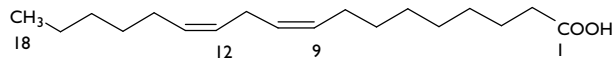


What are Fatty Acids and their Derivatives?

Fatty acids are the main constituents of oils and fats, whose applications are overwhelming. They possess a simple structure consisting of a long hydrocarbonate chain and one or more carboxylic groups. The broadest definition includes all chain lengths, but most natural fatty acids are C_4 to C_{22} , with C_{18} most common. The simplest fatty acids are referred to as saturated fatty acids. They have no unsaturated linkages and cannot be altered by hydrogenation or halogenation. When double bonds are present, fatty acids are said unsaturated, monounsaturated (MUFA) if only one double bond is present and polyenoic (or polyunsaturated fatty acids = PUFA) if they have two or more double bonds generally separated by a single methylene group (methylene-interrupted unsaturation). Some uncommon polyunsaturated fatty acids have two adjacent double bonds separated by more than one methylene group; they are named polymethylene-interrupted fatty acids (Fig. I.1). Systematic names for fatty acids are too cumbersome for general use, and



shorter alternatives are widely used. A general way to describe these compounds is using two numbers separated by a colon, which give, respectively, the chain length and number of double bonds: octadecenoic acid with 18 carbons and 1 double bond is therefore 18:1 (Table I.1). The position of double bonds is indicated in a number of ways: explicitly, defining the position and configuration; or locating double bonds relative to the methyl end shown as $n-x$ or ωx , where x is the number of carbons from the methyl end. Another way to indicate the position of double bond is using Δx , which designated the number of carbons from the carboxyl end. Nowadays, the $n-x$ or ωx designation is preferred [1].

Physically, most of these fatty acids are liquid at room temperature. The different properties are to a large extent related to saturation or unsaturation presence. Generally, solid fats are indicated by a dominance of saturated fatty acids and liquid oils are evidence of a high level of unsaturated fatty acids [2].

Table I.1

Nomenclature and structure of common fatty acids.

Fatty Acid	Common Name	Formula
4:0	Butyric	$\text{CH}_3(\text{CH}_2)_2\text{CO}_2\text{H}$
6:0	Caproic	$\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}$
8:0	Caprylic	$\text{CH}_3(\text{CH}_2)_6\text{CO}_2\text{H}$
10:0	Capric	$\text{CH}_3(\text{CH}_2)_8\text{CO}_2\text{H}$
12:0	Lauric	$\text{CH}_3(\text{CH}_2)_{10}\text{CO}_2\text{H}$
14:0	Myristic	$\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{H}$
16:0	Palmitic	$\text{CH}_3(\text{CH}_2)_{14}\text{CO}_2\text{H}$
18:0	Stearic	$\text{CH}_3(\text{CH}_2)_{16}\text{CO}_2\text{H}$
18:1 9c	Oleic	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{CO}_2\text{H}$
18:2 9c12c ¹	Linoleic	$\text{CH}_3(\text{CH}_2)_4(\text{CH}=\text{CHCH}_2)_2(\text{CH}_2)_6\text{CO}_2\text{H}$
18:3 9c12c15c ¹	α -Linolenic	$\text{CH}_3\text{CH}_2(\text{CH}=\text{CHCH}_2)_3(\text{CH}_2)_6\text{CO}_2\text{H}$
22:1 13c ¹	Erucic	$\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_{11}\text{CO}_2\text{H}$
20:5 5c8c11c14c17c ¹	EPA ²	$\text{CH}_3\text{CH}_2(\text{CH}=\text{CHCH}_2)_5(\text{CH}_2)_2\text{CO}_2\text{H}$
22:6 4c7c10c13c16c19c ¹	DHA ²	$\text{CH}_3\text{CH}_2(\text{CH}=\text{CH}(\text{CH}_2)_6\text{CH}_2)_2\text{CO}_2\text{H}$

¹c stands for cis double-bond geometry.²Abbreviations of the systematic names eicosapentaenoic acid and docosahexaenoic acid

