Tallow Quality Testing

An introductory guide

Commodity Inspection Services

Titre of Tallow

Titre is the solidification point of the mixed fatty acids of which tallow is comprised. In simple terms it reflects the hardness or softness of the tallow. Hard fats contain more saturated fatty acids while soft fats and oils have a higher unsaturated component. The titre test can give an indication of the species origin of the tallow, for example, approximate Titre values for the three main species are:

Ovine:	42 – 45 Degrees Celsius
Bovine:	40 – 42 degrees Celsius
Porcine:	36 – 40 Degrees Celsius

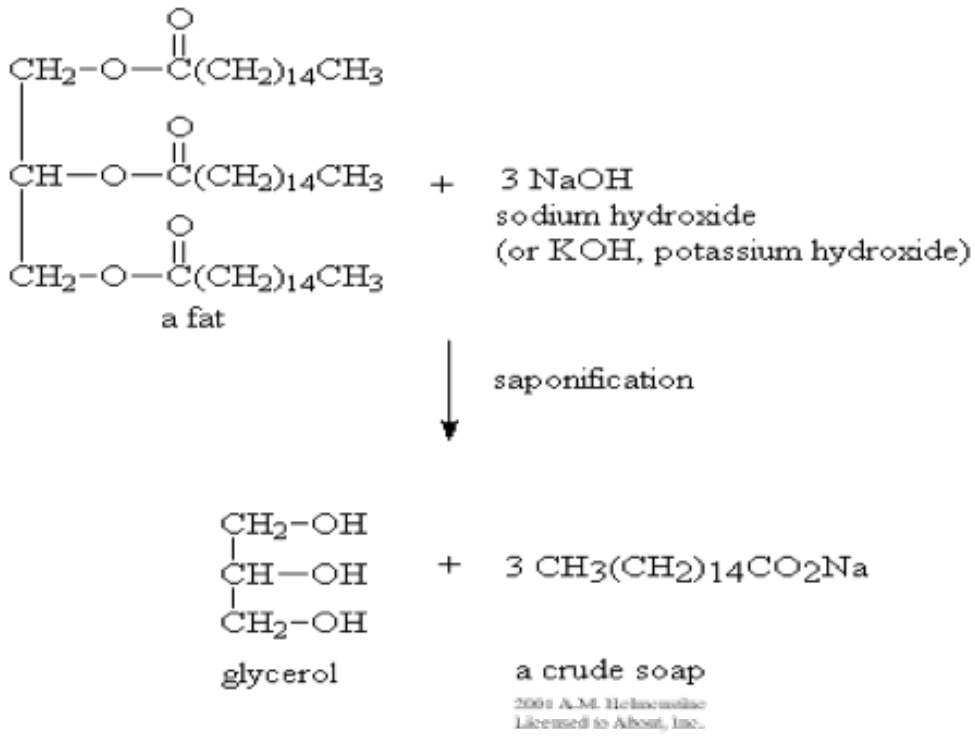
The test can also provide an indication of whether tallow has been contaminated with a vegetable oil or other soft oil.

How:

Titre is determined firstly by completely saponifying the tallow with a solution of potassium hydroxide dissolved in glycerol. The soap mixture is then treated with a strong acid (sulphuric) splitting off the free fatty acids. It is then washed with water to remove any free soluble soap and glycerol followed by drying to remove any excess moisture. The free fatty acid is then placed in a titre test tube with a thermometer and stirred uniformly whilst being cooled. When the fatty acid starts to go cloudy the temperature will rise slightly until it reaches a peak. This is the titre value.

Titre of Tallow

Example of the saponification process of a fat with sodium hydroxide is shown below:



Example of the saponification process of a fat with sodium hydroxide is shown below:

The crude soap is then treated with sulphuric acid to yield:
CH3(CH2)14CO2Na + H2SO4 → CH3(CH2)14CO2H (free fatty acid) + Na+(aq) + HSO4-(aq)

Purpose

In the tallow industry, the titre value is of great importance as the hardness of the fat will have a direct relationship with the hardness of the product in which it is to be used, be it margarine, shortening, candles or soaps to name a few. The titre test can give an indication of the species origin of the tallow.

Free Fatty Acid (FFA)

Tallow is comprised of a mixture of long chain fatty acids combined with glycerol to form triglycerides. Chemical change can take place by way of hydrolysis, oxidation or bacterial and enzymatic attack giving rise to quality issues.

