

Analytical tools for renewable fuel spill response

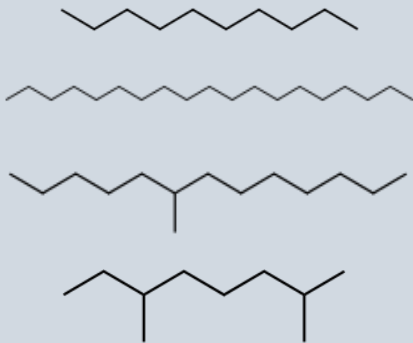
MARTICE VASQUEZ, PHD

OSPR LABORATORY PROGRAM

Outline

- Highlight chemical differences between renewable diesel and biodiesel
- Traditional tools and approaches for fingerprinting petroleum and renewables
- Work being done at OSPR Petroleum Chemistry Laboratory on renewable diesel

Renewable diesel



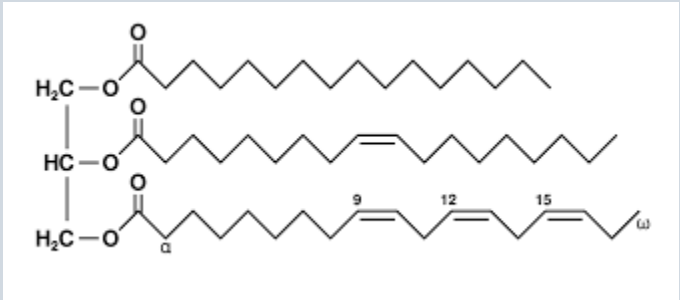
Linear and
branched chain
hydrocarbons

+



Renewable
Propane

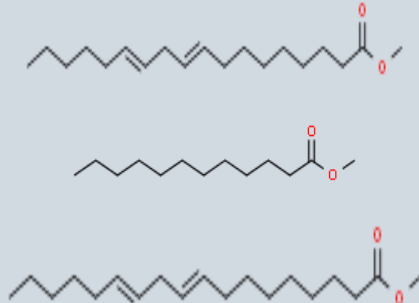
Vegetable and Animal Fats:
Triglycerides



Hydrotreatment
Isomerization

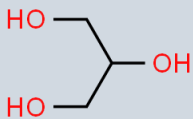
Transesterification

Biodiesel



Fatty Acid
Methyl Ester
(FAME)

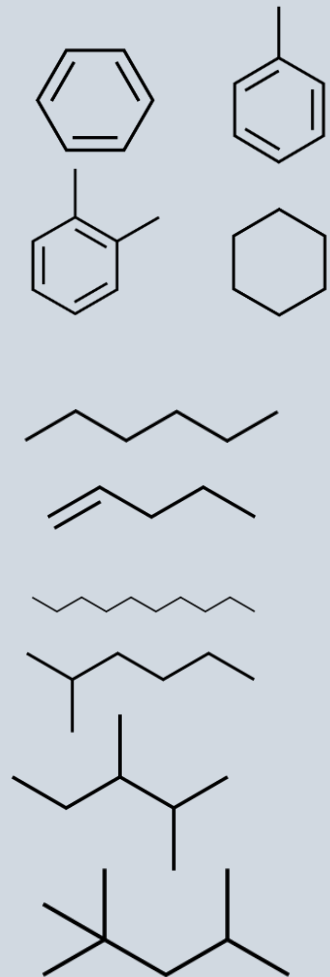
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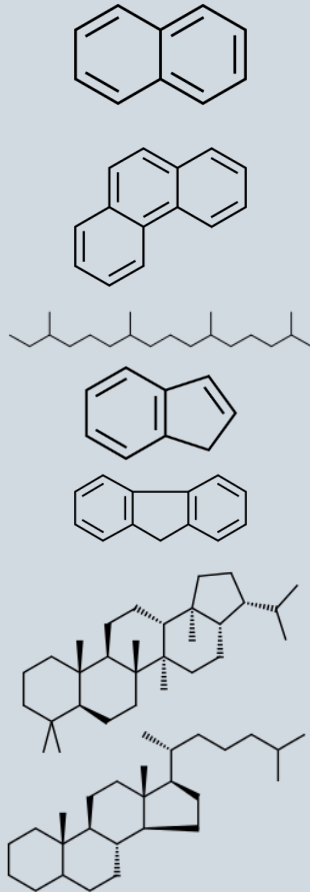
Glycerol

Tools for Analysis and Fingerprinting – GC/MS, GC/FID

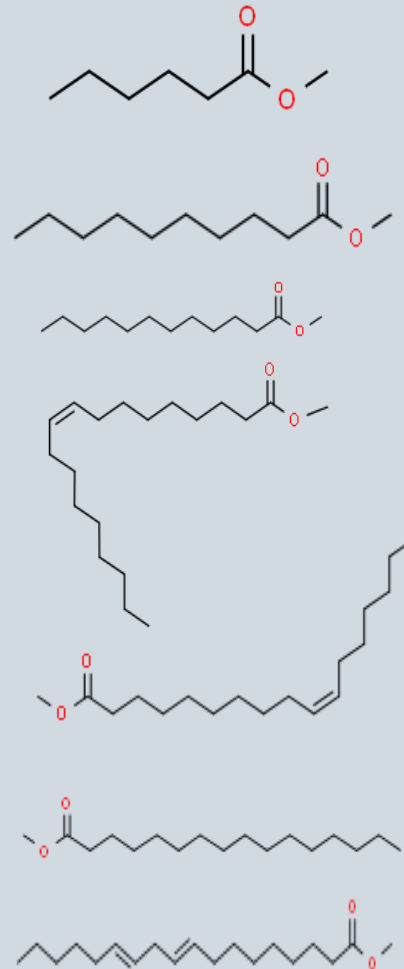
Gasoline (C6-C12)