Sources of fatty acids and their derivatives

Most of fatty acids are obtained from the hydrolysis of hard animal fats (tallow), coconut, palm kernel and soybean oils and from the fractional distillation of crude tall oil (a byproduct of Kraft pulping of pine wood). Other fatty acids are derived from petroleum [3]. Over the years, the production of edible oil fats and oils has soared, with vegetable sources now dominating the field formally held by butter and lard. In 1950 the food fat marketed in United States was split approximately equally between animal fats (lard, tallow and butter) and edible vegetable oils. Twenty years later in 1970, edible vegetable oils accounted for three-fourths of the total and

animal fats only one-fourth. Vegetable oils became dominant mainly because of competitive pricing for vegetable oil, increased hydrogenation capacity, consumer preference shifts from butter to margarine, and nutritional concerns regarding cholesterol and saturated fats [4].

Significant amounts are encountered in the oils and fats of commercial importance, as it is shown in Table 1.2. Regarding linoleic acid and linolenic acid, specifically, alpha-linolenic acid, their dietary oil sources are listed below. Note that fish oil is not the only source of omega-3 acids, since flaxseed contains also an important relative amount [5-9].

Linoleic Acid (Omega 6 family)

- Safflower
- Sunflower
- Corn
- Soya
- Evening primrose
- Pumpkin
- Wheat germ

Alpha-Linolenic Acid (Omega 3 family)

- Linseed (flaxseeds)
- Rapeseed (canola)
- Soya beans

Importance of fatty acids and derivatives. Applications

In the human body, PUFAs are important for maintaining the membranes of all cells; for making prostaglandins which regulate many body processes which include inflammation and blood clotting. Another requirement for fat in the diet is to enable the fat-soluble vitamins A, D, E and K to be absorbed from food; and for regulating body cholesterol metabolism. Fatty acids are important for living organisms, since

Table 1.2

Some sources of fatty acids.

Fatty Acid	Significant Sources
4:0	Butter, dairy fats
6:0	Coconut, palm kernel
8:0	Coconut, palm kernel
10:0	Coconut, palm kernel
12:0	Coconut, palm kernel
14:0	Coconut, palm kernel
16:0	Cottonseed, palm
18:0	Cocoa butter, tallow
18:1 9c	Cottonseed, olive, palm, rape
18:2 9c12c	Corn, sesame, soybean, sunflower
18:3 9c12c15c	Linseed
20:1 13c	High erucic rape
20:5 5c8c11c14c17c ¹	Fish and animal fats
22:6 4c7c10c13c16c19c ¹	Fish and animal fats

they are used as energy stores or hydrophobic parts of biological membranes. The stocks of living organisms can be met either by biosynthesis or by dietary supply. Saturated and monounsaturated fats are not necessary in the diet as they can be made in the human body. Two polyunsaturated fatty acids (PUFAs) that cannot be

made in the body are linoleic acid and alpha-linolenic acid. They must be provided by diet and are known as essential fatty acids. Their metabolism leads to EPA (eicosapentaenoic acid) and DHA (docosahexaenoic acid) [10].

The main application and interest of omega-3 compounds is their extensively studied anti-carcinogenic properties. The elevated number of cancer diagnoses has generated an enormous amount of research in order to try to decrease or avoid its exterminating effects in the society [11].

Omega-3 compounds are scarcely presented in vegetable oils, if compared to the amount of omega-6. However, they are extremely important due to medical applications [12], so a procedure to produce them from omega-6 is a good optional new source. Several international research groups are using gene technology to produce omega-3 PUFA oils rich in EPA and DHA [13, 14]. This fact may inevitably produce a negative public reaction. Then, a chemical reaction to obtain them is then a good alternative, also from the point of view of social impact.

On the other hand, the reduction of non-environmental friendly emissions is required in order to prevent worse effects for the environment, such as, greenhouse effect. An alternative combustible has been found in the fatty acid field, especially fatty acid esters. This fact supposes another relevant application, which recently provokes a large emerging research work. Although our work is not directly related to biodiesel field, the obtained results, such as thermal stability and reactivity, may be used in a nearby future to deeply understand these compounds [15, 16].

Finally, it is a must to briefly comment the already-extended application of fatty acid and their derivatives as cosmetic constituents [17-19].

