

# VARNISH FORMING PROPERTIES OF SUNFLOWER OIL AND HOW THEY RELATE TO ITS USE AS FUEL IN DIESEL TRACTORS

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Sunflower oil has the inherent ability to polymerize (cross link) to form a solid insoluble film which, in automotive terminology, is often referred to as varnish or gum. As used here, the terms varnish, gum and film are synonymous. This characteristic is a disadvantage for its use as a fuel.

A fuel textbook states, "Chemical instability results from the presence in fuel of unsaturated hydrocarbons containing more than one double bond in their molecular structure. These compounds react with air or with each other to form rubberlike substances called gums (varnish) causing engine difficulties (Popovich and Hering, 1959)." Sunflower oil is basically this type of compound, and the same statement could be made for it. In diesel engines, polymerization of unburned sunflower oil on injectors, piston ring grooves and in lubricating oil are three areas of concern.

Sunflower oil is primarily a triester of glycerol, often called a triglyceride. The compound has three branches as opposed to being a single straight chain compound. Each of the three branches is a fatty acid, mostly 18 carbon atoms in length. In sunflower oil of North Dakota origin, approximately 70 percent of the branches are linoleic acid, which has 18 carbon atoms and two double bonds; 20 percent are oleic acid, 18 carbon atoms and one double bond and less than .5 percent is linolenic acid, 18 carbon atoms and three double bonds. The composition of sunflower oil grown in a warmer climate has less linoleic and more oleic branches. Table 1 gives the typical fatty acid composition of common fats and oils, including both northern and southern grown sunflower oil.

TABLE 1. TYPICAL FATTY ACID COMPOSITION OF FATS AND OILS

Fat or Oil	SATURATED				UNSATURATED			
					one double bond	two double bonds	three double bonds	
	Average Composition, %				Palmitoleic	Oleic	Linoleic	Linolenic
	Lauric	Myristic	Palmitic	Stearic				
Animal								
Butter	2.5	11.1	29.0	9.2	4.6	26.7	3.6	—
Lard	—	1.3	28.3	11.9	2.7	47.5	6.0	—
Plant								
Corn	—	1.4	10.2	3.0	1.5	49.6	34.3	—
Cottonseed	—	1.4	23.4	1.1	2.0	22.9	47.8	—
Linseed	—	—	6.3	2.5	—	19.0	24.1	47.4
Olive	—	—	6.9	2.3	—	84.4	4.6	—
Peanut	—	—	8.3	3.1	—	56.0	26.0	—
Soybean	0.2	0.1	9.8	2.4	0.4	28.9	50.7	6.5
Sunflower (ND)	—	—	5.0	5.0	—	20.0	69.0	—
Sunflower (Texas)	—	—	5.0	5.0	—	50.0	38.0	—
Safflower	—	—	7.0	3.0	—	13.0	76.0	—
Hi Oleic Safflower	—	—	5.0	2.0	—	75.0	16.0	—
Rapeseed (Canola)*	—	—	4.0	2.0	—	60.0	21.0	11.0
Rapeseed (non-Canola)	—	—	3.0	1.0	—	15.0	13.0	—

\* Also contains 18% eicosenic (20 carbon, 1 double bond), and 47% erucic (22 carbon, 1 double bond).

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## VARNISH FORMING PROPERTIES IN GENERAL

Extensive research has been conducted on the varnish forming properties of vegetable oils. Rheineck and Austin (1968) note that the ultimate quality of a varnish is a function of the amount of unsaturation of the vegetable oil. A compound that has no double bonds is referred to as being saturated. The straight chain molecule in diesel fuel are of this type. Those with double bonds are unsaturated. Table 1 shows that sunflower oil is highly unsaturated or polyunsaturated. Research has shown that sunflower oil has superior film forming properties because it is so unsaturated.

In vegetable oils, a measure of the unsaturation is the iodine value. This value is measured in centigrams of iodine that will react with a gram of vegetable oil. Vegetable oils have been classified according to iodine value by Jamieson (1954) as follows:

Drying . . . . .	140 or greater
Semi-Drying . . . . .	125 to 140
Non-Drying . . . . .	125 or less

Drying oils will dry to satisfactory films at 50-95°F. Semi-drying oils give a tacky film at these temperatures but convert to better films when baked at 150-200°F for 15 to 30 minutes. Temperatures are higher than this in an engine.

The average iodine value for sunflower oil has been 130, so it was generally referred to as a semi-drying oil. However, sunflower oil produced in North Dakota in 1981 has an iodine value of 140 (National Sunflower Association, 1981), which classifies it as a drying oil.

Table 2 gives the iodine value of various vegetable oils.

TABLE 2. VEGETABLE OIL IODINE VALUES

Vegetable Oils	Iodine Value
N.D. Sunflower (1981 avg.)	140
Texas Sunflower	110
Cottonseed	105
Peanut	95
Olive	85
Rapeseed (not Canola)	85
Rapeseed (Canola)	115
Soybean	130
Soybean (Partially hydrogenated, from grocery store)	115
Corn	125
Linseed	190
Safflower	145

Note: Different sources give slightly different values

## NATURE OF POLYMERIZATION

Polymerization is the chemical bonding of two or more molecules to give a larger molecule. This is the process through which paints harden and plastics are formed. Polymerization may form in several ways. The oil molecule may absorb oxygen and form products by autoxidation which cross link to produce insoluble hard films (West et al., 1966).