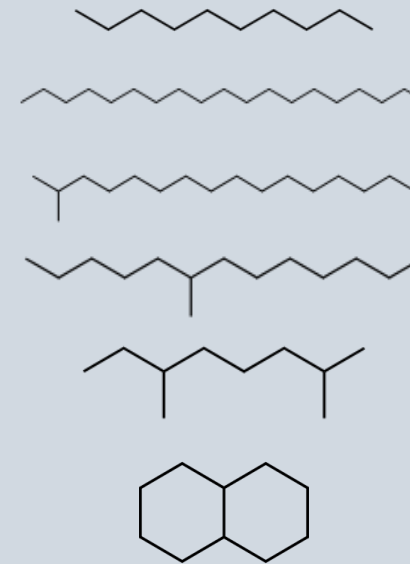
Petroleum
Diesel(C10-28)
and Oil



Biodiesel (FAME)*

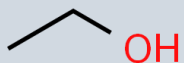


Renewable Diesel
(C10-C20)



No documented approach for
fingerprinting renewable diesel

Ethanol



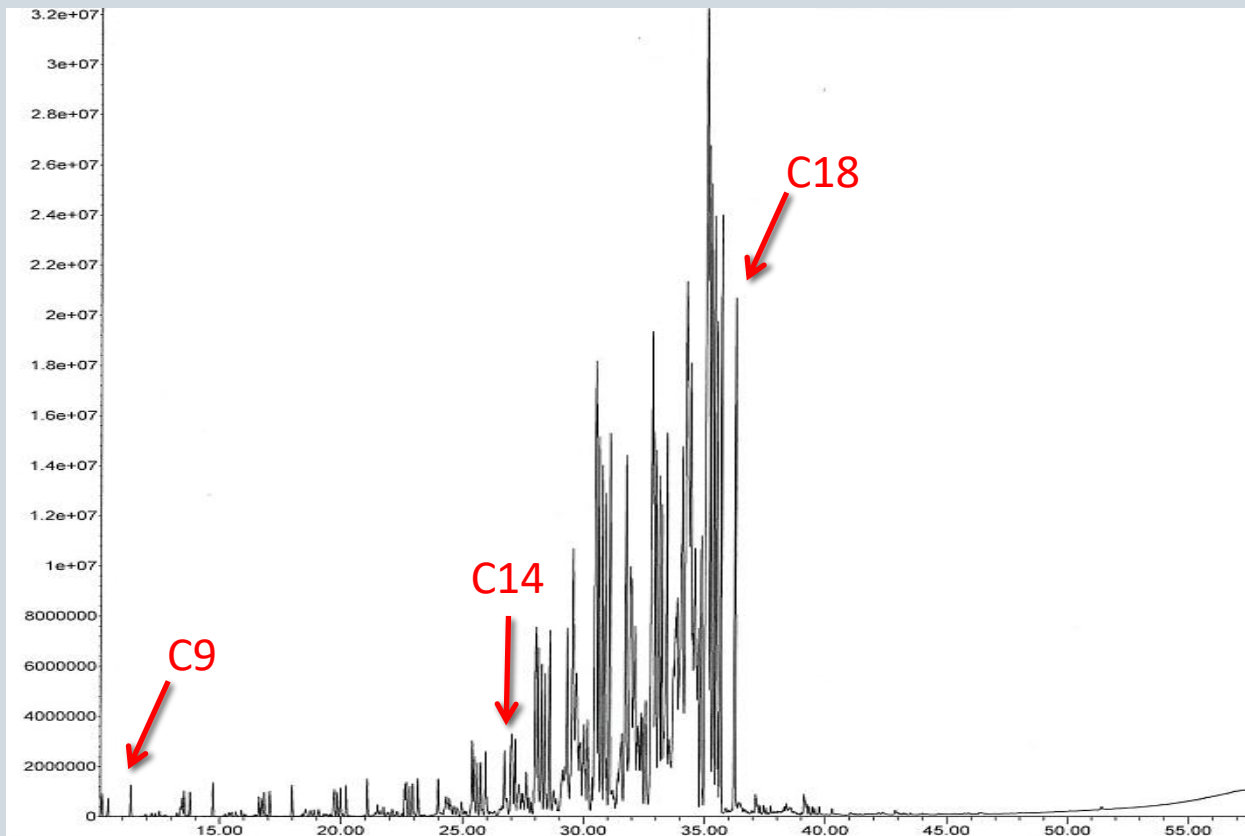
*Infrared Spectroscopy

Main Project Objectives

1. Evaluate the applicability of current petroleum spill analytical methodologies for characterization and fingerprinting of renewable diesel spills.
 - a. Can we differentiate renewable diesel from petroleum diesel? Renewable diesel from Biodiesel?
 - b. What about mixtures?
 - c. Can we fingerprint renewable diesel?

