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REVIEW ARTICLE

Cooking oil rancidification during deep frying causes health hazards

Prof. Dr. Dhrubo Jyoti Sen

Department of Pharmaceutical Chemistry, Shri Sarvajanik Pharmacy College, Gujarat Technological University, Arvind Baug, Mehsana-384001, Gujarat, India

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ABSTRACT

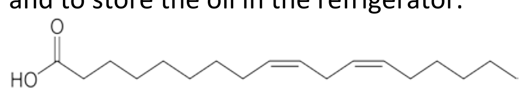
Many factors can affect the tendency of oil to become rancid. The first is too much exposure to air. Since oxidative rancidity is the most likely kind of rancidity to affect food oils, always want to keep those oils in bottles that are tightly capped. A tightly capped bottle will help prevent oil from being unnecessarily exposed to oxygen. The next factors are heat and light. Since both of these factors can also speed up the rancidity process, protection from heat and light are also important when it comes to your food oils. With respect to light best bet is to purchase oils in bottles made from darker (tinted) glass (usually dark brown or dark green glass). Oils can be stored in a cabinet that is lightproof. Many heat sensitive oils are best kept in the refrigerator where the temperature remains continuously low. Protecting of food oils from light and heat is a moment-by-moment process. For example, it means paying attention to the cooking place where it is placed a bottle of oil when using it in a recipe. Oil can't be placed directly above a stove that is turned rancidification due to the increased risk of damage from heat. It also a trouble of capping the bottle whenever not pouring oil from it because if the cap is open then the thermolabile oil will undergo oxidation followed by rancidification and will become too hard to cap the bottle mouth.

Keywords: saturated fat, unsaturated fat, ω-3 fatty acids, ω-6 fatty acids, linoleic acid, α-linolenic acid, PUFA, rancidification, free radical, lipid peroxidation, malonaldehyde

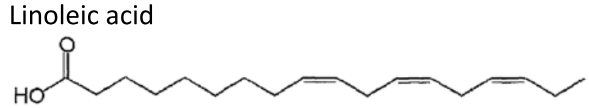
INTRODUCTION

The chemical composition of oil is also a key factor in the risk of rancidity. Here the basic principles involve saturated and unsaturated fat. The more saturated fat contained in oil, the high susceptible it is to rancidity.[1] The greater the amount of unsaturated fat in oil, the more likely less to become rancidity. Since the healthiest plant oils are all highly unsaturated, they are especially less to susceptible to rancidity.[1,2]

Some unsaturated oils, like extra virgin olive oil, are a little less susceptible to rancidity because a larger amount of their unsaturated fat falls into a special category called "monounsaturated." Extra virgin olive is about 75% monounsaturated, which is somewhat unusual for plant oil.3 Plant oils usually have more polyunsaturated fat than monounsaturated fat and that is one reason why they are particularly susceptible to rancidity. While the highly monounsaturated nature of extra virgin olive oil doesn't mean that it can be forget ten about the issue of rancidity, it does mean that this unique oil is a little more stable than oils that have much fewer monounsaturates. Both ω-3 and ω-6 fatty acids are always polyunsaturated. When it comes to plant oils, if you are trying to make sure that your diet contains an ample supply of ω-3s, you are always at the lowest risk for rancidity. Flaxseed oil, for example, contains about 15 grams of α-linolenic acid per ounce. α-linolenic acid is a polyunsaturated ω-3 fatty acid not found in a wide variety of foods, and it's the basic building block for all other ω-3 fatty acids. Many food scientists look upon the α-linolenic acid found in flaxseeds oil as the most delicate part of its composition that needs to be protected from oxidative rancidity. In a case like flaxseed oil, where the chemical composition of the oil places it at great risk for rancidity, it's best to avoid any type of heating at temperatures above 150°F (66°C) and to store the oil in the refrigerator.[1]



Linoleic acid



Linolenic acid

Deep frying is a cooking method in which food is submerged in hot fat (e.g., oil). This is normally performed with a deep fryer or chip pan; industrially, a pressure fryer or vacuum fryer may be used. Deep frying

