A great discussion of olive oil chemistry by Guido Costa in simple terms

Herewith my contribution on FATTY ACIDS AND ACIDITY: Olive oil is composed mainly of triacylglycerols (triglycerides). Chemically speaking, these are molecules derived from the natural esterification of three fatty acid molecules with a glycerol molecule. The glycerol molecule can simplistically be seen as an "E-shaped" molecule, with the fatty acids in turn resembling longish hydrocarbon chains, varying (in the case of olive oil) from about 14 to 24 carbons atoms in length. Thus the triacylglycerols can, for our purpose, be visualized as elongated E-shaped molecules, each with three long extensions, being the three fatty acid chains "attached to each horizontal bar of the E".

Please note that we are dealing here with fatty acids forming part of the triacylglycerols molecule. They are distinct from FREE FATTY ACIDS, which we'll talk about later!

Various fatty acids are found in nature. They differ in length (number of carbon atoms in the chain) as well as in the type of chemical bonds found within the chain. Mostly these carbon-carbon bonds in the chain are "single" bonds, comprising 2 electrons shared between adjacent carbon atoms. However, in certain of the fatty acids, some of the bonds are "double bonds", where 4 electrons are shared between adjacent carbon atoms. The fatty acids that have no double bonds in their chains are called "saturated" fatty acids (all the carbons in their carbon chain are "saturated" by hydrogen atoms). Examples of saturated fatty acids are Palmitic Acid (16 carbons long), Stearic Acid (18 carbons long) and Arachidic Acid (20 carbons long). The fatty acids that have one carbon-carbon double bond somewhere along their length are called monounsaturated fatty acids (one carbon-carbon bond which is not fully saturated with hydrogens), i.e. one of the bonds available at each of 2 adjacent carbons is now used to form a double bond between themselves instead of being used to bond externally to hydrogen atoms. Examples of monounsaturated fatty acids are Palmitoleic Acid (16 carbons long) and our famous Oleic Acid (18 carbons long). Oleic acid is the most abundant fatty acid found in nature. The double bond in Oleic acid occurs in the mid position of the molecule, between carbon 9 and carbon 10.

I don't want to make this sound too complicated, but as soon as one brings a double bond into the picture, one must bear in mind that, unlike the single bonds (wherein the molecular chain has complete rotational freedom of movement in the bond axis), the double bond is a rigid bond insofar as it does not allow rotation around its longitudinal axis. Thus, with each double bond, one introduces what are called isomers. These have the same chemical structure, but different stereochemistry. In other words, the shape of the molecule differs, and so does its chemical reactivity (and effect on health). This leads to things like "trans" fatty acids (TFA's) and "cis" fatty acids (CFA's). Trans fatty acids are normally produced when oils are artificially and chemically converted into margarines. They are said to raise LDL's (the "bad" cholesterol) and lower HDL's (the "good" cholesterol), and are thus to be avoided. Oleic acid is a cis fatty acid, and more specifically a cis monounsaturated C18 acid. Cis means the rest of the chain is "on the same side" of the bond axis as the carbon chain prior to the double bond, and trans means "on opposite sides" of the bond axis. Wow, is there anyone still reading this!?

Well, we're not yet finished. Now for polyunsaturated fatty acids. If you've understood the above, they're a simple extension - just more than one double (unsaturated) bond along the length of the fatty acid carbon chain. In olive oils the maximum number of double bonds per fatty acid is three, whereas one can get up to six unsaturated double bonds in certain fatty acids derived from fish. Generally, however, the greater the number of double bonds in the fatty acid, the more unstable, and more easily broken down by heat, light, etc. That's why olive oil, made up predominantly of monounsaturated Oleic Acid, is so much more heat-stable than the highly polyunsaturated seed oils. Olive oil can, for example, be re-used substantially more often in frying than other seed oils (including canola, which has about three times the amount of polyunsaturation than olive oil). An example of a polyunsaturated fatty acid with two unsaturated double bonds along its carbon chain is Linoleic Acid (18 carbons long). Linolenic Acid has three double bonds in its carbon chain, and is also 18 carbons long.

Triacylglycerols are normally composed of a mixture of three of the some of the above-mentioned fatty acids. Most prevalent in olive oil is the oleic-oleic-oleic (OOO) triacylglycerol, followed, in order of incidence, by palmitic-oleic-oleic (POO), then oleic-oleic-linoleic (OOL), then palmitic-oleic-linoleic (POL), then stearic-oleic-oleic (SOO), etc.

Now lets look ACIDITY, which is probably the most fundamental quality measurement of an edible oil.

As we know, freshly pressed oil, made from sound, healthy, freshly picked olives, normally has a pretty low "acidity", in the order of well under 0,5%. This "acidity" is the result of a degree of breakdown of the triacylglycerols due to a chemical reaction called hydrolysis, in which free fatty acids are formed. (In exceptional circumstances, even oils made from fresh, healthy olives can have significant amount of acidity, caused by anomalies during the actual biosynthesis of the oil in the olive fruit). Once the oil has been extracted, however, carelessness can lead to a very significant further breakdown of the triacylglycerides into fatty acids - these "broken off" fatty acids being called FREE FATTY ACIDS. Sometimes just one of the three fatty acids breaks off, leaving a diacylglycerol. If two fatty acids break off a certain triacylglycerol, we're left with a monoacylglycerol. If all three break off, we're left with glycerol.

Factors which lead to a high free fatty acidity in an oil are: fruit fly infestation of fruit, delays between harvesting and extraction, especially if the fruit has been bruised or damaged during harvesting, fungal diseases in the fruit (gloesporium, macrophoma, etc.), prolonged contact between oil and vegetation water (after extraction), etc. Thus we see that the traditional way in which olives are/were stored in heaps/silos to encourage enzymatic breakdown of cell structure so as to facilitate oil release (as practiced in Portugal, etc.) is certainly not conducive to producing a high quality, low acid oil.

The free fatty acidity is thus a direct measure of the quality of the oil, and reflects the care taken right from blossoming and fruit set to the eventual sale and consumption of the oil.

Measurement of FFA (free fatty acidity) is a very simple procedure. The principle is based on dissolving the free fatty acids present in a carefully weighed sample of oil into a mixture of solvents (usually alcohol/peroxide-free ether), and then titrating, with constant stirring, against a standard alkali solution (usually standardized Potassium Hydroxide) in the presence of an acid/base indicator (usually phenolpthalein). The results are presented as grams Oleic Acid per 100 grams oil, commonly known as the free fatty acidity (ffa or acidity) of the oil (in %).