Obtaining by separation

Since omega-3 compounds are present in some vegetable oils, as already exposed in previous paragraphs, separation processes to achieve their isolation from vegetables have been also reported [20-22].

The use of fluids at supercritical conditions followed by chemical treatment was proposed [20]. Other studies proposed their isolation by chromatographic techniques followed by chemical treatment, as well [21].

As usual in separation procedures regarding compounds with further application with humans, hazardous trace-compound presence was a relevant inconvenient.

Besides, the experimental set-up required, in most cases, specific equipment which may increase the production costs.

Our study intends to offer a 'cleaner' and more safety obtaining procedure of such compounds. Furthermore, a simple continuous system is another option to these complex systems.

Reactivity of fatty acids and their derivatives

Although fatty acids and their derivatives have been extensively studied, three reactions are briefly exposed in this part: hydrogenation, dehydrogenation and isomerization. They are commented because of their direct or indirect relation to our work.

The hydrogenation of vegetable oils is an important reaction. The molecule complexity of fatty acids and their derivatives allows that hydrogenation occurs in two different parts of the molecule: in the unsaturated hydrocarbonate chain or in the organic functional group of carbon I. The hydrogenation of fatty acids and their methyl esters to give place to fatty acid alcohols is also an important industrial process [23]. For obvious reasons, our attention will be centred in the hydrogenation of the unsaturated chain. Hydrogenation of fats and oils is one of the first commercial hydrogenation processes [24, 25]. Not many years after it was shown that double bonds in light hydrocarbons could be hydrogenated in the vapour phase using nickel or noble metal catalysts. A patent concerning a liquid phase hydrogenation process for fats and oils was registered by Normann in 1902. Hydrogenation industrial processes are usually performed in liquid phase and using nickel, whether supported kieselguhr or silica [26]. Although there are some continuous described processes, most of hydrogenation reactions are carried in batch reactors [27-29].

Biochemistry works regarding desaturation of fatty acids are numerous [30-34]. The number of references mentioning dehydrogenation of vegetable oils in a catalytic way is extremely scarce. Floyd [35] referred to aromatization of linoleate, while Wang et al. refer [36] suggested that linoleate was initially dehydrogenate into linolenate when performing the study of the hydrogenation of linoleate using bimetallic Cu:Ni catalysts in a batch reactor. Bernas et al. [37] suggested that dehydrogenation of fatty acids could be a hydrogen source, when studying isomerization of linoleic acid.

The presence of one or more unsaturations along the hydrocarbonate chain can give place to an important amount of isomers by isomerization reaction of fatty acids [37-40]. Lately isomerization of fatty acids has significantly become more interesting due to the recent research concerning the conflicting human effect of *trans* isomers [41, 42]. However, some of them are associated to anticarcinogenic and antioxidative effects [37, 39, 40].

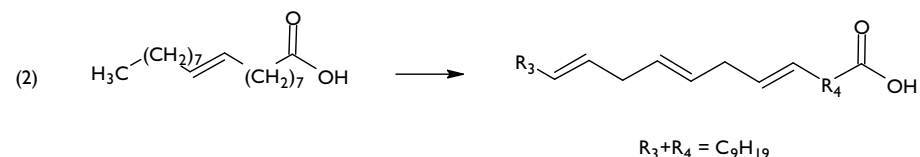
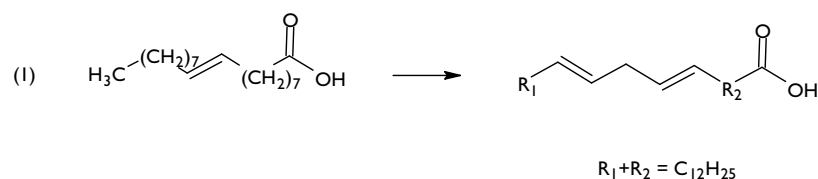
Thermodynamics