It has been claimed (Chipault, et al., 1951) that the rate of oxidative reaction is as follows:

triolein (all three branches oleic)	trilinolein (all three branches linoleic)	trilinolenin (all three branches linolenic)
1	to	120
	to	330

A molecule with the three branches being linoleic would be 120 times more reactive than a molecule with three oleic branches. Approximately 25 percent of the molecules in N.D. sunflower oil have all three linoleic branches (Formo et al., 1979). These are highly reactive molecules in the presence of oxygen. Cross linking occurs in all three dimensions resulting in a hard insoluble varnish. An engine has an oxygen rich atmosphere, so the lower the percentage of linoleic and the higher the percentage of oleic branches, the better for use as a fuel.

Cross linking of oil molecules is also achieved by thermal or peroxide (the absence of oxygen) induced polymerization (Solomon, 1977). Heating the oil in the absence of air will also cause molecules to polymerize. In a diesel engine, any unburned sunflower oil will polymerize and form a hard film either in the presence of air or when heated in the absence of air.

Catalysts can play a major role in speeding up polymerization. These catalysts are commonly called "driers" in the paint and varnish industry. Metal ions which act as catalysts included lead, cobalt, manganese, iron, zinc, aluminum, vanadium, copper, nickel and chromium. As little as 0.005 percent of some of these ions is all that is required in paints to fully catalyze the drying process (Solomon, 1977). Driers may reinforce or supplement each other, and combinations of driers frequently lead to shorter drying times than can be obtained using any amount of a single drier (Formo et al., 1979). Unburned sunflower oil would come in contact with many of these metal ions in an engine.

Sulphur dioxide is another compound that greatly enhances polymerization (Severson, 1948). It is available from the sulphur in diesel fuel when blends of sunflower oil and diesel fuel are used.

## SUMMARY AND RECOMMENDATIONS

One of the problems that can occur when North Dakota sunflower oil is used as a fuel in diesel engines is the polymerization of unburned oil. Conditions required for polymerization to a hard, insoluble varnish are: high temperature, oxygen rich atmosphere, presence of metal catalysts, sulphur in diesel fuel and extended drying time. An engine would have all of these.

Several alternatives involving non-drying oils should be considered. Partial hydrogenation of sunflower oil to change most linoleic branches to oleic, resulting in an iodine value in the range of 70 to 80, would seem to be

the best for North Dakota sunflower oil at present. Breeding would accomplish the same, but requires several years of time.

The oil from sunflower grown in the south or in other warm climates such as Australia and South Africa has a lower linoleic acid content. If the iodine value of this oil is 125 or less, the problem would be minimized.

Other vegetable oils that are low in linoleic acid such as rapeseed, high oleic safflower and peanut oil are also good choices.

To eliminate oxidation, literally thousands of antioxidants have been identified. However, massive amounts of expensive antioxidants would probably be required. An antioxidant would not eliminate the problem of thermal polymerization.

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Plants need land and compete with other resources that are required for food production. It can be expected that there will be increasing public debate about the use of an edible oil product for fuel use. David Bartholomew, manager of the oilseeds division for Merrill, Lynch, Pierce, Fenner, & Smith of the Chicago Board of Trade, points out that from the beginning of time, man has used the productivity of agriculture as a source of fuel for the provision of motive power for on-farm and off-farm use. It has been only since the 1930s that the U.S. shifted from horses and mules to the use of petroleum-powered implements and vehicles that did not use food for fuel. Seen in this light, it should be said that petroleum is the "alternative" fuel, instead of vegetable oil and alcohol as being alternatives. The U.S. made the shift just about 50 years ago when the government adopted a cheap petroleum policy as a stimulant to mechanization and industrialization. Presently, some form of renewable energy sources must begin to take the place of the nonrenewable sources.

Unfortunately, alternative fuels are not yet economically competitive with petroleum-based fuels. In April, 1982, No. 2 diesel fuel cost \$1.11 per gallon compared to \$1.65 per gallon for 200 proof ethanol and \$2.07 per gallon for sunflower oil. Clearly, diesel fuel is the least expensive. However, comparing costs for the alternate fuels, it is important to remember that ethanol contains only 84,000 BTU per gallon as compared to 138,000 BTU per gallon for No. 2 diesel fuel and 131,000 BTU per gallon for sunflower oil. So sunflower oil will provide 100,000 BTU's of energy for \$1.58 whereas it will cost \$1.96 for ethanol to provide the same amount of energy.

Even though vegetable oils are not yet economically competitive with diesel fuel, they may be competitive in the future. The price ratio of soybean oil to diesel fuel was 4.6:1 in 1971 and increased to 10.7:1 in 1973. Since then the price ratio has decreased. In February, 1982, the crude soybean oil price hit 17.8 cents per pound or \$1.37 per gallon. In the future vegetable oils may cost about the same as No. 2 diesel fuel. In some parts of the world, vegetable oils cost less than diesel fuel today.

So even though it is hard to get excited about the use of alternative fuels, we need to continue our research on renewable energy sources. The U.S. is in the midst of a temporary oil glut. Crude-oil imports have declined by 25 percent in the past two years. Successful energy conservation and the recession have dampened the market for petroleum. Refineries are now running at only about 65 percent of capacity. Many people are now saying the oil crisis is over. Yet the most dangerous thing is to draw long-term conclusions from short-term events. James Cook points out in the March 15, 1982, issue of FORBES magazine that the so-called glut is only a correction and not a change in the fundamental conditions of supply. It is not the coming of spring, but that rare sunny day in January. The U.S. needs a synfuels program—oil shale, coal gasification and liquefaction—every bit as much as it ever did. Not only does such a program serve to warn OPEC that there really are limits to how high its prices can go, it also offers hope of providing the U.S. with the energy security it needs in the event of a disruption in worldwide supplies. Clearly, the U.S. has to conduct research before vegetable oil can become an accepted fuel. But vegetable oil fuels look like a sleeper in the research and development program for synthetic fuels.