Corresponding author:** *Prof. Dr. Dhrubo Jyoti Sen* **||** ***E-mail: *dhrubosen69@yahoo.com*

is classified as a dry cooking method because no water is used. Due to the high temperature involved and the high heat conduction of oil, it cooks food extremely quickly. If performed properly, deep-frying does not make food excessively greasy, because the moisture in the food repels the oil. The hot oil heats the water within the food, steaming it; oil cannot go against the direction of this powerful flow because the water vapor pushes the bubbles toward the surface. As long as the oil is hot enough and the food is not immersed in the oil for too long, oil penetration will be confined to the outer surface. However, if the food is cooked in the oil for too long, much of the water will be lost and the oil will begin to penetrate the food. The correct frying temperature depends on the thickness and type of food, but in most cases it lies between 175–190°C (347–374°F).[2,3]

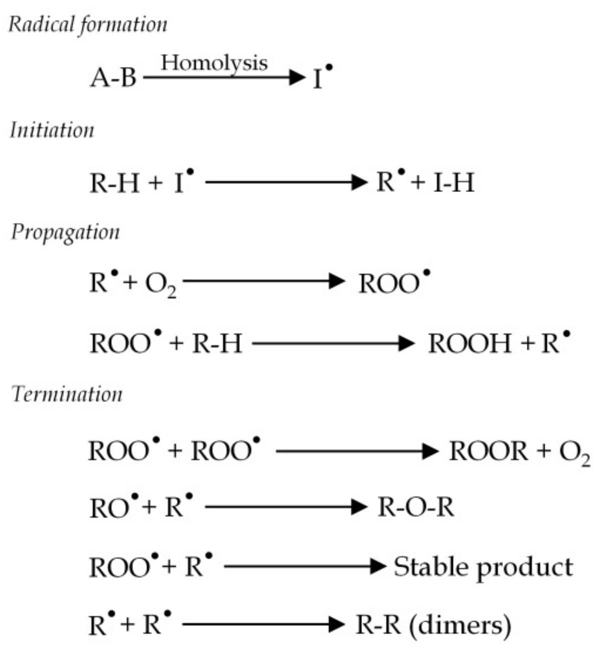


Figure 1: Steps of rancidity

Overheating or over-using the frying oil leads to formation of rancid-tasting products of oxidation, polymerization and other deleterious, unintended or even toxic compounds such as acrylamide (from starchy foods). Deep-frying under vacuum helps to significantly reduce acrylamide formation, but this process is not widely used in the food industry due to the high investment cost involved.

Some useful tests and indicators of excessive oil deterioration are the following:

- Sensory: Darkening, smoke, foaming, thickening, rancid taste and unpleasant smell when heating.
- Laboratory: Acidity, anisidine value, viscosity, total polar compounds, polymeric triglycerides.

Instruments that indicate total polar compounds, currently the best single gauge of how deep-fried an object is, are available with sufficient accuracy for restaurant and industry use.

Cooking oil is flammable and fires may be caused by it igniting at too high a temperature because unsaturation part present in cooking oil takes up oxygen and epoxy fractions are formed which is further converted into peroxide then hydroperoxide and finally into rancid free radicals followed by dimer formation (Figure-1). Further, attempts to extinguish an oil fire with water cause an extremely dangerous condition, a boil over, as it causes the water to flash into steam due to the high heat of the oil, in turn sending the burning oil in all directions and thus aggravating the fire. Instead, oil fires must be extinguished with a non-water fire extinguisher or by smothering. Other means of extinguishing an oil fire include application of dry powder (e.g., baking soda, salt) or fire fighting foam. Most commercial deep fryers are equipped with automatic fire suppression systems using foam.