In the following part, a brief evaluation of the thermodynamical aspects of the different dehydrogenation reaction of fatty acids and derivatives is presented. Regarding the following general equation to determine the enthalpy of chemical reactions and the standard formation enthalpy values of the concerning compounds [41-43]:

$$\Delta H_{\text{reaction}}^{\circ} = \sum \Delta_f H_{\text{products}}^{\circ} - \sum \Delta_f H_{\text{reactants}}^{\circ}$$

$$\Delta_f H_{\text{linoleic acid}}^{\circ} = -634 \text{ kJ/mol} \quad \Delta_f H_{\text{oleic acid}}^{\circ} = -764.8 \text{ kJ/mol} \quad \Delta_f H_{\text{linolenic acid}}^{\circ} = -508.8 \text{ kJ/mol}$$

And considering the following reactions using oleic acid:

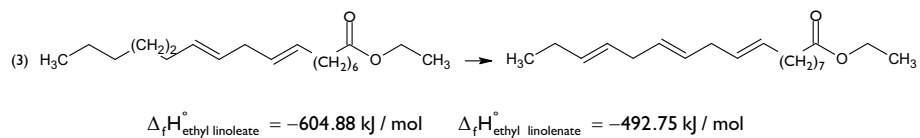


Then, the enthalpy of previous reactions can be respectively calculated:

$$\Delta_f H_{(1)}^{\circ} = 130.8 \text{ kJ/mol} \quad \Delta_f H_{(2)}^{\circ} = 256 \text{ kJ/mol}$$

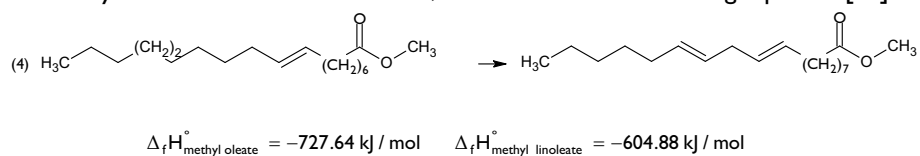
Since ethyl linoleate was also used as starting material for the catalytic reaction, the reaction thermodynamic is also calculated assuming the same value of formation

enthalpies for methyl and ethyl linoleate. The equation and its enthalpy are shown as follows [44]:



$$\Delta_f H_{(3)}^\circ = 112.13 \text{ kJ/mol}$$

Another available starting material is methyl oleate. Anyhow the reaction thermodynamics are not so convenient, as shown in the succeeding equation [45]:



$$\Delta_f H_{(4)}^\circ = 122.76 \text{ kJ/mol}$$

In all cases, dehydrogenation reaction appeared to be an endothermic reaction which suggested the inclusion of an external effect to favour its thermodynamics.

References

- [1] F. Shahidi, ed., *Bailey's Industrial Oil and Fat Products*, John Wiley & Sons, Inc, 2005.
- [2] E. Ramírez Rangel, Contribution to the Study of Heterogeneous Catalytic Reactions in SCFs: Hydrogenation of Sunflower Oil in Pd Catalysts at Single-Phase Conditions, PhD Thesis, Universitat Politècnica de Catalunya, 2005.
- [3] www.rohmhass.com (2002).
- [4] R. D. O'Brien, in: *Fats and Oils*, Technomic Publishing Co., Inc., United States of America (1998).
- [5] http://www.vegansociety.com/html/food/nutrition/e_fatty_acids.php (2003)
- [6] <http://www.cyberlipid.org/glycer/glyc0064.htm#top> (2003)
- [7] <http://www.scientificpsychic.com/fitness/fattyacids.html> (2003)
- [8] <http://www.fatsoflife.com> (2003)
- [9] <http://www.fda.gov/cder/foi/label/2004/216541bl.pdf> (2003)
- [10] U. N. Das, *Prostaglandins Leukot. Essent. Fatty Acids*, 70 (2004) 539.
- [11] S. H. Landis, T. Murray, S. Bolden, P. A. Wingo, *Cancer J. Clin.* 49 (1999) 8.
- [12] P. Nichols, *Lipid Technology*, 16 (2004) 11.
- [13] B. Qi, T. Fraser, *Nature Biotechnology*, 22 (2004) 739.
- [14] A. Abbadi, *The Plant Cell Preview*, 16 (2004) 1.
- [15] <http://www.chemstations.net/documents/BiodieselWhitePaper.pdf> (2006)
- [16] http://www.journeytoforever.org/biofuel_library/VegetableOilsKnothe.pdf (2006)
- [17] <http://ec.europa.eu/enterprise/cosmetics/inci/incich9.htm> (2006)
- [18] S. S. Shapiro, K. Martin, US Patent 6372791, 2000, to Johnson & Johnson Consumer Companies, Inc.
- [19] <http://www.freepatentsonline.com/5215759.html> (2006)
- [20] Z. Liu, H. Ge, X. Kong, Patent number, CN 2003-113398, 2003.
- [21] K. Iwata, T. Yamada, S. Moriguchi, S. Kawasaki, Patent number, 19881202, 1988.
- [22] Y. Gao, X. Li, L. Hu, T. Zhu, *Zhongcaoyao*, 13 (1982) 385.
- [23] K. Y. Cheah, T.S. Tang, F. Mizukami, S. Niwa, M. Toba, Y. M. Choo, *JAOCS*, 59 (1992) 410.
- [24] R. R. Allen, in: *Bailey's Industrial Oil and Fat Products*, John Wiley & Sons, Inc, 1982.

