^{1}H Nuclear Magnetic Resonance Determination of the Yield of the Transesterification of Rapeseed Oil with Methanol

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ABSTRACT: The formation of fatty acid methyl esters by transesterification with methanol can be monitored by ^{1}H nuclear magnetic resonance spectroscopy; this accurate determination is simpler than chromatographic methods.
JAOCS 72, 1239–1241 (1995).

KEY WORDS: Diesel fuels, methyl esters, NMR spectroscopy, transesterification.

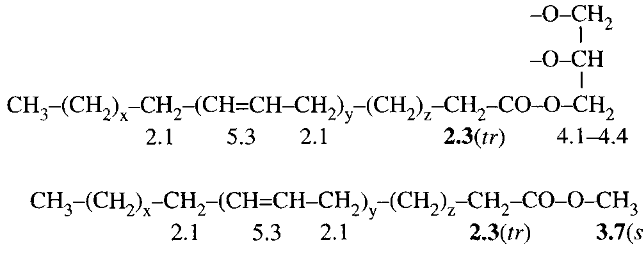
The production of biofuels for diesel engines relies on the transesterification of vegetable oils from soybean or rapeseed by light alcohols, such as methanol or ethanol. The reaction requires inorganic strong bases as catalyst (1,2).

In the course of our studies on the use of organic strong bases as catalysts for the transesterification of rapeseed oil with methanol, we developed a reliable and fast method to monitor the rate of the transesterification reaction.

The usual methods are gas–liquid chromatography and high-performance liquid chromatography; though they are used also to determine the intermediary mono- and diglycerides, they require derivatization of the samples and/or tedious calibrations (3,4).

We decided to investigate ^{1}H nuclear magnetic resonance (NMR) spectroscopy to quantitate directly the methyl esters in the reaction mixture and then the yield of the reaction, without any derivatization of the samples.

The assignments of chemical shifts of protons for glycerides and for methyl esters are summarized in Scheme 1:



$$\begin{array}{lllll}
 & & & & \mathrm{{-}O{-}CH_2} \\
 & & & & \mathrm{{-}O{-}CH} \\
\mathrm{CH_3{-}(CH_2)_x{-}CH_2{-}} & \mathrm{(CH{=}CH{-}} & \mathrm{CH_2)_y{-}(CH_2)_z{-}} & \mathrm{CH_2{-}CO{-}O{-}} & \mathrm{CH_2} \\
\qquad\qquad 2.1 & 5.3 & 2.1 & \mathbf{2.3}(tr) & 4.1\text{–}4.4 \\
 & & & & \\
\mathrm{CH_3{-}(CH_2)_x{-}CH_2{-}} & \mathrm{(CH{=}CH{-}} & \mathrm{CH_2)_y{-}(CH_2)_z{-}} & \mathrm{CH_2{-}CO{-}O{-}} & \mathrm{CH_3} \\
\qquad\qquad 2.1 & 5.3 & 2.1 & \mathbf{2.3}(tr) & \mathbf{3.7}(s)
\end{array}$$

SCHEME 1

The relevant signals chosen for integration are those of methoxy groups in the methyl esters at 3.7 ppm (singlet) and of the α-carbonyl methylene groups present in all fatty ester derivatives at 2.3 ppm. The latter appears as a triplet, so accurate measurements require good separation of this triplet and the multiplet at 2.1 ppm, which is related to allylic protons.

This depends on the resolution of the spectrometer; thus, the spectra of samples of methyl esters, oil, or mixtures of them were obtained on a series of 80, 100, 200, and 250 MHz equipment. Good resolution (see Fig. 1) is already obtained at 100 MHz, but preferentially a 200 MHz instrument is used. Integrations were recorded only when a good resolution was obtained (see Fig. 1, c and d).

The terminal methyl group might also be considered, but it appears as a broad superposition of triplets between 1.1 and 0.8 ppm; signals in the vicinity were preferred.

A general procedure for the transesterification is as follows: A mixture of 4 g oil, 0.5 g methanol, and 2 molar% of the catalyst is vigorously stirred at 70°C in a screw-cap vessel; after cooling at the required time, the upper layer is recovered, washed twice with brine to ensure complete removal of glycerol and alkali, and finally dried over magnesium sulfate. NMR spectra were recorded in $CDCl_3$.

Pure methyl ester was obtained by repeating this procedure twice with sodium hydroxide as catalyst. After 45 min heating, the lower phase was discarded, and the same amount of methanol and catalyst as above was added; heating was performed again in 45 min. The purity of the methyl ester mix is 98 ± 2% as checked by NMR and gel permeation chromatography; furthermore, no visible glyceryl-related signals were found at 4.1–4.4 ppm.