Spilled hot cooking oil can also cause severe, even fatal, burns.[2] The higher temperatures and tendency of oil to stick to the skin make spilled hot cooking oil far more dangerous than spilled hot water. Children are particularly at risk, as they can accidentally pull a pot off the stove onto themselves. Cooking with oil also tends to make a mess, with oil splatters on all adjacent surfaces and oil vapors condensing on more distant surfaces. More detergent is also needed to clean cooking pots and utensils coated in oil. If a bag of opened potato chips in the pantry and by the time the chips tasted “funny”; because of the oils that the chips had been fried in having gone rancid. How did that happen? Fats are stable at room temperature due to their higher saturated fatty acids content. Oils on the other hand are usually liquid at room temperature. The reason is they are higher in mono- and polyunsaturated fatty acids. Rancidity refers to changing the chemical and physical structure of lipids (fats and oils) during cooking temperature (Figure-1). Lipids (Oil/Fat) starts hardening so the physical structures change and rancid form of it is completely different form initial one, so chemical structures change.[2-4] There are two different ways oils can become rancid: hydrolytic rancidity and oxidative rancidity. Hydrolysis of oil/fat the ester bond of triglyceride linkage ruptures and glycerol with free fatty acids release & oxidation of oil/fat the β-carbon gets oxidized by following initiation, propagation and termination steps to form free radical dimer (Figure-1)

Hydrolytic rancidity is when oils are partially catalyzed to free fatty acids (FFA), mono- and diglycerides. Usually the causes are enzymes (lipases) and microorganisms (lipases-producing, like Candida albicans). Lipases are enzymes, which break down fats into monoglycerides (digest fats). All oils and fats are susceptible to hydrolytic rancidity, but the ones that can put out off-flavors are the fats with shorter chain fatty acids, like butyric, caproic, caprylic and capric acid. These oils include coconut oil and butter. Other highly-saturated fats, like cocoa oil, usually smell offensive and it's easy to find out if they have become rancid; coconut oil (90% saturated) can go rancid by way of hydrolytic rancidity. Oxidative rancidity is the result of a chemical reaction between the fats in oil and oxygen. The rancidity from oxidation is always accompanied by off-flavors and odors due to the formation of peroxides, carbonyls, aldehydes, trienes (low-molecular-weight volatile compounds). Oxidative rancidity occurs primarily in oils with saturated fats rather than monounsaturated (MUFA) and polyunsaturated fats (PUFA) because saturated oils have no double bonds. Unsaturated oils have one or more double bonds between carbon atoms (they have missing hydrogen atoms) that can't be easily oxidized by oxygen from the air. Polyunsaturated fats have two or more double bonds and thus are stable to oxidative rancidity than saturated fats. In other words, the higher the level of unsaturation in oils, the lesser the possibility and the speed of oxidative rancidity because unsaturation point has stable σ-bond and weak π-bond and π bond is formed by sharing of electrons which form covalent bond whereas σ bond is formed by strong sharing of electrons by formation of strong covalent bond which suppress the action of π bond during heat. So more saturated oil/fat is sensitive to oxidative rancidification compared to unsaturated oil/fat.

Apart from oxygen, other catalysts causing oxidative rancidity include metal ions (iron), heat and light. Oxidation of oils starts even before the oils are extracted from fruits (olive, avocado), seeds (sunflower, hemp, flax), grains (corn) or legumes (soy). Some methods of extraction speed up oxidation and rancidity. For example, expeller pressed oils become rancid during the process of extraction because of the higher temperatures during the process. Cold-pressed oils are less rancid by the time they get to store shelves.[3]

Common cooking oils that are most prone to rancidity from oxidation due to high saturated fat content are the following in this order:

Safflower<Hemp<Sunflower<Flax<Corn<Soybean<Cotton seed

Safflower oil (less viscous & light)

Cottenseed oil (more viscous & denser)

More saturated fat~More rancidification

More unsaturated fat~More stable

So, to answer the question "how does cooking oil become rancid". It can become rancid:

1. If stored in light, clear bottles, in tins with a large air bubble at the top, at higher storage temperature or at direct sunlight
2. During cooking, especially if it is highly saturated. The higher the temperature (like in frying), the faster it oxidizes by β-oxidation (Figure-1)
3. During storage, if attacked by lipase-producing bacteria and microorganisms
4. If passed through machines or vessels, made of or containing iron

Heat depletes the nutrient content of foods. It modifies the protein, carbohydrates and fats into less effective and sometimes harmful, compounds.