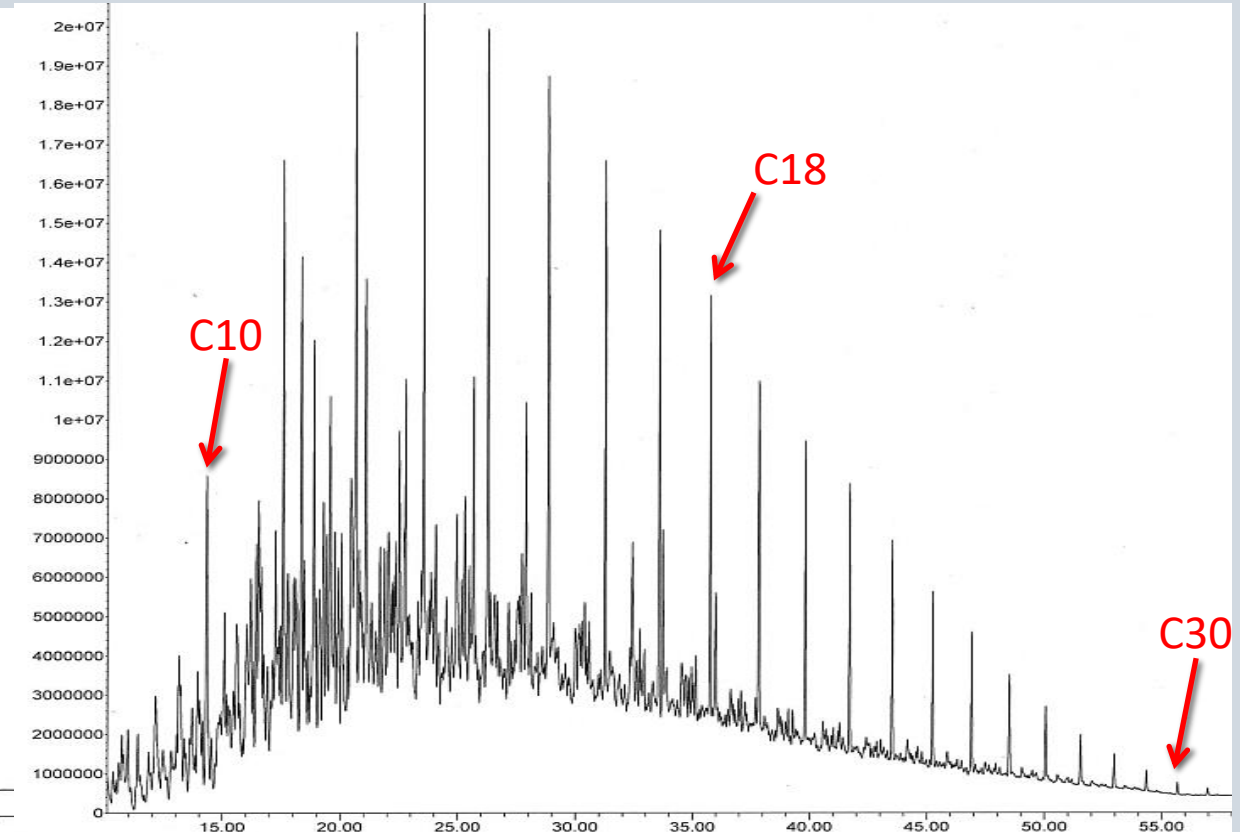
Can we tell the difference between renewable diesel and petroleum diesel using our traditional full scan GCMS screening?

Traditional GC can be used to confirm and characterize renewable diesel



100% Renewable Diesel

- Carbon range C9 – C18, majority of signal C15–C18
- Extreme abundance C17 – C18, easily overloading detector