- [25] R. R. Allen, *JAOCS*, 58 (1981) 166.
- [26] K. Nielsen, H. J. M. Hansen, V. R. Nielsen, *JAOCS* 37 (1960) 271.
- [27] L. F. Albright, *Chem. Eng.*, 9 (1967) 197.
- [28] L. F. Albright, in: *Modern Chemical Technology*, a reprint from *Chemical Engineering*, McGraw-Hill, New York (1967).
- [29] S. G. Sourelis, *JAOCS*, 33 (1956) 492.
- [30] D. R. Tocher, M. J. Leaver, P. A. Hodgson, *Prog. Lipid Res.* 37 (1998) 73.
- [31] J. Shanklin, E. Whittle, B. G. Fox, *Biochemistry* 33 (1994) 12787.
- [32] D. A. Los, N. Murata, *Biochim. Biophys. Acta* 1394 (1998) 3.
- [33] D. J. Murphy, P. Piffanelli, Fatty acid desaturases: structure mechanism and regulation, in: J.L. Harwood (Ed.), *Plant Lipid Biosynthesis*
- [34] P. H. Buist, *Tetrahedron: Asymmetry* 15 (2004) 2779.
- [35] D. E. Floyd, R. F. Paschke, D. H. Wheeler, W. S. Baldwin, *J. Am. Oil Chem. Soc.* 33 (1956) 609.
- [36] Q. Wang, J. Yao, J. Rong, . Huang, C. Yuan, *Catal. Lett.* 4 (1990) 63.
- [37] A. Bernas, N. Kumar, P. Mäki-Arvela, N. V. Kul'kova, B. Holmbom, T. Salmi, D. Y. Murzin, *Appl. Catal. A: Gen.* 245 (2003) 257.
- [38] C. Litchfield, J. Lord, J. E. Isbell, A. F. Reiser, *JAOCS*, 40 (1963) 553.
- [39] M. Kreich, P. Claus, *Angew. Chem. Int.* 44 (2005) 7800.
- [40] A. Bernas, P. Laukkanen, N. Kumar, P. Mäki-Arvela, J. Väyrynen, E. Laine, B. Holmbom, T. Salmi, D. Y. Murzin, *J. Catal.* 210 (2002) 354.
- [41] C. M. Oomen, M. C. Ocke, *Lancet*, 357 (2001) 746.
- [42] H. F. Rase, in: *Handbook of Commercial Catalysts: Heterogeneous Catalysts*, CRC Press, Boca Raton, FL (2000).
- [43] D.W. Rogers, O. P. A. Hoyte, R. K. C. Ho, *J. Chem. Soc. Faraday Trans. I*, 74 (1978) 46.
- [44] J. B. Pedley, R. D. Naylor, S. P. Kirby, *Thermochemical Data of Organic Compounds*, Chapman and Hall, New York, 1986, 1-792.
- [45] L. Keffler, J. H. McLean, *J. Soc. Chem. Ind.* 17 (1935) 178.