Hydrolytic Rancidity

Hydrolytic rancidity occurs when water splits fatty acid chains away from the glycerol backbone in triglycerides (fats). The chemical term is ester hydrolysis. Usually this hydrolysis process goes unnoticed, since most fatty acids are odorless and tasteless. When, however, the triglyceride is derived from short chain fatty acids, the released carboxylic acid can confer strong flavors and odors. A particular problem arises with butter, which contains triglycerides with a high content of butyric acid derivatives.

Hydrolytic rancidity leads to increased FFA resulting in higher losses on refining and thus reducing the value of the product.

Oxidative Rancidity

Oxidative rancidity is associated with the degradation by oxygen in the air. Via a free radical process, the double bonds of an unsaturated fatty acid can undergo cleavage, releasing volatile aldehydes and ketones. The presence of these and other compounds in the tallow results in off flavours and odours which can cause consumer acceptance and palatability problems in food and animal feed applications. This process can be suppressed by the exclusion of oxygen or by the addition of antioxidants. Oxidation primarily occurs with unsaturated fats.

Free Fatty Acid (FFA)

Microbial Rancidity
Microbial rancidity refers to a process in which microorganisms, such as bacteria, produce enzymes such as lipases which break down fat.

The FFA test is a measure of the hydrolytic rancidity in fats. During hydrolysis, one or more of the fatty acid chains can be detached from the glycerol. The detached fatty acid is Free Fatty Acid (FFA). The hydrolysis of triglycerides in rendering is accelerated by the presence of bacteria in raw material and in finished product. From bacteria, fat splitting enzymes are produced which accelerate hydrolysis. It is important that the time between slaughter and rendering is kept to a minimum and that fines and other matter which might harbour micro organisms are removed from the tallow as completely as possible before storage.

How:
FFA is obtained by direct titration with standard alkali (sodium hydroxide). The tallow is firstly dissolved in neutralized isopropanol with the aid of a hotplate. The amount of FFA in the sample is determined from the volume of standard alkali required to neutralise the tallow. Phenolphthalein indicator is used to determine the end-point (pink) of the titration.

Chemistry:
Example of a free fatty acid reacting with a standard alkali (sodium hydroxide):
$CH_3(CH_2)_{14}CO_2H$ (free fatty acid) + $NaOH \rightarrow CH_3(CH_2)_{14}CO_2Na + H_2O$

Purpose:
FFA is a basic quality parameter for fats and oils. It is used to calculate expected refining yields. When refining, the free fatty acids are removed and form part of the “refining losses”. The higher the FFA, the higher the losses and the lower is the value of the tallow.

FAC

The natural colour of tallow is pale yellow which results from the presence of carotenoid compounds. However the colour of the finished product may be altered by the presence of other compounds and by the way in which the product is treated. For example, a greenish colour can be imparted to tallow by the presence of chlorophyll derived from grass in paunch material. In better quality tallow of light colour, paunch contents will have been washed away before processing. However, overheating during processing or rapid and/or prolonged heating in storage can cause scorching and fixing of some of the natural pigments onto the molecular structure of the tallow. Carotenoids and other pigments darken to produce a red-brown colour which is extremely difficult if not impossible to remove effectively by bleaching.

FAC is specified in AOCS Official Method Cc 13a-43 as a single numbered colour scale and is approved by the Fat Analysis Committee of the American Oil Chemist Society. It is a test for the determination of the Raw Colour of Fats. The scale includes 26 colour standards designated by odd numbers from 1 to 45. They are divided into 5 groups:
Scale 1 – 1, 3, 5, 7 and 9 (light coloured tallow)
Scale 2 – 11, 11A, 11B and 11C (predominately yellow tallow)
Scale 3 – 13, 15, 17 and 19 (dark fats with a red cast)
Scale 4 – 21, 23, 25, 27 and 29 (dark fats, predominately green)
Scale 5 – 31, 33, 35, 37, 39, 41, 43 and 45 (very dark fats, predominately red)
The FAC colour is reported as “not darker than” the higher of the two colours between which the sample falls.

How:
FAC colour can be determined in two ways:

- Lovibond 3 – Aperture Comparator or,
- Lovibond PFX880 Tintometer (Instrument currently used by CIS)

FAC

Lovibond 3 – Aperture Comparator
The Aperture Comparator is used for visually determining the FAC colour of sample with the use of coloured glass standards. The sample and two adjacent standards are view simultaneously. The two standards are set to two limiting colours to determine whether the sample is within tolerance.

Lovibond Tintometer
The Tintometer determines the FAC colour of tallow automatically. The operator only needs to select operating parameters.

Purpose:
The FAC colour test is important as it provides a guide to raw material quality, processing control and storage and handling care.

Moisture

Moisture is a term used to describe the amount of water in the tallow.