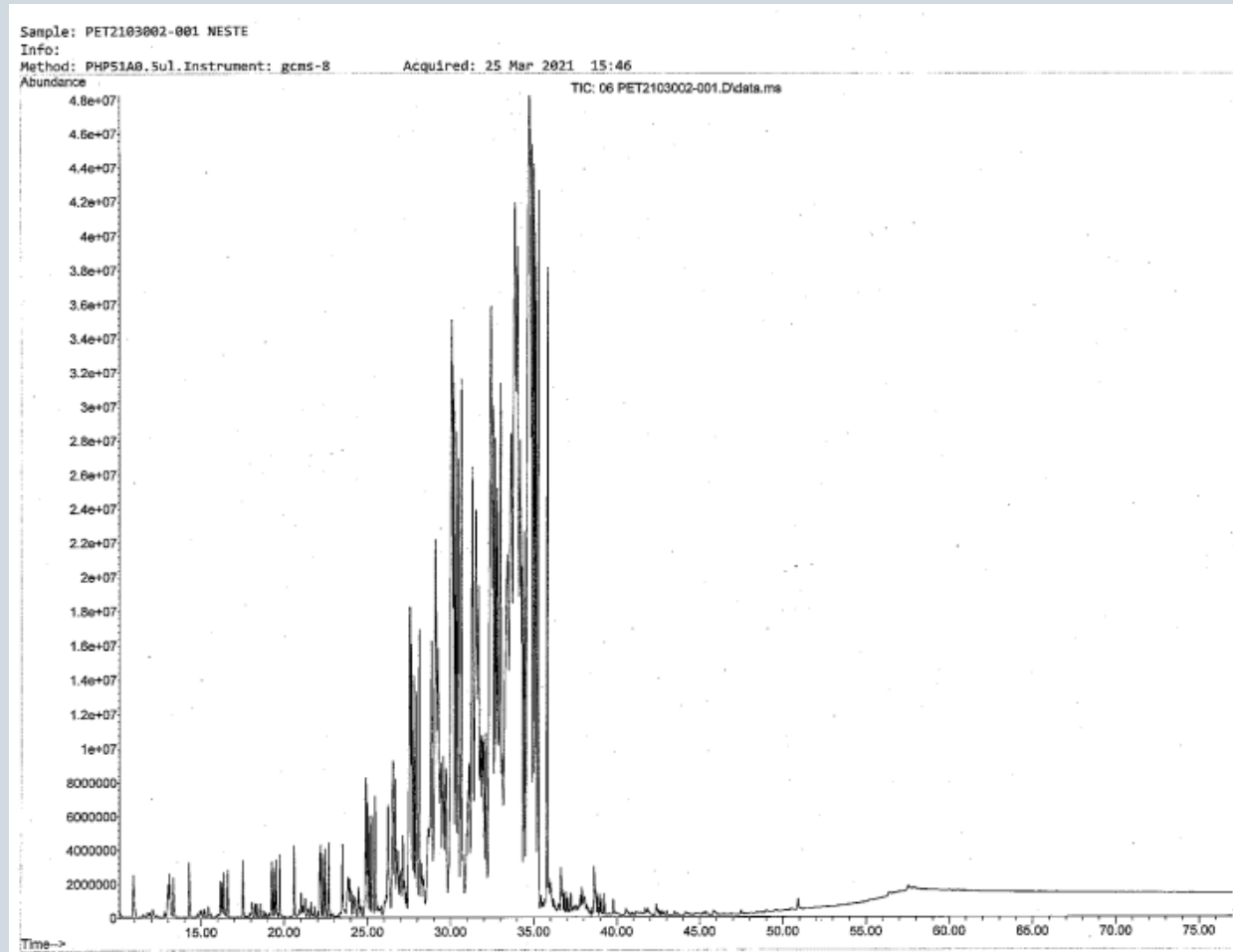


100% Petroleum Diesel

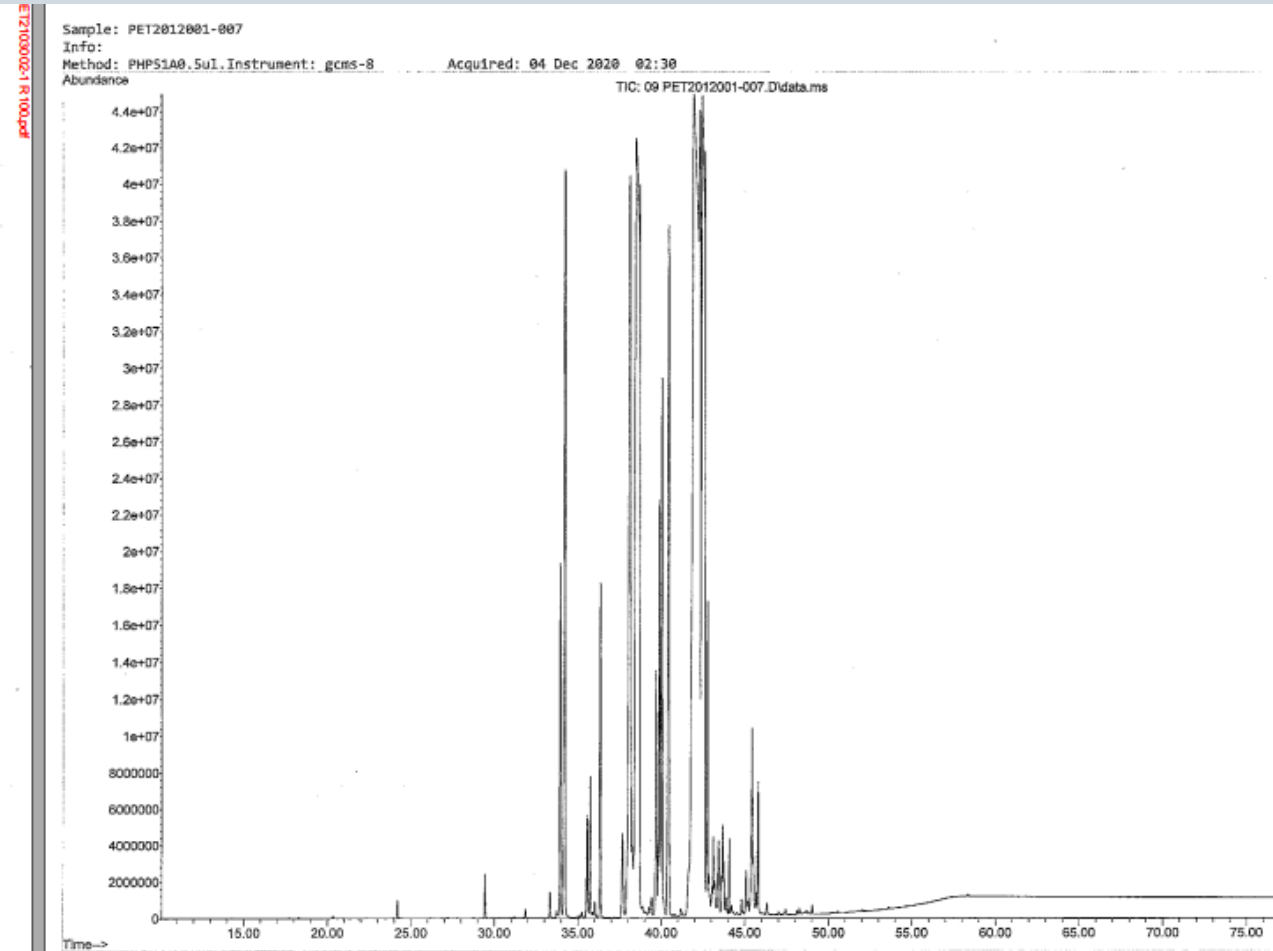
- Carbon range: ~C9 – C28
- UCM is present for the majority of carbon range

Can we tell the difference between renewable diesel and biodiesel using our traditional full scan GCMS screening?