Figure 2: Deep fry

Cooking food in fat or oil changes the overall PUFA content in several ways:

1. The PUFAs in the oil used for frying, baking, roasting or broiling (grilling) are altered by heat into trans- fatty acids and other harmful molecules
2. The PUFAs in the food being cooked are transformed to a varying extent into other compounds
3. The food being cooked is enriched with PUFAs from the cooking oil

The degree and complexity of the changes depend on the cooking method.

Frying causes the largest changes because of the high temperatures involved and the interactions that take place between the food and the cooking oil. Fats and oils that are high in saturated fatty acids and monounsaturated acids are more suitable for frying because they are more stable when heated. Use coconut oil, palm oil, butter, cocoa butter, olive oil or canola oil.

From a PUFA perspective, frying is much more complex than baking or grilling because:

- Frying involves the use of oil, which itself is changed by the cooking process
- Exchanges take place between the oil in the pan and the fat, water and other nutrients in the food
- A hard crust is usually formed which inhibits fat uptake by the food to varying degrees

Frying of food it has to be considered:

- Using alternative cooking methods on some occasions
- Using a wok and adding water before the oil to keep the cooking temperature low
- Using saturated or monounsaturated oils as suggested above
- Frying the food for shorter periods
- Replacing the frying oil after each use

Baking, roasting and broiling (grilling)

Baking, roasting and broiling (grilling) food generally have less impact on its PUFA composition than frying. The same principles apply in terms of which types of oil to use.

Does it matter which type of cooking oil we use?

Apart from the issue of instability described above, research has shown that the type of cooking oil used directly affects the ultimate PUFA content of the cooked food. Deep-frying in olive oil enriches the food in oleic acid while deep-frying in sunflower oil enriches the food in LA, therefore impacting the ω-3 to ω-6 ratio adversely. Choose your cooking oil with care: Frying foods in corn, sunflower, safflower or soya oil enriches the food with LA, resulting in an adverse ω-3 to ω-6 ratio. Choose palm oil, butter, olive oil, canola oil, rapeseed oil or coconut oil to help maintain a more healthy PUFA balance.[4]

You can improve your ω-3 to ω-6 balance by using canola, rapeseed, olive or palm oil instead of oils that have a much higher LA content. Although coconut oil has no ALA, it has one of the lowest LA contents and has other advantages, including very good heat stability and high resistance to rancidity due to its high saturated fat content. Canola and rapeseed oil have the best ω-3 to ω-6 ratios. Olive oil and palm oil are even lower in LA content although they contain very little ALA and hence have a less well balanced ω-3 to ω-6 ratio. Lipid peroxidation refers to the oxidative degradation of lipids. It is the process in which free radicals "steal" electrons from the lipids in cell membranes, resulting in cell damage. This process proceeds by a free radical chain reaction mechanism. It most often affects polyunsaturated fatty acids, because they contain multiple double bonds in between which lie methylene bridges ($-CH_2-$) that possess especially reactive hydrogens. As with any radical reaction, the reaction consists of three major steps: initiation, propagation, and termination. Initiation is the step in which a fatty acid radical is produced.

Table 1: Cooking oils

Cooking Oils	**α-Linolenic % by weight of total Fatty Acids**	**Linoleic % by weight of total Fatty Acids**	***n*-3 to *n*-6 Ratio**
Coconut Oil	0.0	1.5	NA
Canola Oil	9.2	18.7	1 to 2.0
Rapeseed Oil	7.3	14.6	1 to 2.0
Soybean Oil	7.8	53.2	1 to 6.8
Olive Oil	0.6	10.0	1 to 16.7
Palm Oil	0.3	9.4	1 to 31.3
Corn Oil	0.9	57.0	1 to 63.3
Sunflower Oil	0.5	68.2	1 to 136.4
Cottonseed Oil	0.3	53.3	1 to 177.7
Sesame Oil	0.2	43.3	1 to 216.5
Peanut Oil	None	31.4	NA
Safflower Oil	None	77.7	NA