The calibrations were made with $CDCl_3$ solutions that contained known amounts of rapeseed oil and methyl ester mix. The yields were calculated by assuming average molecular weights of 293 for an ester unit of oil and of 294 for the methyl esters. The averaged molecular weight for an ester unit of 293 was calculated from the saponification index (I_s = 191.5) (5). The yields for transesterification are obtained directly from the area (A) of the selected signals:

$$Y\% = 100 \cdot (2A_1/3A_2) \tag*{[1]}$$

where A_1 and A_2 are the areas of the methoxy and the methyl-

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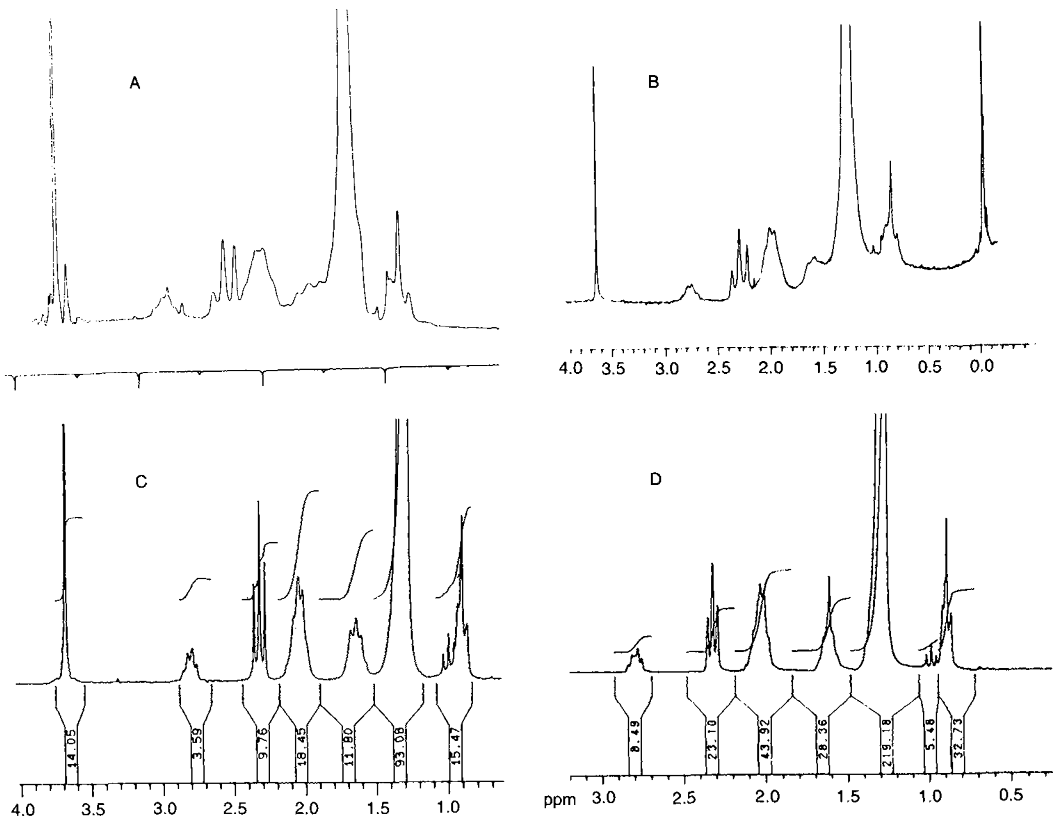

FIG. 1. Pulsed nuclear magnetic resonance spectra of rapeseed oil and methyl esters mix in $CDCl_3$; a) methyl esters at 80 MHz; b) oil and methyl esters at 100 MHz; c) methyl esters at 200 MHz; and d) oil at 250 MHz.

ene protons, respectively. Comparisons between the calculated and measured values are given in Table 1.

The agreement between the values calculated from the weights and those from the ^1H NMR spectra data is good; so, the rate of the transesterification reaction can be monitored, within 2% of error, on samples withdrawn from a reaction mixture.

Thus, without knowing the exact amount of the intermediary mono- and diglycerides, it is possible to determine the amount of methyl esters that formed in the transesterification of triglycerides with methyl alcohol; the precision is determined by the accuracy of the integration of NMR signals.

ACKNOWLEDGMENTS

Financial support from the Centre National de la Recherche Scientifique (C.N.R.S.), the European Community (contract C1I*-CT92-009) and ONIDOL (Paris) is gratefully acknowledged. Dr. A. Forestiere and G. Hillion (Institut Français du Pétrole) are acknowledged for providing chromatographic data.

TABLE 1
Comparisons of Simulated Yields from ^1H Nuclear Magnetic Resonance (NMR) Data

mmol Oil (mg)[a]	305 (89.5)	272 (79.8)	206 (60.4)	135 (39.7)	69 (20.3)	35 (10.3)	
mmol Methyl ester (mg)[b]	33.7 (9.9)	79 (23.2)	131 (38.4)	224 (66)	277 (81.5)	306 (90.1)	—[c]
Yield from weight (%)[d]	9.9	22.5	38.9	62.4	80.1	89.7	96.2[e]
Yield from NMR (%)[f]	9	22	39	62	80	90	96

[a] Rapeseed oil from Robbe (Compiègne, France); averaged molecular weight = 293 calculated from the saponifiaction index. The numbers in parentheses are mg.

[b] Methyl ester from a 2 × 45 mn transesterification for at 70°C with 15% excess of MeOH and 1% NaOH as catalyst; 98% of methyl ester from chromatographic data.

[c] Sample of methyl ester from the Institut Français du Pétrole (Solaize, France).

[d] 100 • [mmol methyl esters]/[(mmole methyl esters) + (mmole oil)].

[e] Methyl esters content estimated by chromatography; the sample contains 1.5 and 2.26% of residual mono- and diglycerides, respectively.

[f] Measured with an expanded scale between 4.0 and 2.0 ppm; according to the reproducibility of integration, values are given at ±2%.

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[Received January 5, 1995; accepted June 13, 1995]