Traditional gas chromatography can be used to confirm and characterize RD samples



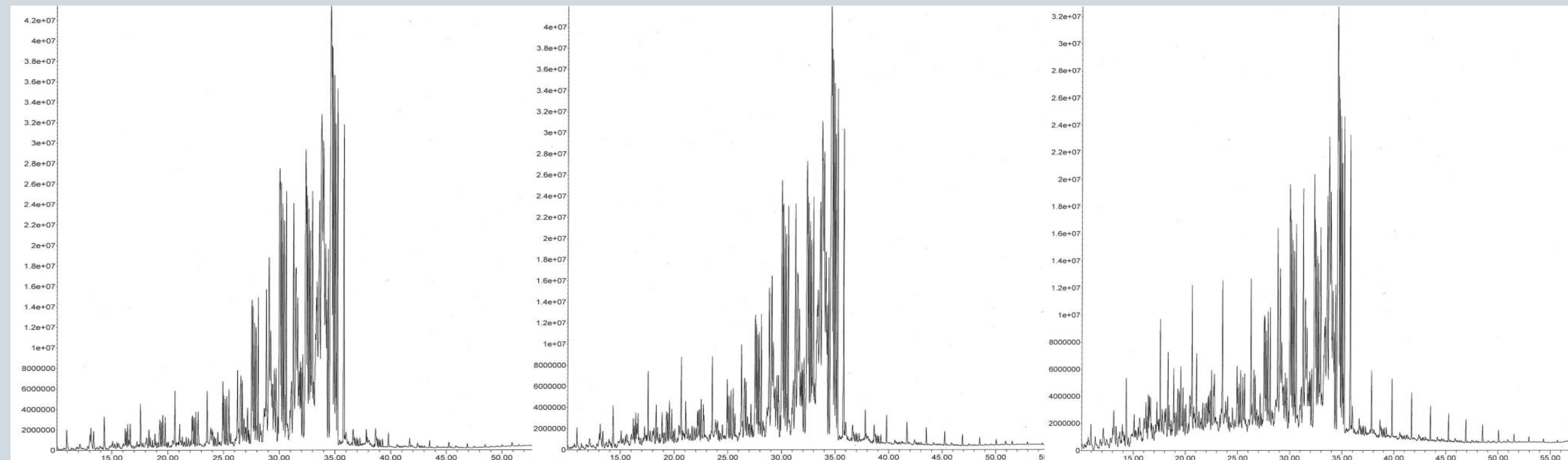
100% Renewable Diesel



100% Biodiesel

What about mixtures of renewable diesel
and petroleum diesel?

We can tell if there is a mixture between the two qualitatively but can not say what percentage the mixture is petroleum diesel vs renewable diesel



90% Renewable Diesel; 10 % Diesel

75% Renewable Diesel; 25 % Diesel

50% Renewable Diesel; 50 % Diesel

We can not distinguish between “old” and “new” carbon using GCMS

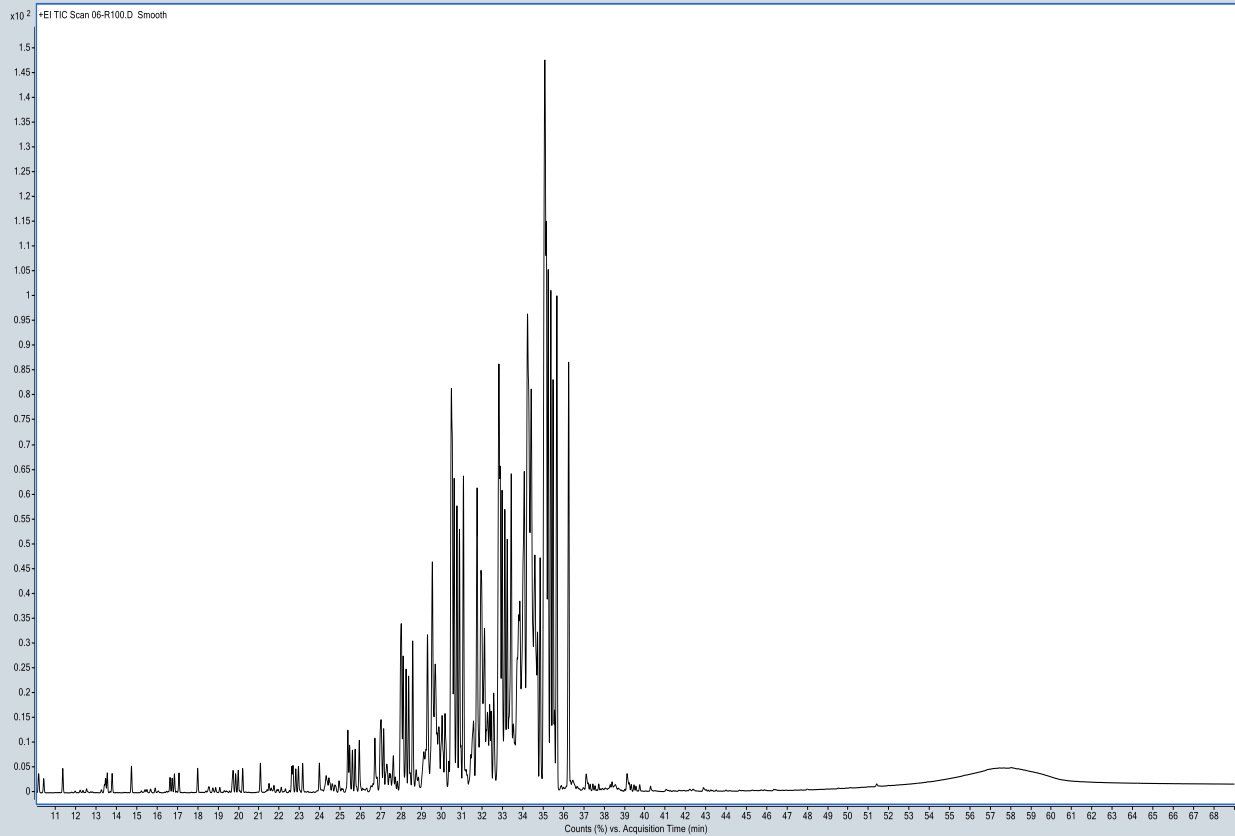
- ^{14}C Isotopic analysis is required to quantitate percentages in a mixture of renewable and petroleum diesel.
- When organisms stops growing, the ^{14}C begins to decline ($t_{1/2} = 5730$ years)
- Fossil diesel no longer contains ^{14}C isotope and the portion of new organic material can be detected.
- Accelerator Mass Spectrometry (AMS) or Liquid Scintillation Counting (LCS)