The most notable initiators in living cells are reactive oxygen species (ROS), such as OH· and HO_2, which combines with a hydrogen atom to make water and a fatty acid radical. The fatty acid radical is not a very stable molecule, so it reacts readily with molecular oxygen, thereby creating a peroxyl-fatty acid radical. This radical is also an unstable species that reacts with another free fatty acid, producing a different fatty acid radical and a lipid peroxide, or a cyclic peroxide if it had reacted with itself. This cycle continues, as the new fatty acid radical reacts in the same way. When a radical reacts with a non-radical, it always produces another radical, which is why the process is called a "chain reaction mechanism". The radical reaction stops when two radicals react and produce a non-radical species. This happens only when the concentration of radical species is high enough for there to be a high probability of collision of two radicals. Living organisms have different molecules that speed up termination by catching free radicals and, therefore, protecting the cell membrane. One important such antioxidant is vitamin E. Other anti-oxidants made within the body include the enzymes superoxide dismutase, catalase, and peroxidase. The end products of lipid peroxidation are reactive aldehydes, such as malondialdehyde (MDA) and 4-hydroxynonenal (HNE), the second onebeing known also as "second messenger of free radicals" and major bioactive marker of lipid peroxidation, due to its numerous biological activities resembling activities of reactive oxygen species.[5]

How to slow down rancidity in cooking oils?

To slow rancidity from hydrolysis and oxidation:

•store cooking oils in dark or covered/wrapped bottles away from direct sunlight, or in metal tins with the oil nearing the top of the tin

•store cooking oils in cool and dark places – best refrigerated (keep in mind that highly monounsaturated oils, like olive oil will become semi-solid at low temperatures)

•use lower cooking temperatures (with the right cooking oils – below) and DO NOT reuse oils for cooking or frying!

•in commercial applications, with the use of natural (polyphenols, ascorbic acid, mixed tocopherols) or synthetic antioxidants, added to oils.

What oils should you use for cooking?

The best oils for cooking are those that are highly unsaturated or primarily monounsaturated in this order:

•coconut oil (warning: low smoke point – use lower cooking temperatures)

•butter, organic (or ghee – clarified butter)

•palm oil

•lard

•extra-light olive oil

•pomace oil

•extra-virgin olive oil (lower smoke point)

CONCLUSION:

We all know that oil that has gone bad smells rancid and tastes stale, but what are the health effects of using rancid vegetable oil in cooking? Does spoiled oil contain some toxic substances that makes eating food containing rancid oil dangerous, or is it just unpleasant to the palate? Plant-based oils, such as safflower oil and sunflower oil, contain plenty of polyunsaturated fatty acids (PUFAs) which oxidize easily in the presence of light, heat, or oxygen in the air. Many of the oxidation products of PUFAs have been reported to have cytotoxic (toxic to cells) and mutagenic (capable of changing the DNA) effects. Cytotoxic and mutagenic substances are commonly known to increase the risk of cancer. Edible oils – such as extra-virgin olive oil, almond oil and sunflower oil – are excellent dietary sources of vitamin E. For example, just one tablespoon of extra-virgin olive oil contains nearly 2 milligrams of vitamin E, which corresponds to a whopping 10% of the reference daily value for vitamin E. Vitamin E is a powerful antioxidant that can protect the human body from dangerous free radicals that have been linked to an increased risk of numerous diseases and health problems. However, rancid oil appears to be capable of depleting vitamin E levels. A 1996 study published in the journal Aquaculture Research reported that blood levels of α-tocopherol acetate (a type of vitamin E) increased significantly in African catfish when the fish were given extra doses of α-tocopherol, but that those levels saw a significant drop when the fish were given rancid oil to eat. Polyunsaturated fatty acids (PUFAs) include the essential fatty acids, including the super-healthy ω-3s that are being touted by nutritionists and health gurus around the world. However, compared to fats that are rich in saturated fatty acids (such as coconut oil or butter), edible oils that are rich in PUFAs are highly unstable and prone to oxidation. This means that many healthy, plant-based sources of dietary fat – such as hemp seed oil, walnut oil, grape seed oil, and unrefined safflower and sunflower oils – can go rancid within a very short period time. Oils like olive oil, avocado oil, and macadamia nut oil, on the other hand, have a longer shelf life due to their lower concentration of PUFAs and higher concentration of monounsaturated fatty acids (MUFAs).

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