Determination of Iodine Value in Ethylic Biodiesel Samples by ^{1}H-NMR

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Abstract: *An alternative method for the determination of iodine value in biodiesel samples obtained via ethylic route is proposed in this work. The method is based on the ^{1}H NMR spectra where areas of the hydrogen signals observed at specific chemical shifts are integrated. The results demonstrated that there is a good correlation between data obtained by the traditional method and ^{1}H NMR (r^2 = 0.9389 and r = 0.9691). The model was considered satisfactory and applicable to ethylic biodiesel samples obtained from different raw materials.*

Introduction

Petroleum derivatives, actual base of the world energy matrix, are causing serious problems to the environment, such as the increase of greenhouse effect.[1] As a potential alternative fuel source, biodiesel is currently being considered world-wide to be use in diesel cycle engines.[2,3] It can be produced by the chemical reaction of vegetable oils or animal fats with an alcohol in the presence of a catalyst, resulting in long chain fatty acid alkyl esters (biodiesel).[4,5,6] Glycerol is also obtained as a by-product.[7,8,9] Aiming its use as a fuel, the produced biodiesel must meet a series of physical-chemical specifications parameters established by the Brazilian Petroleum, Natural Gas and Biofuels Agency – ANP. Among them is the iodine value which indicates the unsaturation degree of the fuel, expressing its trend to oxidize.

The iodine value expresses the unsaturation degree of the fatty acid alkyl esters. The higher the iodine value, the more extensive is the unsaturation degree, meaning a higher number of double bonds in the biofuel.[10] The Resolution ANP 42/04 do not establishes limits for the iodine value of biodiesel samples but ask the producers to report it.[11] However, a high iodine value indicates a higher potential for biodiesel degradation, either through thermal oxidation or free radical attack. The traditional method for the determination of iodine value uses the methodology described by the American Oil Chemist Society – AOCS.[12]

A study using Hydrogen Nuclear Magnetic Resonance (^{1}H NMR) spectra of biodiesel samples produced through ethylic route was carried out in this work. The areas of the different types of hydrogens appearing at different chemical shifts in the spectra were integrated and treated mathematically. The

method studied was applied to biodiesel samples obtained from several vegetable oil seeds and animal fats in order to test its applicability.

Experimental

Samples

Biodiesel samples were obtained from commercial vegetable oil through transesterification reaction using ethanol as the alcohol source. The biodiesel was prepared by mixing together 54 mL of freshly prepared sodium ethoxide (54 mL of ethanol plus 30 mg of 0.1N NaOH) and 100 g of cottonseed oil previously heated to 65°C. Raw material was previously heated to melt when animal fat was used. The reaction was carried out under constant stirring during 40 minutes. The reaction mixture was heated up to 80°C for 15 min until complete ethanol evaporation. Hexane was added to extract the biodiesel phase. Then, the hexane was evaporated and the biodiesel recovered, dried in anhydrous sodium sulfate and characterized.

^{1}H NMR

Spectra were recorded on a Varian Mercury-300 spectrometer operating at 300 MHz at room temperature. The samples were diluted in deuterated chloroform ($CDCl_3$), in a concentration around 10% (v/v) of the biodiesel in 0.7 mL of $CDCl_3$ with a very small amount of TMS as internal reference standard in a 5 mm NMR tube. The spectrum was acquired using 16K data points, spectral width of 14 ppm, acquisition time of 3.6 s, 1.3 s of relaxation delay, 45º of pulse width and 16 scans. Total time for the acquisition of one spectrum was about 90 s.

Results and Discussion

Figure 1 shows a typical ^{1}H NMR spectrum of an ethylic biodiesel. A direct measure of the unsaturation degree of the samples is obtained from the ^{1}H NMR spectra by integrating the olefinic hydrogen signals between δ 5.40 and 5.26 ppm (**L**). The hydrogens from methyl groups are shown in the region between δ 0.50 and 1.00 ppm. The CH_2 protons of the ethoxy groups are observed in the region between δ 4.10 – 4.32 ppm of chemical shift (**R**).

Signals in the range of δ 0.5 – 2.8 ppm are due to the other methylenic hydrogens of the fatty acid ester chain (**M**).[12]

Total % of Ethyl Esters (%EE)

The calculation of the ethyl ester yield (%EE) was carried out, dividing the integral value of the area of the ethylic CH_2 group at δ 4.2 ppm of the ^{1}H NMR spectra by the integral area of the alpha CH_2 at 2.2 ppm and multiplying the result by 100.