Can we fingerprint renewable diesel?

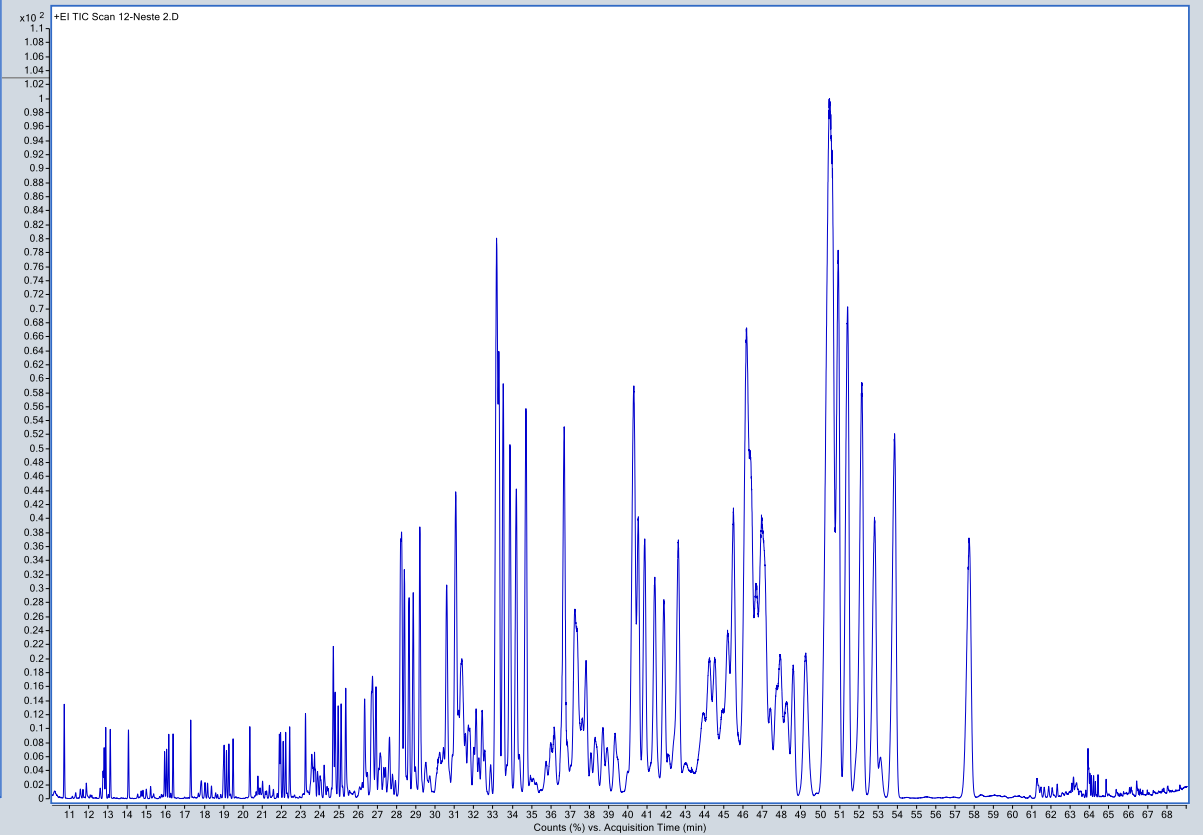
Fingerprinting Renewable Diesel?

- RD lacks biomarkers and PAHs used for petroleum fingerprinting
- Linear and branched hydrocarbons dominate the signal
- Some work we are doing at the Petroleum Chemistry Lab to fingerprint RD