How:
Moisture is determined by measuring the loss of weight upon heating the sample at 110˚C. Moisture is expressed as a percentage.

Purpose:
Pure tallow is moisture free, however as water is used in its processing a small amount is usually present in the finished product. The level of moisture in the tallow is dependent on the efficiency of washing and clarifying procedures used after rendering. High levels of moisture are detrimental to the quality of tallow as they accelerate the rate of hydrolysis and oxidation.

Insoluble Impurities

Insoluble impurities are materials that are suspended in the tallow. They usually consist of a combination of tissues, protein fines, finely grounded bones, hair and manure.

How:
Insoluble impurities are determined by dissolving the tallow in kerosene and vacuum filtering the fatty solution to leave behind the impurities. The weight of this is recorded to determine the percentage of impurities per weight of sample.

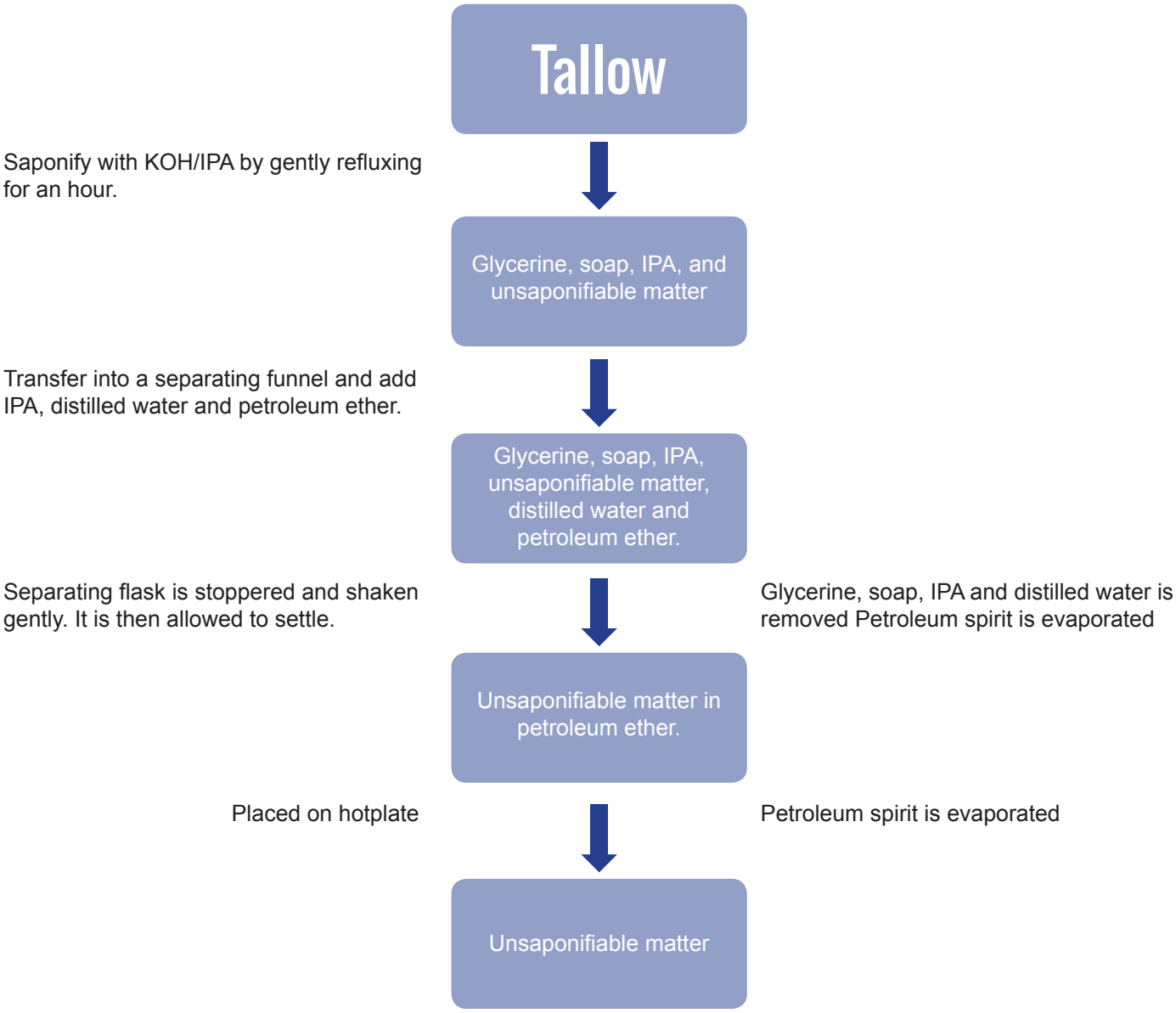
Purpose:
Insoluble impurities are harmless when dry. However when wet, they can support hydrolysis of triglycerides which in turn, form free fatty acids. The formation of free fatty acid reduces the quality and value of tallow.

