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Chemistry Magazine: Trans-Forming Food

Trans Forming Food

BY BARBARA MAYNARD



As the evidence mounts that trans fats are unhealthy for the heart, chemists are working on a slew of replacements for these ubiquitous food ingredients.

Imagine a substance so dangerous to human health that the National Academy of Sciences states that “a tolerable upper intake level of zero” is prudent. Imagine, too, that Americans eat enough of this substance to account for 2.6% of our daily intake of calories. Don’t you think there would be a huge public outcry?

Instead, the mounting evidence on the unhealthy effects of trans fats has been met with more of a low murmur. New York City recently banned trans fat from restaurant food. Chicago, too, is considering an outright ban. Even this year’s Girl Scout cookies will carry a label proclaiming zero grams of trans fats per serving. But many consumers don’t know what trans fats are, how much they are eating, or why that’s not such a good idea. Nonetheless, chemists and plant geneticists are hard at work developing replacements for this latest dietary villain.

The term “trans fat” is shorthand for trans fatty acid. A fatty acid is a long chain of carbons with a carboxyl group at one end. Attach three fatty acids to a glycerol molecule, and you have a triglyceride, commonly known as fat.

Some fats, like butter, are solid at room temperature, whereas others, like olive oil, are liquid. The difference lies in the bonds holding the carbon chain together. Some fatty acids contain only single bonds connecting the carbon chain. In that case, the chain is saturated with hydrogen, and therefore is called a saturated fatty acid. Butter, lard, and most other animal fats, along with tropical oils such as palm and coconut, contain a high percentage of saturated fatty acids.

On the other hand, fatty acids with one or more double bonds between carbons are referred to as unsaturated. Olive oil is largely oleic acid, which is known as a monounsaturated fatty acid because it contains only one carbon-carbon double bond. Any fatty acid with two or more carbon-carbon double bonds is called polyunsaturated. Alpha-linolenic acid, found in salmon, soy, and canola, is a common example of a polyunsaturated fatty acid.

Saturated fats have been associated for years with heart disease. This association stems from the tendency of saturated fats to raise the levels of cholesterol found in low-density lipoproteins (LDL), the so-called “bad” cholesterol. As health-



Walter Willett

David Dzisiak
DOW AGROSCIENCES LLC

conscious consumers learned to avoid saturated fats, movie theaters felt the heat for popping corn in coconut oil, and fast food restaurants looked for something other than animal fat for frying foods. Luckily, or so it was thought at the time, a cheap and healthy alternative was waiting in the wings—partially hydrogenated vegetable oils.

Bubbling hydrogen through unsaturated vegetable oils in the presence of a catalyst saturates some of the double bonds, making the oil act more like a saturated fat. However, the high temperatures used for partial hydrogenation also tend to convert the remaining double bonds from the natural *cis* isomer to the *trans* configuration—a difference in whether the hydrogens lie on the same side of the bond (*cis*) or opposite sides (*trans*). *Trans* fatty acids are produced naturally in ruminant stomachs, but by far most of the *trans* fats in today's food supply are created by partial hydrogenation.

Since their introduction in the early 1900s, partially hydrogenated oils have found their way into just about everything—crackers, cookies, fried foods, pretzels, muffins, soups, salad dressings, and the list goes on. Even an Eskimo treat called *agutak*, traditionally made with seal oil or caribou fat, berries, fish, and other local foods, is now often made with Crisco—possibly the most recognizable partially hydrogenated oil on the market—in place of the animal fat.

Unfortunately, decades after consumers and food processors alike switched en masse to “healthier” partially hydrogenated vegetable oils, evidence is mounting that *trans* fats are even worse for coronary health than are saturated fats. Not only do *trans* fats raise LDL-cholesterol, but they also lower the proportion of cholesterol found in high-density lipoproteins (HDL), the so-called “good” cholesterol. This one—two cholesterol punch is bad enough, but evidence suggests that *trans* fats have an even greater effect on coronary health than would be expected from their effects on cholesterol levels alone. A recent [review article](#) published in the *New England Journal of Medicine* reported that *trans* fat consumption also promotes inflammation and impairs the function of the cells that line blood vessels, both of which are associated with cardiovascular disease.

Global Response

In response to mounting evidence of the damaging effects of *trans* fats, health organizations worldwide have issued guidelines calling for drastic reductions in the amount of *trans* fats we consume. The World Health Organization recommends that *trans* fat consumption be less than 1% of total energy intake, whereas the National Academy of Science's Institute of Medicine recommends that people consume as little *trans* fat as possible while maintaining adequate nutrition.

