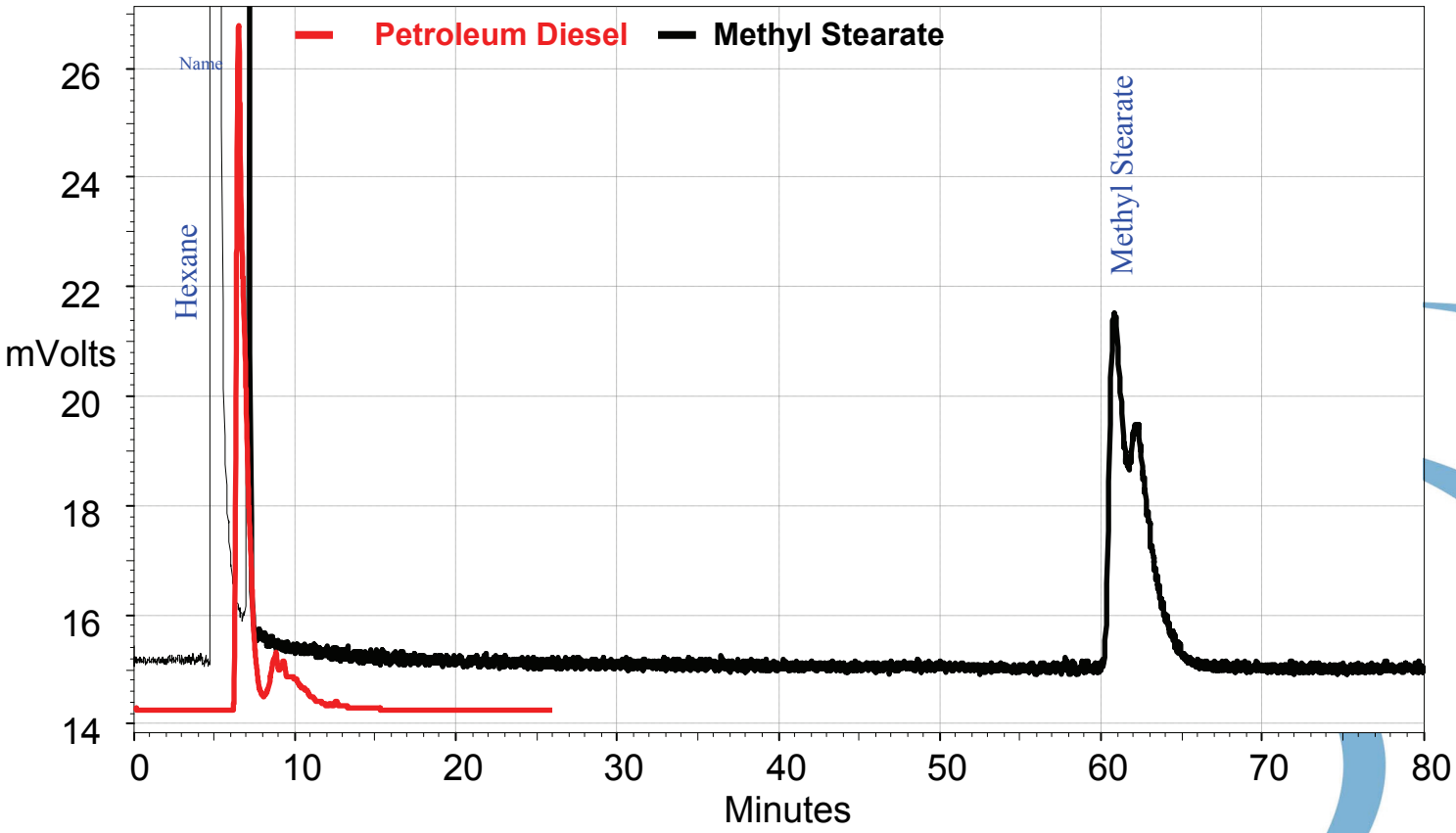
SFC Instrumentation

- SFC system
  - Pressure and temperature programmable
  - Precision Injection
    - More repeatable results compared to methods like FIA
  - Flame Ionization Detection
  - Automated Column Switching

Goals of This Study

- Separate and identify main biodiesel fractions without derivatization
- Separate biodiesel from petroleum diesel
  - Still be able to quantify aromatic content of petroleum diesel
- Quantify all of the fractions

FAMEs Highly Retained on Silica Column



Conditions:

50 cm X 1 mm 5 µm 60 Å

Oven 40°C

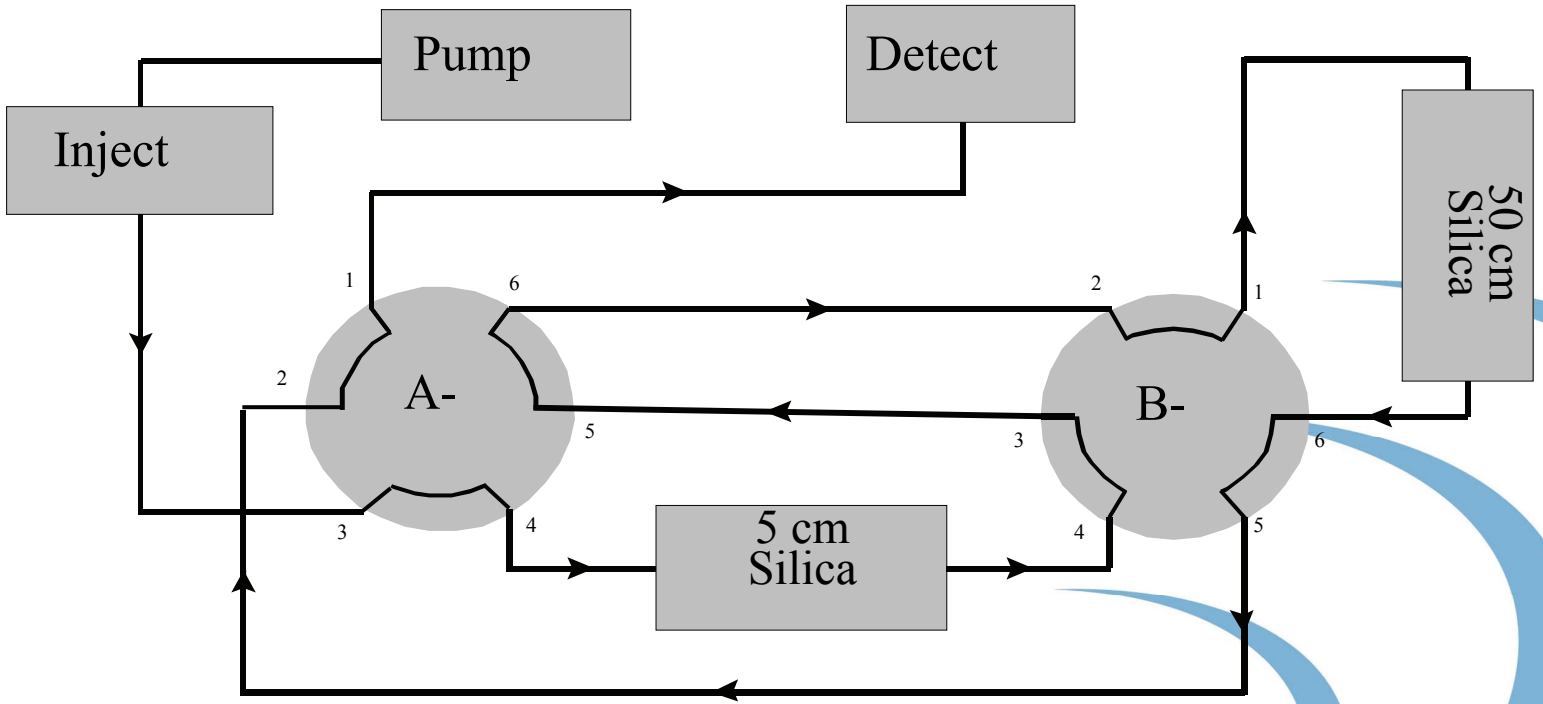
Pump 200 ATM

FID 400°C

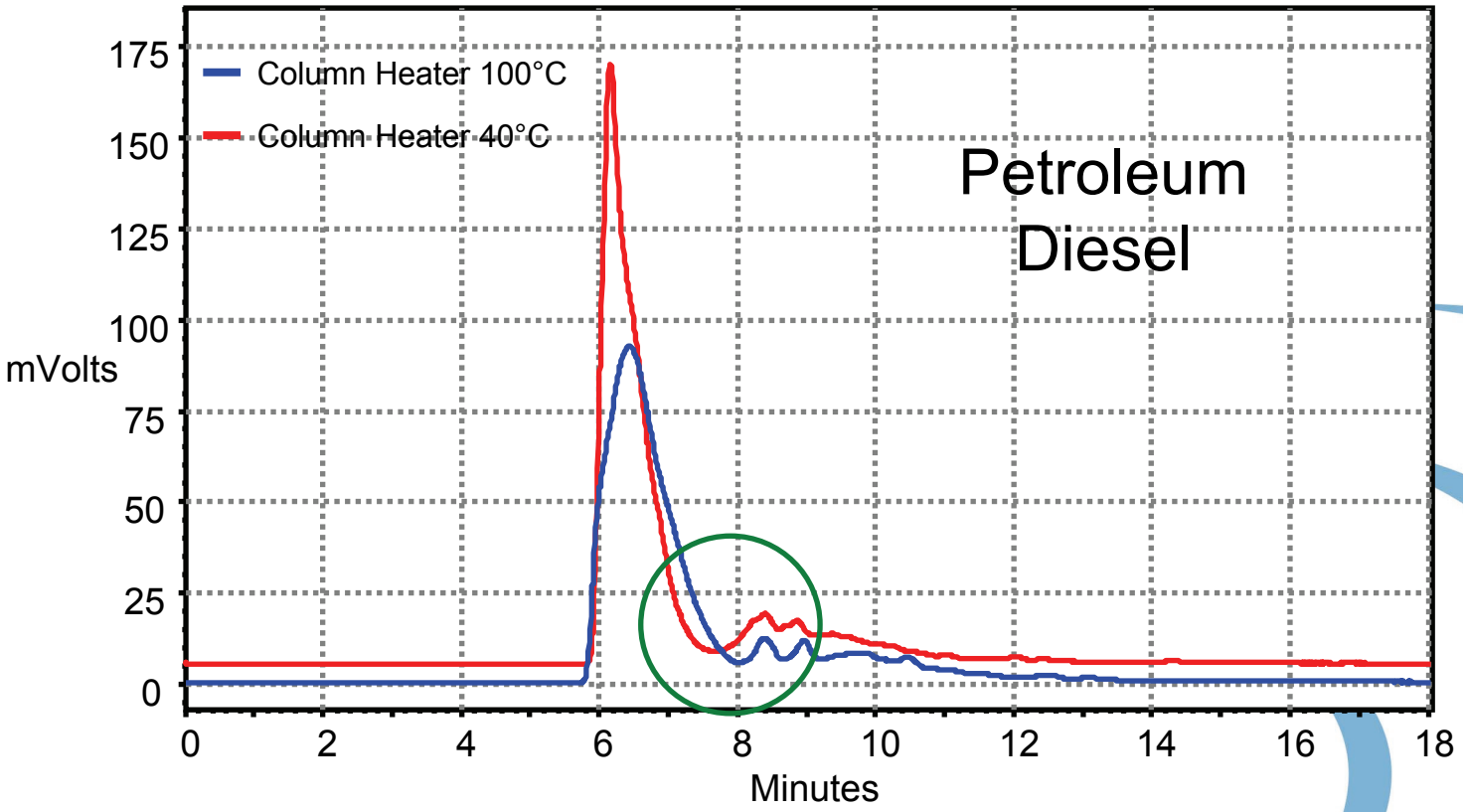
Ways to Affect Selectivity

- Temperature
  - Elevated temperature disrupts hydrogen bonding
- Pressure
  - Increasing the pressure increases the solvent strength
- Columns
  - Stationary phase
    - Silica
    - PVA

Valve Configuration



Effect of Temperature on Silica Column Separation



Conditions:

Column A, 5 cm X 1 mm 5 µm 60 Å In separate column heater

Column B, 50 cm X 1 mm 5 µm 60 Å at oven temperature

Oven 40°C

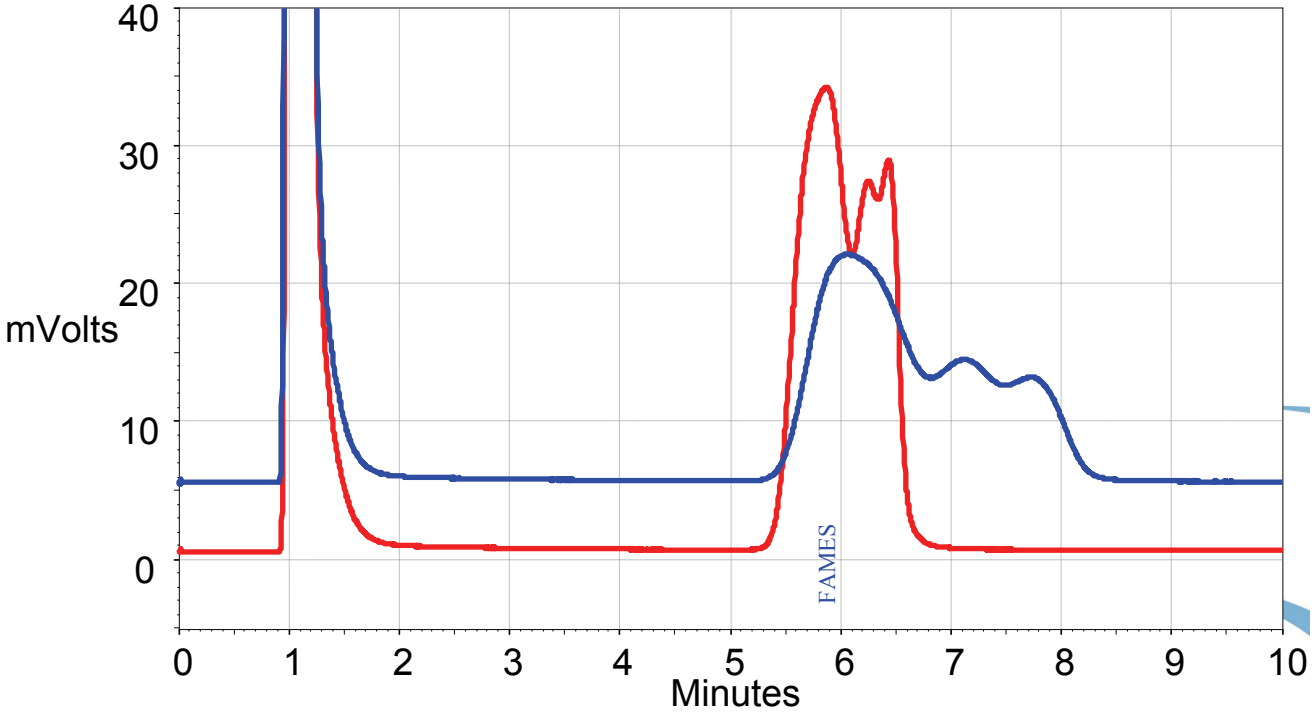
Pump 200 atm

FID 400°C

Red Trace Column Heater 40°C

Blue Trace Column Heater 100°C

Effect of Pressure



Conditions:

Column A: 5 cm X 1 mm 5 µm 60 Å

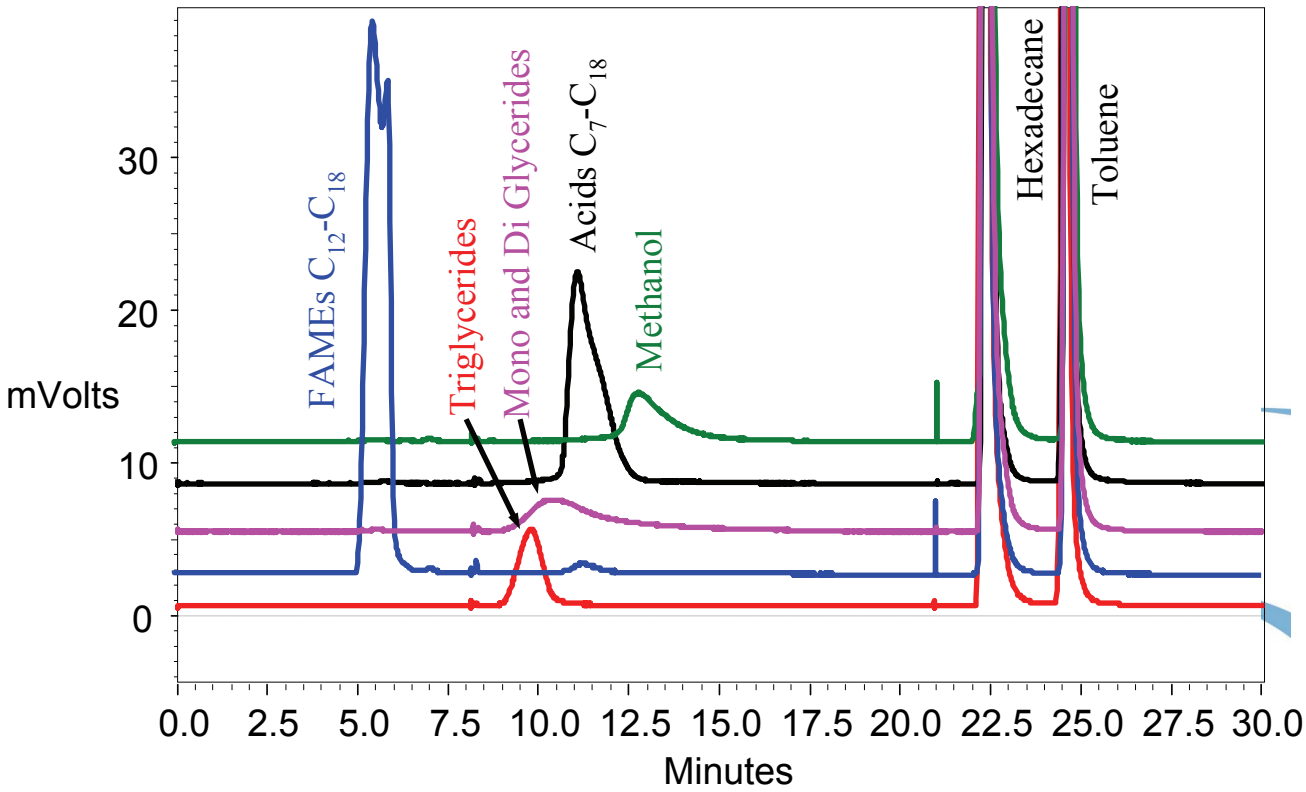
Oven: 40°C

Fame Mix C_{12}-C_{18}
Pump:
200 atm for 4.8 Minutes
Ramped to 400 atm at 50 atm/Minute
Held until 10 Minutes

Fame Mix C_{12}-C_{18}
Pump:
200 atm for 10 Minutes

FID: 400°C

Separation of Biodiesel Components



Conditions:

Column A: 5 cm X 1 mm 5 µm 60 Å

Column B: 50 cm X 1 mm 5 µm 60 Å

Oven: 40°C

Pump:
200 atm for 4.8 Minutes
Ramped to 400 atm at 50 atm/Minute
Held until 17 Minutes
Ramped from 400 atm to 200 atm
Held for 19 Minutes

FID: 400°C

Valve B 0 to 4.8 min.

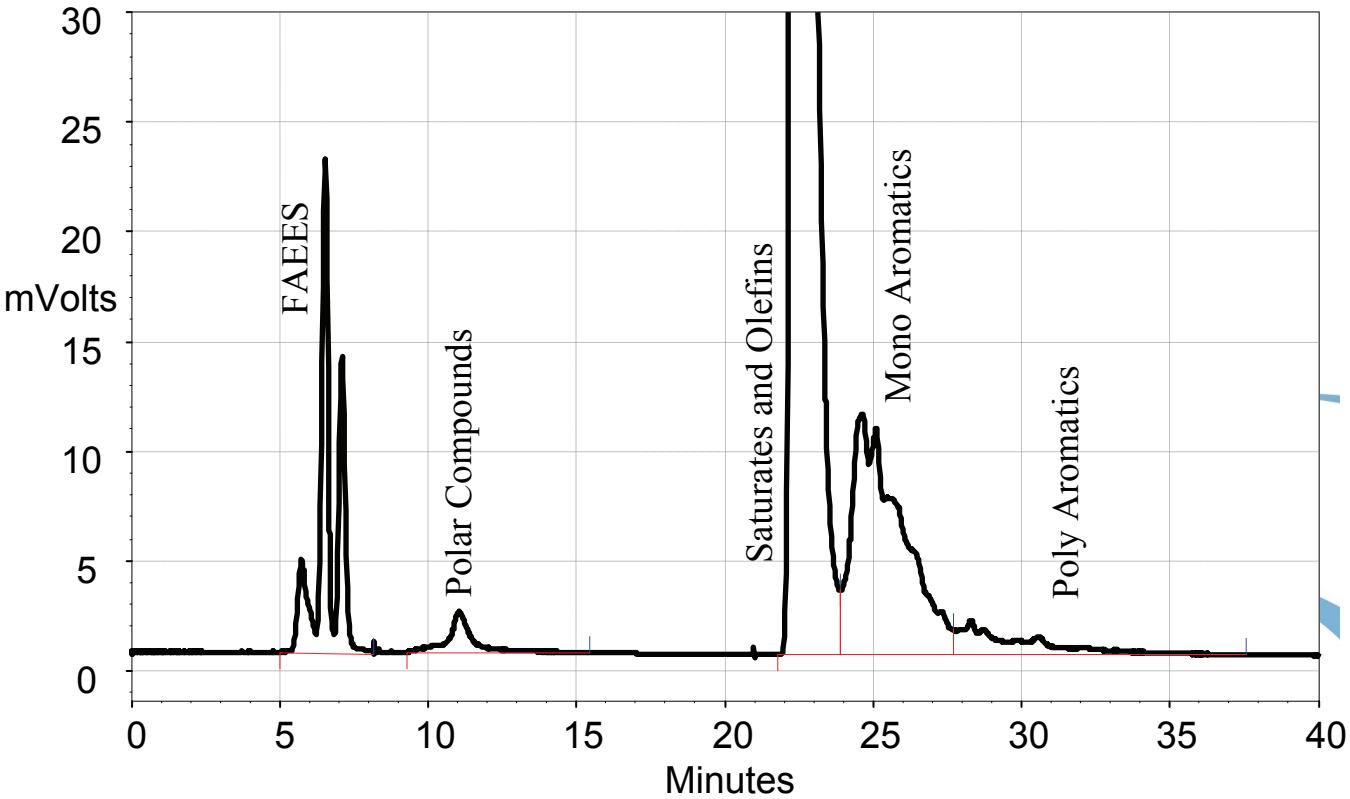
Valve A 8.2 to 21 min.

