NMReady

Preparation of Biodiesel

Incorporating NMR instrumentation into undergraduate laboratories increases students' understanding of fundamental and practical characterization techniques.

The NMReady™ benchtop spectrometer offers a portable and affordable option with a network accessible, easy-to-use interface that can be easily incorporated into teaching laboratories.

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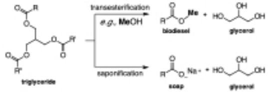
A Modern Undergraduate Experiment: Preparation of Biodiesel

Incorporating laboratory experiments that are applicable to current events can heighten students' interest while also increasing their understanding of relevant scientific challenges that our society faces. The synthesis of biodiesel and the search for sustainable, renewable energy sources is pertinent today!

Biodiesel is straightforward to prepare, and the standard transesterification can be done via a number of procedures (*e.g.,* conventional, microwave), with different feedstocks (*e.g.,* reused/filtered oil, soy, olive) and with various catalysts (KOH, K_2CO_3). This reaction is complicated by saponification byproducts that can be formed with excess water.



Procedure:

Although there are numerous procedures available, we selected:

Weigh out approximately 3 g of oil. Assume that the oil feedstock has an average molar mass of 880 g/mol & calculate the amount of anhydrous K_2CO_3 required such that it is 6% of the mass of oil. Add 6 mmol of anhydrous MeOH for every mmol of oil used. Heat the mixture to 60 °C for 40 minutes.

After the reaction is complete, the mixture should be allowed to cool before the slow addition of acetic acid.

Using a separatory funnel, isolate the biodiesel & wash it three times with warm water. The biodiesel fraction can then be then be collected & dried with $MgSO_4$ and filtered. The volume and weight of the biodiesel should be measured and recorded, followed by boiling point determination. Other techniques, such as optical rotation can also be used to assess reaction completeness.

Key Concepts:

organic synthesis, transesterification, stoichiometry, byproduct formation, optical rotation, separation, neutralization, percent yield, boiling point

Students' Discussion:

From this, students are expected to discuss the reaction, reaction completeness, byproduct formation, and comment on the purity of their reaction.

The use of NMR Spectroscopy provides additional evidence for understanding the reaction, reaction monitoring, observing any byproduct formation, and introducing kinetics.

Modify this Modern Experiment with the NMReady:

1) Add 0.5 mL of *d*-$CHCl_3$ to 10 clean, dry NMR tubes.
2) Weigh oil feestock into a beaker equipped with a stirbar.
3) Add MeOD to the oil and stir until well mixed. Heat to 60°C.
4) Add K_2CO_3 and stir for 30 sec.
5) Take a 0.1 mL aliquot of the reaction mixture and add to the first pre-prepared NMR tube.
6) Acquire a ^1H spectrum with the following parameters.

SW = 12 ppm	ns = 4 scans
delay time = 1 sec	total time = 20 sec

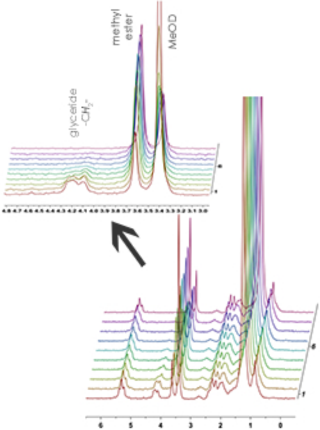
Save the file under a name stipulating the time interval it was taken.

7) Take a 0.1 mL aliquot every 4-5 min, add to an NMR tube and acquire a spectrum with the same parameter for the next 45 min.

Additional Concepts:

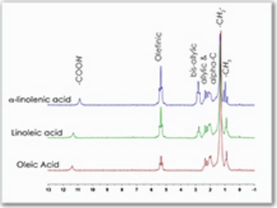
NMR sample preparation, NMR data acquisition & analysis, NMR characterization, reaction monitoring, byproduct formation, competing reactions, kinetics

Example of 60 MHz ^1H NMR Results:



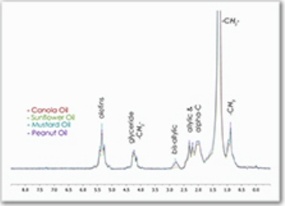
Extended Discussion:

1) Assign all the ¹H NMR resonances for the following spectra.



2) What is the chemical composition of edible oils? What percentage of ω-3, 6 and 9 are present in your feedstock oil?

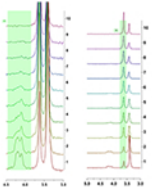
3) Assign the below peaks in the spectra of edible oils. Highlight the difference between the free fatty acids and oils.



4) Assign all resonances in the biodiesel reaction monitoring ¹H NMR spectrum you took. What functional groups are present?

5) What peaks disappear during the reaction? Which appear? Is this consistent with the mechanism of the reaction?

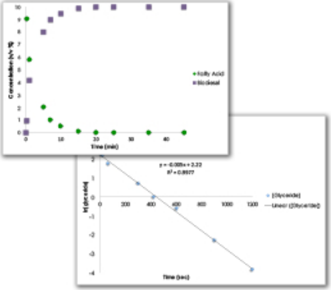
6) Integrate these peaks and tabulate.



Time (sec)	Integration of Glyceride	Integration of Methyl Ester
0	4.14	0
15	3.87	0.41
60	3.25	2.31
300	1.8	7.08
420	0.88	7.87
600	0.49	8.55
900	0.09	8.63
1200	0.02	9.23
1500	0.01	9.44
2100	0	9.45
2700	0	9.42

7) Make a speciation plot of time vs. species concentration.

8) Pick the integral of the glyceride [G(t)] and plot as a function of time: for (a) [G(t)]; (b) ln[G(t)]; and (c) 1/[G(t)]. What do these say about the kinetic order of the reaction?



9) Why do we use MeOD? What would the spectra look like if we used MeOH? d_4-MeOH?

10) Assess the purity of the synthesized biodiesel.

11) Can you differentiate the biodiesel components? How does it compare to the oil starting material?

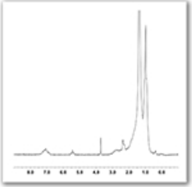
12) Why is transesterification necessary? Why aren't oils used as a fuel in transportation? What differences are noticable between the starting material and the product?

13) What is the reported heating value of biodiesel? How does this compare to the current fuels? Gasoline? Diesel?

14) Assuming methyl linoleate ($C_{19}H_{34}O_2$) is the main component, calculate the standard enthalpy, entropy and Gibbs free energy of the reaction.

15) What would the ¹H NMR spectrum of diesel look like?

16) B5 and B20 biodiesel blends are common. How would you distinguish between biodiesel and diesel components using proton NMR spectroscopy. Assign peaks on the spectrum below highlighting which fuel source they originate from.



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References:

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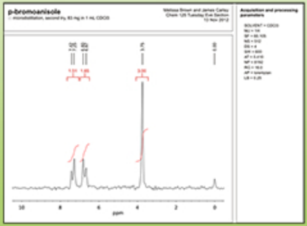
Data Accessibility:

NMReady outputs to a networked drive and has a print option. Students can process and print in third party software, like Mestrelab™, or use the NMReady directly. An example of data to be incorporated into a lab report processed and printed directly from the NMReady is presented below:



For additional ideas of how to incorporate the NMReady™ benchtop spectrometer into undergraduate laboratories please see:

1) Synthesis of Aspirin
2) Aldol Condensation
3) Determination of Acid Dissociation Constants

available at:

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