Denmark has been the world leader in abolishing *trans* fats—or “killer fats,” as they are known there. In 2004, the government there issued rules limiting *trans* fats to no more than 2% of any prepared food's fat content, a level that effectively eliminated *trans* fats from the Danish diet. The restrictions have not deprived people of any favorite foods, according to Steen Stender, professor of preventive cardiology at the Gentofte University Hospital in Copenhagen.

“We have French fries from McDonald's,” he says. “We still have the wafers and we still have the microwave popcorn, but it doesn't contain *trans* fat.” Danes even still have Danishes. “They flake in exactly the same way as the ones with *trans* fat,” Stender adds. “So, we miss nothing. I don't know of any product that has disappeared. No loss in quality of life is experienced when removing *trans* fat. It's an endangered fatty acid in Denmark.”

But Denmark's *trans* fat legislation may itself be endangered. The European Union has made a case against Denmark, claiming that the *trans* fat limit is a hindrance to free trade among the countries.

Mark Matlock (ACS '82) is standing next to an instrument developed by ADM to measure the oxidative stability of vegetable oils.
ADM



Mun Yhung Jung



Steen Stender



To address growing concerns about *trans* fats, Wendy's restaurants replaced the partially hydrogenated oils once used to cook their French fries with a

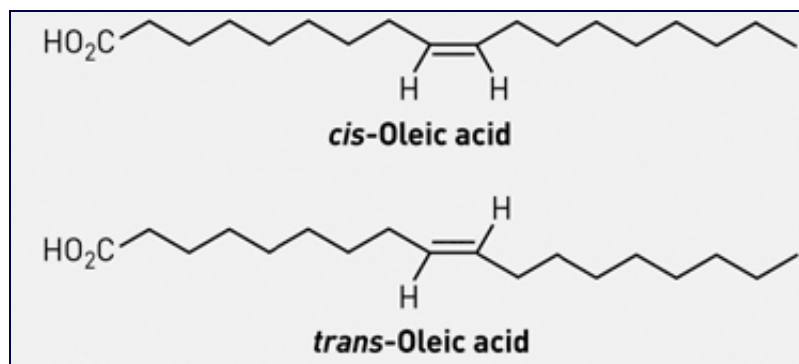
healthier blend of corn
and soy oils in August
2006.

WENDY'S RESTAURANTS



Lipid chemist Mun Yhung Jung uses a laboratory-scale hydrogenator, like the one shown here, to investigate new ways to partially hydrogenate vegetable oils with substantially lower trans fat content. (Click on image to enlarge)
MUN YHUNG JUNG

In North America, anti-trans fat efforts are warming up. In 2005, Canada became the first country to impose mandatory labeling of trans fat content in prepackaged food. In June 2006, a Canadian Trans Fat Task Force recommended the country enact limits similar to those in Denmark, but at a higher level of 5% of total fat content. In the United States, labeling regulations went into effect on January 1, 2006, when it became mandatory to list trans fat content per serving on nutrition labels. Remember, though, that a label reading "0 grams of trans fat per serving" may still have up to 0.5 grams per serving.



A monounsaturated fatty acid such as oleic acid, found in olive oil, naturally occurs in the cis configuration, with hydrogen atoms on the same side of the double bond. The trans version of oleic acid has the two hydrogen atoms on opposite sides of the bond. The placement of the hydrogens affects the shape and properties of the fatty acid, and how the body processes it.

CHEMICAL & ENGINEERING NEWS

Given the outcry against trans fats, one wonders why the food industry hasn't dropped them like proverbial hot potatoes laden with butter and sour cream. In Denmark, for instance, McDonald's has reduced trans fats in its frying oil to meet the Danish regulations, but it has not made the same switch in other countries. In response to questions about the difference, McDonald's Corporation issued only the following statement: "We've been working to reduce or eliminate the trans fatty acid content in our vegetable oils, while maintaining the great taste of our world-famous French fries. We are making progress as we work through limitations in the alternatives currently available. In Denmark specifically, to meet the new Danish legal requirements for trans fat content, TFA (trans fatty acid) levels were reduced—but not eliminated—in all applicable foods."

Stender recently published research on trans fatty acid content of fast foods and snacks collected from 26

countries. Identical meals of chicken nuggets and French fries purchased at McDonald's varied in their fatty acid content from less than 1 gram in Copenhagen and Beijing, China, to 10 grams in New York City. Stender found similar variability around the world in fast food from KFC and in snack foods such as microwave popcorn, cookies, and cakes.

The Value of Trans Fats

Partial hydrogenation fills two main roles for the food industry. "One of the reasons we hydrogenate is to improve the stability for frying and for shelf life" explains Mark Matlock, senior vice president for food research at food processing giant Archer Daniels Midland (ADM). Partial hydrogenation reduces the amount of linolenic acid, which oxidizes quickly, producing a rancid taste. However, linolenic acid is also a beneficial omega-3 fatty acid, so extended shelf life comes at the expense of a healthy nutrient.