Valve B 21 to 40 min.

Relative Response

Compound	Mass %	Area %
FAMES	22.67	21.92
Triglycerides	2.53	2.99
Mono and Di Glycerides	4.11	3.95
Acids C_7-C_{18} Mix	12.89	11.72

B10 Fatty Acid Ethyl Ester Biodiesel Made From Peanut Oil Not Distilled



Conditions:

Column A: 5 cm X 1 mm 5 µm 60 Å

Column B: 50 cm X 1 mm 5 µm 60 Å

Oven: 40°C

Pump:
200 atm for 4.8 Minutes
Ramped to 400 atm at 50 atm/Minute
Held until 17 Minutes
Ramped from 400 atm to 200 atm
Held for 19 Minutes

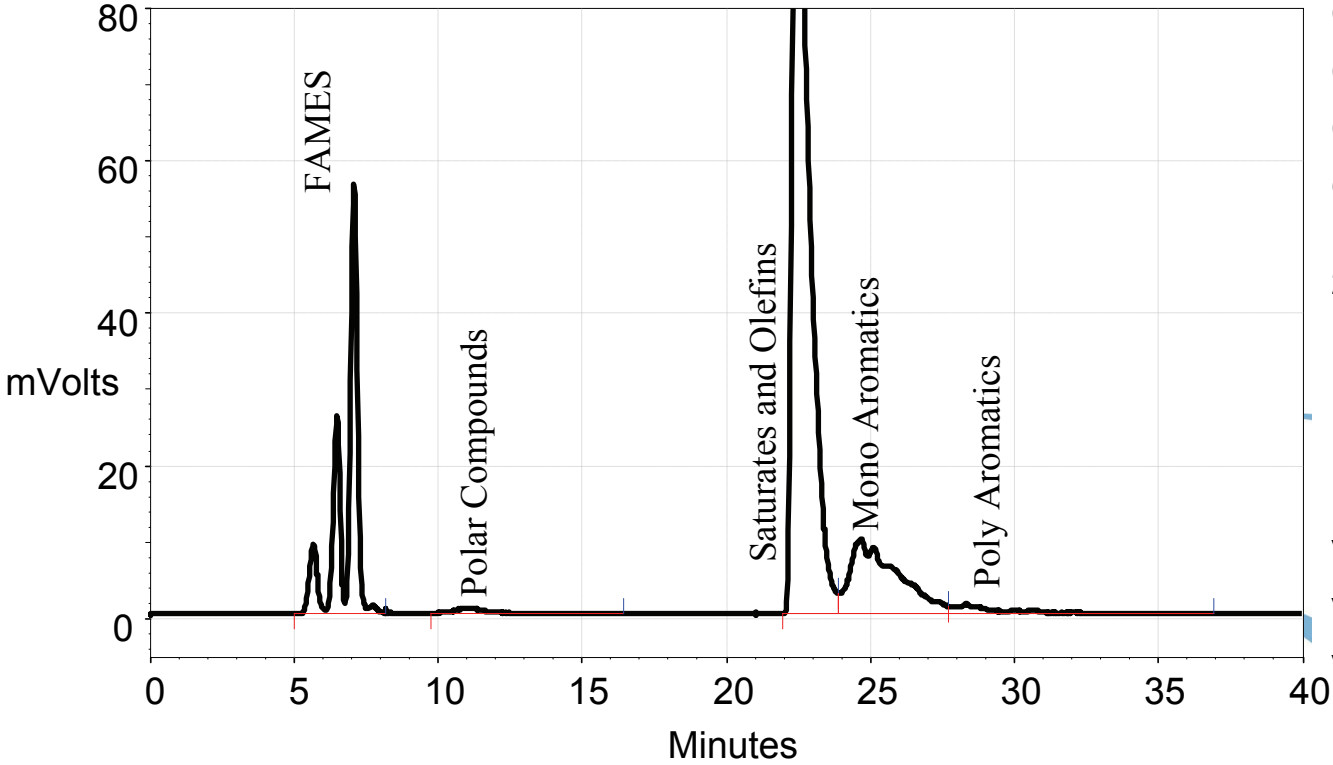
FID: 400°C

Valve B 0 to 4.8 min.

