Determining the iodine value without Wijs

For some years now there has been an activity on the SSERC website about the synthesis and testing of biodiesel [1].

Biodiesels are derived from plant oils and can be used as a cleaner, non-toxic alternative to diesel, though not entirely free from environmental problems. An important property of biodiesel is its chemical stability as this determines how long it can safely be stored and how it might deteriorate under extreme conditions [2]. One measure of the chemical stability of a biodiesel is its Iodine Value. The Iodine Value is a measure of the degree of unsaturation in the fuel - the higher the Iodine Value, the greater the degree of unsaturation and the higher susceptibility to oxidation [3]. More detailed information about biodiesel can be found from an American organisation, Brevard Biodiesel [4].

Iodine value

A common method to establish the Iodine Value is to treat the oil with excess Wijs solution. This contains iodine monochloride dissolved in ethanoic acid and reacts with the unsaturated part of the oil or fat, adding iodine to the molecule.

The greater the number of double bonds, the greater the amount of unsaturation, the less iodine there is left over. The unreacted iodine can then be determined by titration with a standard solution of sodium thiosulphate.

This method is reliable but the solution is expensive to buy ready-made and synthesising it in on site is quite hazardous due to its toxicity.

At SSERC we have developed a simpler, quicker and safer method: add a mixture of ethanolic iodine solution and water to the oil. The iodine and water react with the unsaturated part of the oil, the double bonds, adding iodine and an alcohol group to the molecule [5].

Equipment needed

Each group requires the following, the reagents will be sufficient for about 25 titrations:

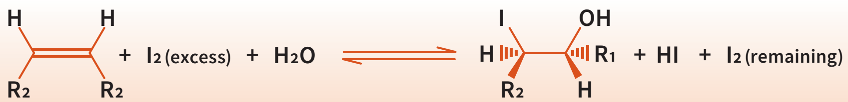
- Access to a 2 dp balance (3 dp or 4 dp balance would be even better).
- Burette.
- 400/500 cm³ conical flasks.
- 2 x 25 cm³ measuring cylinder.
- 1 x 250 cm³ measuring cylinder.
- Oil samples.
- 500 cm³ 96% Ethanol (IDA).
- 375 cm³ Propanol.
- 500 cm³ 0.1 mol l^{-1} Iodine solution in 96% ethanol.
- 1000 cm³ 0.1 mol l^{-1} sodium thiosulphate.*
- Freshly made 1% starch indicator solution.

*The thiosulphate solution should be standardised to determine the exact concentration.

Method

1) Prepare and titrate a blank solution as below but omit the oil. The blank titration only needs to be done once at the start of the experiment.
2) Accurately weigh 0.10-0.17 g of the oil sample into a clean 400 cm³ conical flask.

>>



Any iodine left unreacted is determined by titrating with sodium thiosulphate.

$$2Na_2S_2O_3 + I_{2\,(remaining)} \longrightarrow Na_2S_4O_6 + 2NaI$$

3) Add 15 cm^3 propan-1-ol to the flask and allow the oil to dissolve.
4) Add 20 cm^3 Iodine solution.
5) Add 200 cm^3 cold water (~10°C).
6) Cover with a watch glass and swirl the flask gently for 3-5 minutes.
7) Titrate the solution to a pale yellow colour and then add 2 cm^3 starch solution. Continue titrating to the milky white endpoint ensuring that the flask is well shaken to remove all traces of colour.

Troubleshooting

After the addition of the water a small amount of iodine vapour can be seen in the flask. This can be minimized by using cooled water (~10°C) and only swirling the solution very gently. A watch glass should be used to cover the flask. Any iodine vapour present will disappear as soon as the titration is started. Ensure the conical flasks are completely dry before use – any presence of water will affect the solubility of the oils in the initial stage.

Although ideally a pipette should be used to dispense the iodine solution, the high volatility of the ethanol makes this problematic (ethanol evaporates in pipette, increasing the vapour pressure which forces the solution out of the pipette). In this case it is easier and probably as accurate to use a 25 cm^3 measuring cylinder.

Calculation of the iodine value

2 titrations are carried out, a titration with the oil (T) and a titration without the oil (the blank, B). The difference between the titres in the blank and in the test sample, (B-T), gives the amount of $S_2O_3^{2-}$ equivalent to the I_2 absorbed by the oil.

See equation in next column.

Iodine value equation

Using the equation below we can calculate the mass of I_2 that reacts with 1 cm^3 $S_2O_3^{2-}$.

i.e. 1 cm^3 sodium thiosulphate ≡ a known mass of I_2.

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

Number of moles of $S_2O_3^{2-}$ in 1 cm^3 0.1 mol l^{-1} solution is

1/1000 x 0.100 = 0.0001 moles $S_2O_3^{2-}$

From the equation

2 moles of $S_2O_3^{2-}$ reacts with 1 mole of I_2

Therefore

0.0001 moles of $S_2O_3^{2-}$ reacts with 0.0001/2 = 0.00005 mole of I_2

Mass of I_2 is given by

No of moles = mass I_2/molecular mass of I_2

mass I_2 = no of moles x molecular mass of I_2

= 0.00005 x 254= 0.0127 g

Therefore

1 cm^3 $S_2O_3^{2-}$ reacts with 0.0127g I2

Iodine Value is expressed as a number per 100 g oil

Iodine value = (B-T) x (0.0127) x 100/W

Where

B = blank titre of sodium thiosulphate solution (i.e. no oil present)

T= sample titre of sodium thiosulphate solution

((B-T) gives the amount of $S_2O_3^{2-}$ equivalent to the I_2 absorbed by the oil)
0.0127 is the calculated mass of iodine per cm^3 0.1 mol l^{-1} thiosulphate

W= mass in grams of sample of oil. 100 is used because the Iodine Value is expressed as a number per 100 g of the oil.

Results

Oil	Iodine Value Experimental	Iodine Value range
Olive	91	75-94 [8]
Rapeseed	117	105-126 [7]
Sunflower	129	118-141 [7]
Walnut	135	132-162 [9]

References

[1] https://www.sserc.org.uk/subject-areas/chemistry/chemistry-resources/biodiesel/.
[2] http://www.brevardbiodiesel.org/iv.html.
[3] T.H. Sanders, "Groundnut Oil" Encyclopedia of Food Sciences and Nutrition (2nd Edition), 2003.
[4] http://www.brevardbiodiesel.org.
[5] Aricetti J., Maciel A., Lopes O., Tubino M., "A Simple Green Method for Biodiesel Iodine Number Determination", *Journal of ASTM International*, 2010, **7**, No 1.
[6] Orsavova J., Misurcova L., Ambrozova J., Vicha R. and Mlcek J., "Fatty Acids Composition of Vegetable Oils and Its Contribution to Dietary Energy Intake and Dependence of Cardiovascular Mortality on Dietary Intake of Fatty Acids", *Int. J. Mol. Sci.* 2015, **16**, pages 12871-12890.
[7] Morin J-F. and Lees M., *FoodIntegrity Handbook*.
[8] Simurdiak M., Olukoga O. and Hedberg K., "Obtaining the Iodine Value of Various Oils via Bromination with Pyridinium Tribromide", *Journal of Chemical Education* 2016, **93(2)**, pages 322-325.
[9] R.B.N. Prasad, *Encyclopedia of Food Sciences and Nutrition* (2nd Edition), 2003, pages 6071-6079.