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.

\[ 2 \text{Na}_2\text{S}_2\text{O}_3 + \text{I}_2(\text{remaining}) \rightarrow \text{Na}_2\text{S}_4\text{O}_6 + 2\text{NaI} \]
Iodine value equation
Using the equation below we can calculate the mass of \( I_2 \) that reacts with 1 cm\(^3\) S\(_2\)O\(_3^2^{-}\).

\[
\text{Iodine Value} = \frac{(B-T) \times 0.0127 \times 100}{W}
\]

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\(_2\)O\(_3^2^{-}\) 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 solution
- \( W \) = 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

<table>
<thead>
<tr>
<th>Oil</th>
<th>Iodine Value Experimental</th>
<th>Iodine Value range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Olive</td>
<td>91</td>
<td>75-94 [8]</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>117</td>
<td>105-126 [7]</td>
</tr>
<tr>
<td>Sunflower</td>
<td>129</td>
<td>118-141 [7]</td>
</tr>
<tr>
<td>Walnut</td>
<td>135</td>
<td>132-162 [9]</td>
</tr>
</tbody>
</table>

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 (\(\sim -10^\circ\text{C}\)) 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\(_2\)O\(_3^2^{-}\) equivalent to the I\(_2\) absorbed by the oil.

See equation in next column.