Valve A 8.2 to 21 min.

Valve B 21 to 40 min.

B20 Biodiesel Made From Corn Oil Distilled



Conditions:

Column A: 5 cm X 1 mm 5 µm 60 Å

Column B: 50 cm X 1 mm 5 µm 60 Å

Oven: 40°C

Pump:
200 atm for 4.8 Minutes
Ramped to 400 atm at 50 atm/Minute
Held until 17 Minutes
Ramped from 400 atm to 200 atm
Held for 19 Minutes

FID: 400°C

Valve B 0 to 4.8 min.

Valve A 8.2 to 21 min.

Valve B 21 to 40 min.

Relative Response Total Biodiesel in Petroleum Diesel

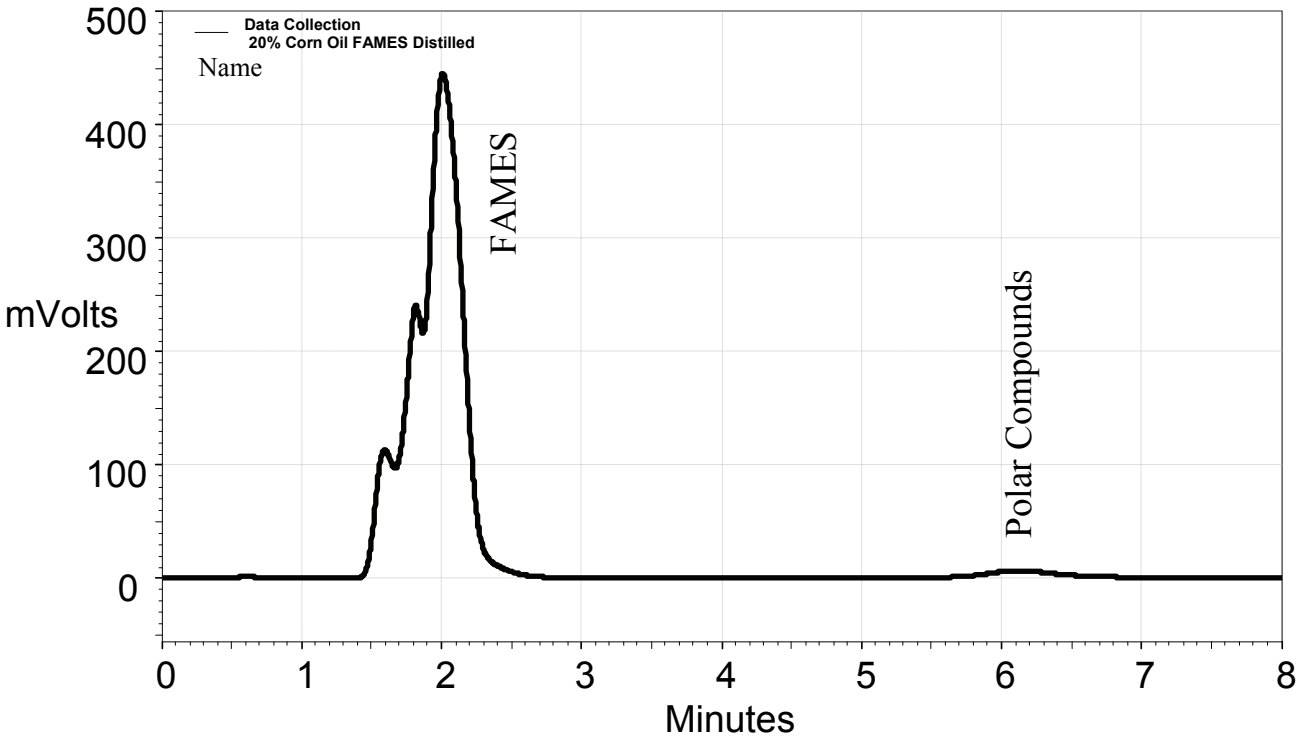
Compound	Mass %	Area %*
Peanut Oil Based	10.03	9.60
Corn Oil Based	20.01	20.73

*No corrections applied

Repeatability Total B20 Biodiesel in Petroleum Diesel

Area%	Fames	Polar Compounds	Total
Run 1	20.00	0.73	20.73
Run 2	20.21	0.62	20.83
Run 3	20.25	0.66	20.90
Run 4	20.27	0.64	20.91
Run 5	20.19	0.68	20.87
Average	20.18	0.67	20.85
STD	0.108	0.042	0.073
%RSD	0.533	6.335	0.350