The results are shown in Table 1, as well as the iodine values analyses performed according to methodologies recommended by ANP.[11]

From the ^{1}H NMR spectra it is possible to determine the iodine value of the samples according to the calculation demonstrated in following session.

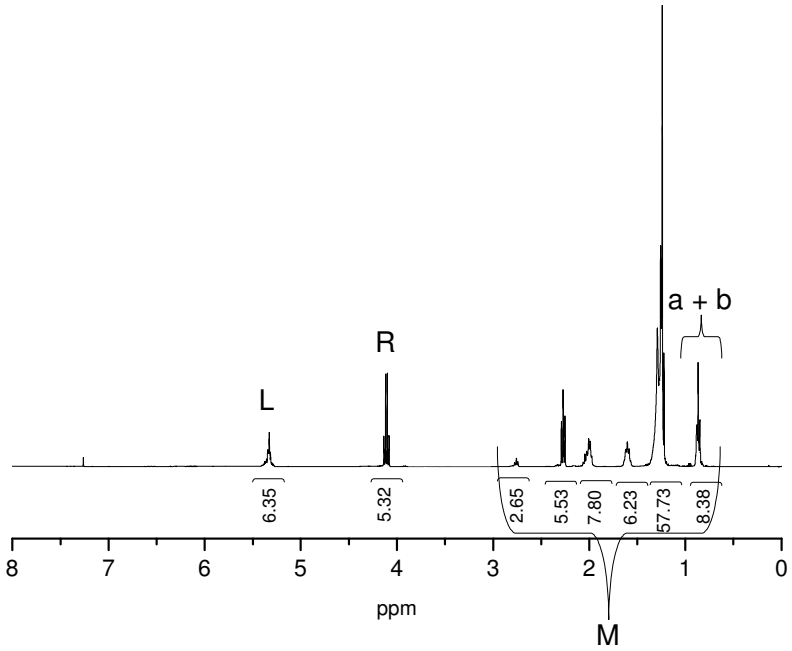

Figure 1. ^{1}H NMR spectrum of cottonseed ethylic biodiesel showing the areas of each signal.

Calculation of the Iodine Value:

From the ^{1}H NMR spectra the integral values at the chemical shift ranges designed as M, R and L (see Figure 1) are obtained. Therefore, it is possible to calculate the average molecular weight of the fatty acid ethyl esters that constitute the biodiesel samples as will be demonstrated below:

1) Firstly an average molecular formula which represents the ethyl esters present in the biodiesel samples and that will be used to calculate the average molecular weight (MW) is written in Eq. 1:

$$MW=C_2H_5(OCO)\text{-}(CH_2)_q\text{-}(CH=CH)_x\text{-}CH_3 \quad \text{(eq.1)}$$

where q and x represent the number of methylenes and olefinic groups present.

2) Substituting the respective atomic weights of all elements in Eq. 1, Eq. 2 is obtained:

$$MW = 88.106 + 14.026q + 26.038x \quad \text{(eq. 2)}$$

3) Calculation of the total number of hydrogens (T):

For the calculation of the total number of hydrogens the hydrogen number which appears in the general average formula of Eq.1, is substituted resulting in Eq. 3:

$$T = 5 + 2q + 2x + 3 \quad \text{(eq. 3)}$$

4) Calculation of the olefinic hydrogen number:

For the calculation of the olefinic hydrogen number, the number of hydrogens directly attached to the double bond carbons are estimated:

$$\sim(CH=CH)_x\sim \qquad O = 2x \qquad \text{(eq. 4)}$$

where O represents the olefinic hydrogen number.

From Equation 4, x can be obtained:

$$x = \frac{O}{2} \qquad \text{(eq. 5)}$$

5) Substituting 5 in 3:

$$T = 2q + O + 8 \qquad \text{(eq. 6)}$$

where T represents the total number of hydrogens.

Isolating q in Equation 6, Eq. 7 is deduced:

$$q = 0{,}5\, x\, (T - O - 8) \qquad \text{(eq. 7)}$$

6) Finally, substituting Eq. 7 and 5 into Eq. MW, Eq. 9 is obtained as a function of T and O:

$$MW = 88.106 + 14.026q + 26.038x \qquad \text{(eq. MW)}$$

$$MW = 88.106 + 14.026\,[0.5(T - O - 8)] + 26.038\left(\frac{O}{2}\right) \qquad \text{(eq. 8)}$$

$$MW = 31{,}999 + 7{,}013\, x\, (T) + 6{,}005\, x\, (O) \qquad \text{(eq. 9)}$$

7) Calculation of the area per hydrogen denominated *variable* **r**:

The area of one hydrogen is calculated dividing the area R of the signal at δ 4.2 ppm (which corresponds to the CH_2 of the ethoxy group) as in Equation 10:

$$r = \frac{R}{2} \qquad \text{(eq. 10)}$$

where R represents the integral value of the signal at δ 4.2 ppm.