Unsaponifiable Matter

Unsaponifiable matter are substances which might be found dissolved in tallow and which cannot be saponified by caustic treatment. Unsaponifiable matter can include high aliphatic alcohols, sterols, pigments and hydrocarbons.

Purpose:
The unsaponifiable matter test determines the amount of material that can not be converted into soap. Soap manufacturing is one of the most common uses of high grade tallow. Therefore this test is a way of determining the yield of soap that can be made from a sample of tallow.

Unsaponifiable Matter



Bleach

Bleached colour is a measure of the amount of pigmentation in the raw material.

How:
Bleached colour is measured after any free fatty acids have been neutralised with sodium hydroxide. The resulting soap is removed by filtration while the neutralised fat is bleached with a standard bleaching earth. After five minutes the bleaching earth is removed by gravity filtration and the tallow is then placed into a Lovibond Tintometer which uses a combination of standard of red, yellow and blue colour that can be superimposed to match the tallow colour.

Purpose:
The bleach test provides a measure of whether tallow can be successfully bleached to the required colour by the end user in his process.

In soap making, tallow is usually bleached before it is saponified therefore highly coloured tallow requiring extensive bleaching can result in product loss as product will be discarded along with spent bleaching earth. Tallow with high residual colour after bleaching can only be used in low value products such as laundry soaps, while those with low residual colour are used in the more valuable white hand soap.

Iodine Value (IV)

IV is a measure of the degree of unsaturation in tallow and is inversely related to titre.
IV measures the amount of iodine (in grams) that will react with 100 grams of tallow. There is no reaction of iodine with saturated fat, iodine will only react with the unsaturated part of the tallow. Hard fats with a high percentage of saturation will have low iodine values and a high titre and alternately, softer or more unsaturated fats will have a higher IV and lower titre.

Iodine Value is inversely related to Titre.

That is:

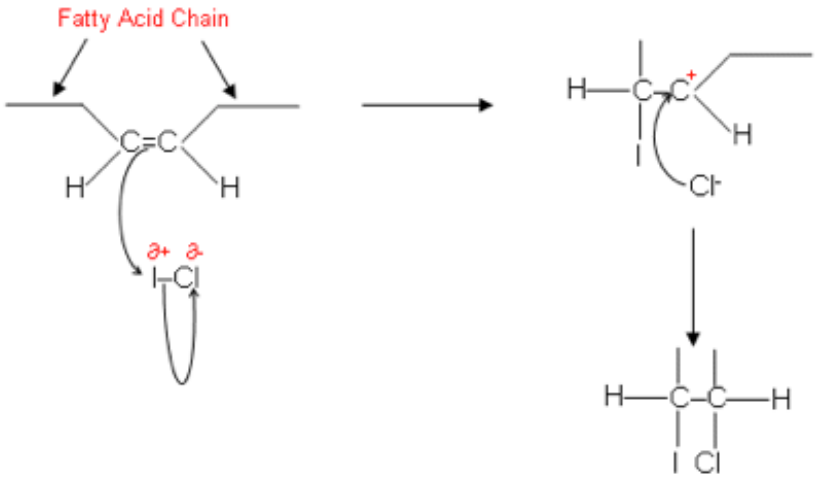
- MORE Iodine →MORE unsaturation→ LOWER solidification → LOW Titre value →SOFT TALLOW
- LESS Iodine → LESS unsaturation → HIGHER solidification → HIGH Titre value→ HARD TALLOW.

How:
IV is obtained by firstly dissolving a weighed sample of tallow in a solvent such a cyclohexane and glacial acetic acid. This solvent is used to allow for the reaction to take place. Next, the tallow is reacted with an excess solution of iodine monochloride in glacial acetic acid (also know as Wij's solution) for 30 minutes. Water is added at completion to dilute the solution. Potassium iodine solution is then added to remove any excess iodine monochloride. This resulting sample is then titrated with standard sodium thiosulphate to determine the IV.

Iodine Value (IV)

Chemistry

Example of the unsaturated part of the tallow reacting with Wij's solution:



Purpose

High IV tallow is more reactive, less stable, softer and more susceptible to oxidation and rancidity. Similarly to Titre, IV can be used as a guide to the species origin of the tallow and to the possible presence of contamination with vegetable oil or other soft oil products.