B100 Biodiesel Made From Corn Oil Distilled



Conditions:

Column: 5 cm X 1 mm 5 µm 60 Å

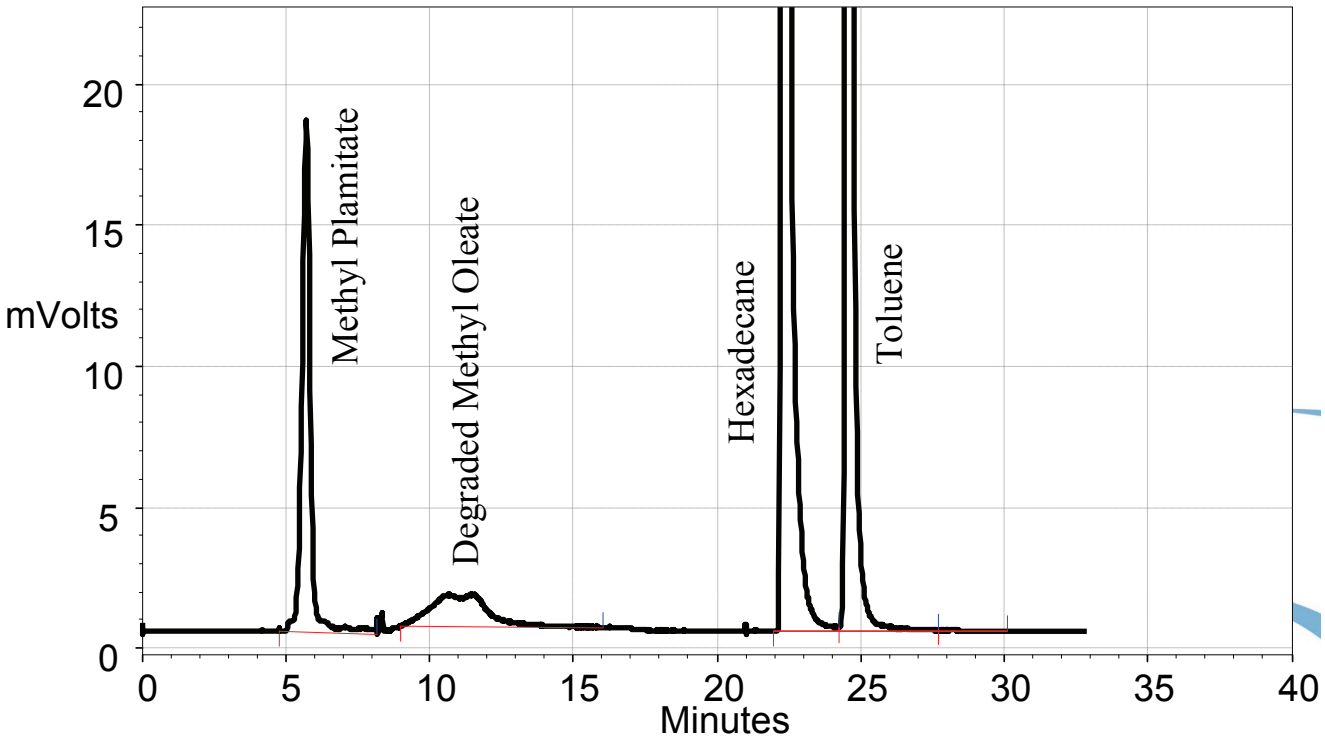
Oven: 40°C

Pump:
400 atm for 15 Minutes

FID: 400°C

Valve A 3 to 15 min.

Degraded Methyl Oleate



Conditions:

Column A: 5 cm X 1 mm 5 µm 60 Å

Column B: 50 cm X 1 mm 5 µm 60 Å

Oven: 40°C

Pump:
200 atm for 4.8 Minutes
Ramped to 400 atm at 50 atm/Minute
Held until 17 Minutes
Ramped from 400 atm to 200 atm
Held for 19 Minutes

FID: 400°C

Valve B 0 to 4.8 min.

Valve A 8.2 to 21 min.

Valve B 21 to 40 min.

Summary Comments

- There is a wealth of information obtained with SFC:
  - Full characterization of petroleum diesel for saturates/olefins, mono and poly aromatics
  - Detail on FAMEs and polar compounds
    - Quantitation of FAMEs and polar compounds
  - Forty minute total analysis time for samples containing petroleum diesel
  - 10 minute analysis for 100% biodiesel
- Future Work
  - Optimization of column lengths
  - Try to get more separation of the polar region allowing quantitation of each group.
  - Shorten the analysis

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