8) Total number of hydrogens (T):

The total number of hydrogens is finally the sum of the integrals L, R and M, divided by r, as in Eq. 11:

$$T = \frac{L + M + R}{r} \qquad \text{(eq. 11)}$$

where T, L, M, R and r have been previously defined.

9) Calculation of the olefinic hydrogen number (O):

The olefinic hydrogen number O is obtained dividing the total area of the olefinic hydrogens L (at δ 5.2 ppm) by r (the area of one hydrogen) as in Eq. 12:

$$O = \frac{L}{r} \qquad \text{(eq. 12)}$$

10) Calculation of the iodine value (IV):

The iodine value I.V. of the biodiesel samples were calculated by means of Eq. 13:

$$I.V = \frac{126.904 \times r}{MW} \times 100 \qquad \text{(eq. 13)}$$

As an example, the method was applied to a cottonseed biodiesel whose ^{1}H NMR spectrum is shown in Figure 1.

1) Calculation of M:

For the calculation of M, the values of the integrals within the chemical shift range of 2.8 and 0.5 ppm of Figure 1 are summed up. Therefore, the value of M for the biodiesel cottonseed sample studied is:

M = 2,65 + 5.53 + 7.80 + 6.23 + 57.73 + 8.38

M = 88.32

2) From Figure 1 it is also possible to get the value of L directly from the integrated area at δ 5.2 ppm:

$$L = 6.35$$

3) The calculation of **r**, is then:

$$r = 5.32 \div 2 \quad r = 2.66$$

4) The calculation of the total number of protons (T) results:

$$T = (88.32 + 6.35 + 5.32)/ 2.66 = 37.90$$

5) The value O for the sample studied is calculated as Eq. 11:

$$O = 6.35 / 2.66 = 2.38$$

6) The average molecular weight (MW) is calculated by Eq. 9:

$$MW = 31.999 + 7.013\ (37.90) + 6.005\ (2.38)$$
$$MW = 312.0$$

7) Finally, it is possible to calculate the iodine value (I.V) applying Eq. 14:

$$I.V = \frac{126.91 \times (2.66)}{312.08} \times 100$$
$$I.V = 108.1$$

Table 1 shows that the iodine value obtained by the traditional AOCS method for the cottonseed biodiesel was 99.92, in good agreement with the value obtained by ^{1}H NMR calculated above. Other results presented in Table 1 indicate that the new method considered for the determination of the iodine value is applicable for biodiesel samples obtained from different raw materials.

The yield of the reaction for each biodiesel sample obtained from the ^{1}H NMR spectra is also shown in Table 1 (%EE) as well as the average molecular weight (MW) calculated for each biodiesel sample.

The results showed in Table 1 indicate that the iodine number obtained by the AOCS Cd 1-25 method correlate well with the ones obtained by ^{1}H NMR. Moreover, the AOCS iodine values were slightly lower than the values obtained by ^{1}H. The yields of the transesterification reaction were considered satisfactory as no values lower than 96% were obtained, demonstrating that the process proposed for the preparation of the biodiesel samples was efficient. Figure 2 shows a good linear correlation between the iodine values obtained from the traditional and ^{1}H-NMR methods:

$$y = 0{,}8948x + 7{,}1022$$

$$[r^2 = 0.9389; r = 0.9691]$$

This fact indicates that the ^{1}H NMR method is a reliable alternative for the determination of the iodine value for ethylic biodiesel samples.

Table 1. Comparison of the iodine values by the traditional AOCS method and ^{1}H NMR. Molecular weights (MW) and ethyl ester concentrations (%EE) obtained by NMR in biodiesel samples from different origins.

Biodiesel Samples	Iodine Value traditional AOCS method	Iodine Value ^{1}H-NMR	MW ^{1}H-NMR	%EE ^{1}H-NMR
Canola	100.0	97,7	325,3	98.2
Cottonseed	99.9	108,1	312,0	96.2
Soybean a1*	105.0	107,6	313,3	99.6
Soybean a2*	87.6	89,1	333,1	98.1
Soybean a3*	97.0	95,9	375,5	97.3
Sunflower	115.0	107,4	312,4	96.3
Corn	107.0	102,4	320,3	96.2
Chicken fat	83.0	85,9	346,3	96.1
Pig fat	71.0	70,6	449,3	96.5

* The three biodiesel samples were produced from three soybean oils samples randomly choosen and designed as: a1, a2 and a3 respectively.