Peroxide Value (PV)

Peroxide value is used as an indicator of the extent of oxidation due to peroxide formation. It is affected by the age of the product, the quality of the raw material as well as processing, storage and transport conditions.

Oxidation takes place through a number of processes in the presence of factors such as heat, fines, metal ions, oxygen and light. Hydroperoxides are formed from the unsaturated fats and a chain reaction starts. Initially, they are formed at a steady rate, which then accelerates rapidly, before slowing down and eventually ceasing, as the peroxides decompose. During the initial stages, the Peroxide Value (PV) of the fat will increase until the reaction terminates, after which it will reduce as other compounds are formed.
The peroxides decompose into a large number of other compounds, including aldehydes, ketones and aromatics, many of which are responsible for off flavours and odours associated with rancidity.

How and Chemistry:
PV is obtained by firstly dissolving a weighed sample of tallow in a solvent of acetic acid and iso-octane. This solvent is used to set an ideal condition for the reaction to take place. Peroxides and other oxidising material react with the iodide (when potassium iodide is added) to liberate iodine. The reaction is then stopped by diluting the mixture with deionised water. The amount of liberated iodine is measured by titrating with sodium thiosulphate. The amount of iodide liberated is expressed as milli-equivalents (meq) of peroxide per 1000g of sample.

Purpose:
PV is used as an indicator of oxidation due to peroxide formation. It can also be used to determine the stability of fats in tests designed to measure the rate at which a fat oxidises. Peroxides in oxidised fats are unstable and are themselves oxidised to other compounds. Fresh fats will have a peroxide value of one to two while rancid fats will typically have a peroxide value of 15 to 20. The PV test measures only peroxide formation. For other compounds resulting from oxidation, alternative tests are required.

Saponification Value

The saponification value is the number in milligrams of potassium hydroxide required to saponify one gram of fat. It is a measure of the average Molecular Weight (or chain length) of all the fatty acids present in the fat. Tallow or oil with predominantly long chain fatty acids have lower Saponification values compared to those containing predominantly shorter chain fatty acids such as the lauric oils.

How:
A sample of tallow is refluxed in potassium hydroxide and iso-propanol solution until the tallow is saponified. Once reflux has been completed, a few drops of phenolphthalein indicator is added and titrated with 0.5N HCl until the pink colour just disappears.

Chemistry:
Example of a fatty acid salt reacting with an acid (hydrochloric):
$CH_3(CH_2)_{14}CO_2K$ (pink) + HCl → $CH_3(CH_2)_{14}CO_2H$ (free fatty acid, colourless) + KCl

Purpose:
The saponification number is of great importance to soap-makers. It provides information concerning the character of fatty acids, in particular the solubility of the resulting soap in water.

Polyethylene Content

Polyethylene in tallow can result from contamination of raw material by items such as plastic bags and livestock ear tags.

The level of polyethylene in tallow is a concern to soap-makers, fatty acid distillers and other users such as biodiesel manufacturers. Polyethylene contamination may lead to discolouration in soaps on drying, as particles may be burnt or charred causing black specks in the finished product. Damage to plant equipment can also occur from solidification of polyethylene particles which can build up in valves and on pipes and other equipment. The level of polyethylene in tallow should be less than 50ppm, but ideally zero.

How and Chemistry:

The tallow is firstly dissolved in a H2SO4/Isopropanol solution. Chloroform is added to separate the polyethylene and any other insoluble matter from the tallow. This is then filtered. To ensure that only polyethylene is collected, the filter paper is dissolved with tetrachloroethylene and any other insoluble matter is removed by vacuum filtration. The polyethylene is then crystallized in cold methanol. The residue is washed, dried and weighed.

Rate of Filtration

Microscopic fines suspended in tallow can cause difficulty in production of soap. Excessive fines can be a result of improper production processes or inadequate settling.

Tallow which will give processing difficulty in slow filtration can be identified by the Rate of Filtration method.

How:
A sample of fat is heated and then filtered at a constant temperature for five minutes. The volume of the filtrate is measured and the rate of flow is determined.

Slip Melting Point - Capillary Tube Method

Tallow does not have a sharp melting point unlike other pure chemical substances due to being made up of a complex mixture of glycerides. The slip melting point of fats is defined as the temperature at which a column of fat in an open capillary tube moves up in the tube when it is subjected to control heating in a water bath.

How:

A capillary tube containing a column of fat which has been crystallized under controlled conditions is immersed to a specified depth in water. The temperature is increased at the rate of 0.5˚C per minute. The temperature at which the column of fat begins rising in the capillary tube is recorded as the slip melting point.