Improve chromatographic resolution

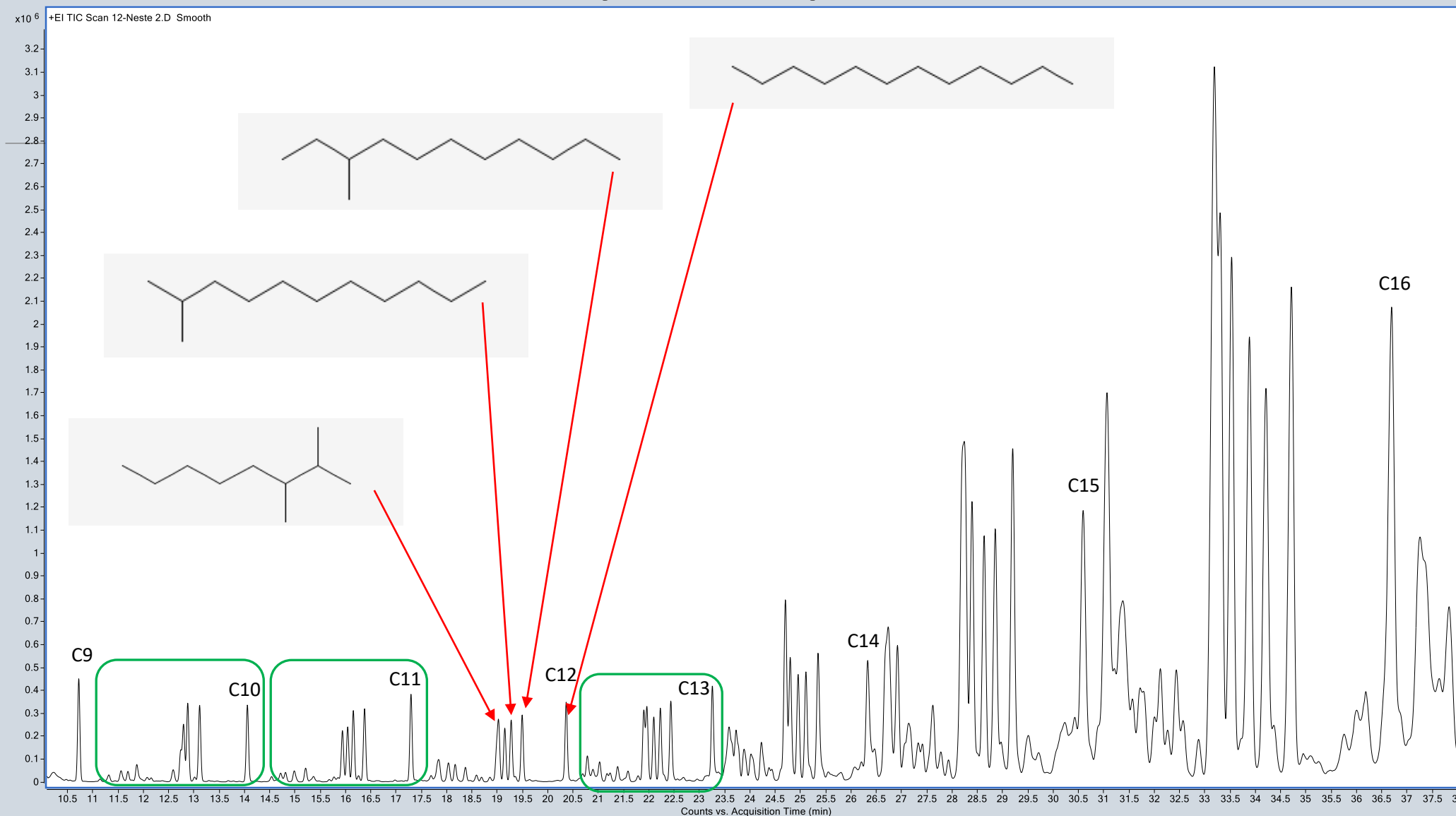


Traditional GC Program for Petroleum Fingerprinting

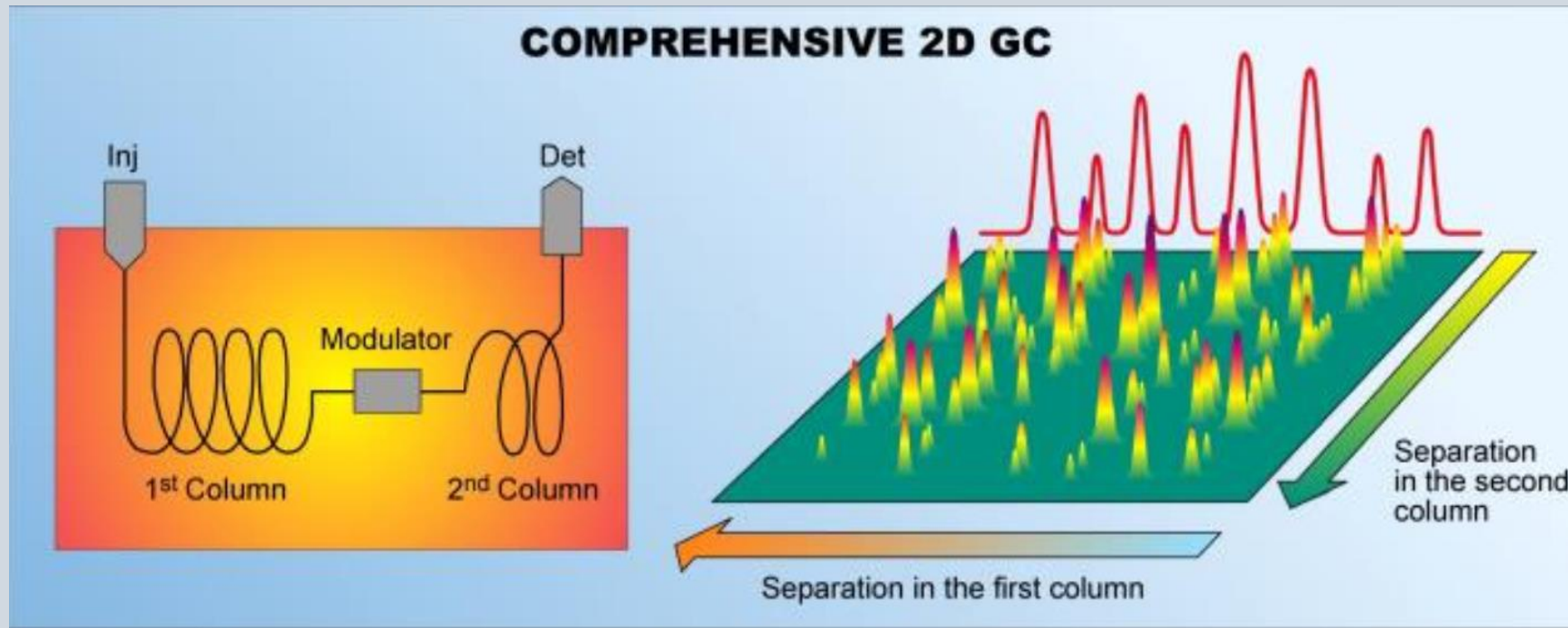


Optimized GC Program for Renewable Diesel Fingerprinting

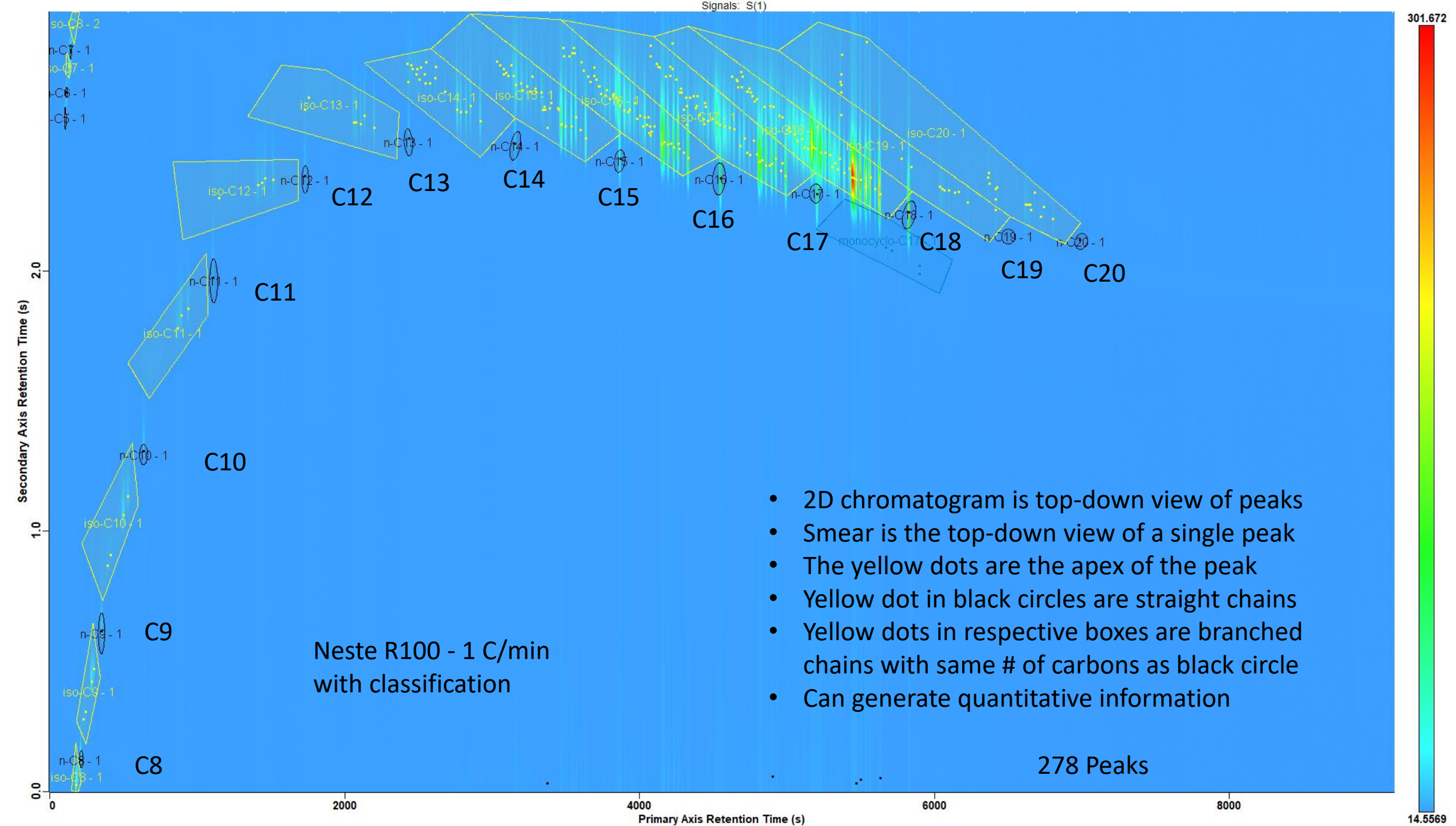
Identify compounds



Do we need 2-dimensional GC?



- Increases resolution – separates peaks within peak
- Sample components separated in 1st column based on polarity
- Sample components separated in 2nd column based on boiling point
- Working with Dr. Petr Vozka of CSU LA to evaluate the ability of 2D GC to pull apart signal



Next Steps - Fingerprinting Renewable Diesel

- Continue to explore quantitative 2D GC application to characterize different renewable diesel samples
- Use quantitative differentiation for comparison of two different renewable diesel samples
- So far, using GCMS (one dimensional GC), no differences in various samples of RD but need to look at more samples, different manufacturers and 2D GC approach
- Continue weathering and mixing studies

Thank you!

Questions?