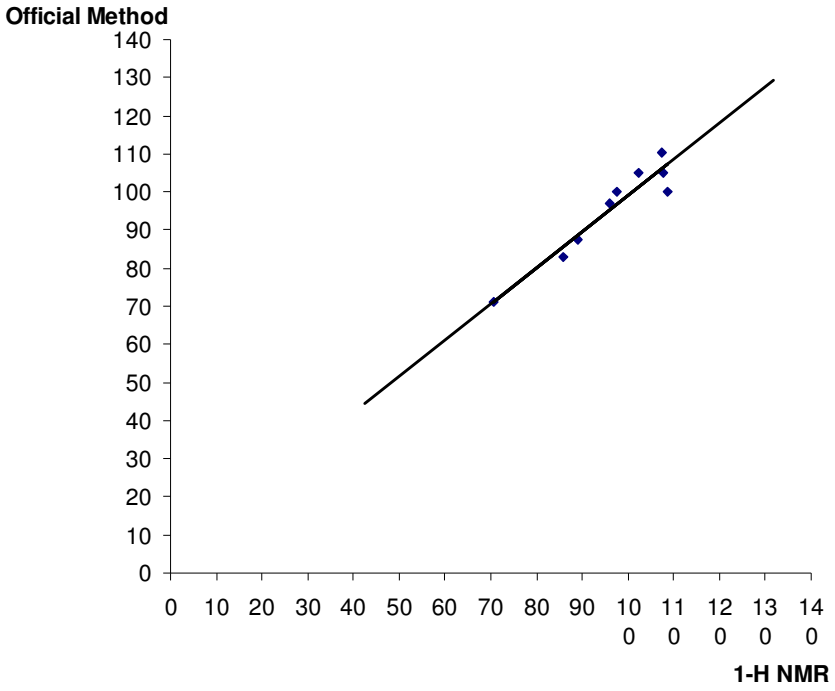

Figure 2. Correlation between official method and ^{1}H-NMR method for determination of iodine value.

Conclusion

The results of the iodine values obtained by ^{1}H-NMR showed good correlation with the classic method. Additionally, the ^{1}H-NMR method can be used also to calculate the average molecular weight of the fatty acid ethyl esters and the yield of ethyl esters produced in the transesterification reaction. The good sensitivity added to rapid results, makes the technique an useful tool for the evaluation of biodiesel samples obtained by the ethylic route.

References

1. Boehman, A. L. *Fuel Processing Technology* **86** (2005) 1057.

2. Hu, J.; Du, Z.; Tang, Z.; Min, E. *Ind. Eng. Chem. Res.* **43** (2004) 7928.

3. Ramadhas, A. S.; Muraleedharan, C.; Jayaraj, S. *Renewable Energy* **30** (2005) 1789.

4. Carraretto, C.; Macor, A.; Mirandola, A.; Stoppato, A.; Tonon, S. *Energy* **29** (2004) 2195.

5. Durán, A.; Lapuerta, M.; Rodríguez–Fernández, J. *Fuel* **84** (2005) 2080.

6. Felizardo, P.; Correia, M.; Joana, N.; Raposo, I.; Mendes, João. *Waste Management* **30** (2005) 1.

7. Ferrari, R. A.; Oliveira, V. S. da; Scabio, A. *Quím. Nova* **28** (2005) 19.

8. Gerpen, J. V. *Fuel Processing Technology* **86** (2005) 1097.

9. Schuchardt, U.; Sercheli, R.; Vargas, R. M. *J. Brazilian Chemical Society* **9** (1997).

10. Candeia, R. A.; Freitas, J. C. O.; Conceição, M. M.; Silva, F. C., Santos, I. M. G.; Souza, A. G. www.biodiesel.gov.br/docs/congressso2006/Armazenamento/AnaliseComparativa2.pdf (Access in August 2007).

11. ANP - National Agency of Petroleum. www.rbb.ba.gov.br/admin/upload/File/Resolucao ANP42, november 24, 2004.pdf (Access in August 2007).

12. A.O.C.S. – American Oil Chemist's Society – cd 1-25, AOCS, 1990.