"The second reason we hydrogenate is to produce solids," Matlock continued. "Soybean oil is a liquid, canola oil is a liquid. If we're trying to make a margarine, we need some solids." Solids are convenient to work with as a spread, and they make icing creamy, crackers crunchy, and croissants flaky.



Canola oil is relatively high in linolenic acid, which is a healthy omega-3 fatty acid but oxidatively unstable. Companies such as Dow AgroSciences are developing low-linolenic acid varieties of canola to address stability issues.
CANOLA COUNCIL OF CANADA



Partially hydrogenated vegetable oils have been widely used for frying foods because of their long shelf life and stability after repeated use. Awareness of the unhealthy effects of consuming the trans fats in these oils is pushing the food industry to find healthier alternatives.
ADM

Partially hydrogenated oils provided an alternative when saturated fats were vilified for their artery-clogging properties—and they did it on the cheap. "One of the great things about partially hydrogenated soybean oil was its price. That's why it was so widely used," Matlock says.

No single solution is likely to replace all the applications that partial hydrogenation currently fills, but a number of options are available or under development. One of the most straightforward ideas for replacing trans fats is to take another look at what Mother Nature, helped by years of traditional plant breeding, has provided. Some available oils, for example, are naturally stable. Corn and sunflower oils both contain less than 1% linolenic acid, making them more stable than soybean oil, which contains 7–8% linolenic acid. "The most plentiful one here in the United States is corn oil," Matlock said. "Another one that is being used is cottonseed oil, which has been around for a long time and is a good frying oil."

The naturally stable oils tend to be more expensive than soy or canola, so selective breeding has been used to create new strains of these two crops. For example, Dow AgroSciences, Inc., has developed a line called Nexera. "Compared to regular canola oil, Nexera contains higher levels of oleic acid and a reduced level of linolenic acid, giving it a fatty acid profile that provides high stability and healthfulness," wrote David Dzisiak, Global Business Leader of Oils for Dow AgroSciences. "The oil derived from Nexera seed is a naturally stable oil with a longer fry life and shelf life."

Dow turned to modern plant biotechnology to speed up the development process. "Biotech tools were used to

identify and track the genes in the new varieties and ensure they are in the new production varieties,” Dzisiak wrote. “By being able to track the genes in the lab versus having to do field trials to grow the candidate varieties and test seed from them, we can save 3 to 5 years of plant breeding time.” In 2007, Dow AgroSciences expects to produce 1 billion pounds of oil from Nexera seed. Other companies have also developed low linolenic strains of soy and canola.

Blending oils from different plants is another way to produce a desirable mix of traits. “There are some customers who don’t need an oil as oxidatively stable as the sunflower, but they can’t use soybean oil directly, so we can blend those two oils together,” Matlock explains. The mixture has a longer shelf life than soybean oil, while also providing more healthful linolenic acid than corn or sunflower. Wendy’s restaurants developed a new blend of corn and soy oil to eliminate trans fats from their fryers in August 2006, but spokesperson Denny Lynch declined to comment further on the mixture.

Despite the grief that palm and coconut oil have received for their saturated fat content, some manufacturers are turning back to them for baking and other applications that require a solid fat. Some data suggest that saturated fatty acids from tropical oils might not be as bad as once thought. Walter Willett, chair of the department of nutrition at Harvard School of Public Health, put the use of tropical oils in perspective. “Where we do need a solid fat, which should mainly be in a few baked goods and margarines, palm or coconut oil are probably the best choices, and if we use these judiciously, the amount in the food supply will be low,” he wrote.

THE ONE *good trans fat*

As food chemists work overtime to produce healthier alternatives to artificial trans fats, some researchers are trying to produce vegetable oils with elevated levels of a natural trans fat. Conjugated linoleic acid, or CLA for short, is a natural component of some animal fat that has been shown in animal models to fight cancer, prevent heart disease, and boost the immune system.

In fact, CLA is an exception to the U.S. Food and Drug Administration’s nutrition labeling regulation—CLA levels do not need to be included in the listing of trans fat per serving. Research is ongoing to develop a method of hydrogenation that could boost the CLA content of vegetable oils without raising other trans fats. However, Walter Willett, chair of the Department of Nutrition at Harvard School of Public Health, has written that it is premature to say whether increased consumption of CLA is helpful, harmful, or neutral to human health.

—BM

New Hope for Hydrogenation

The idea of hydrogenating vegetable oils to produce an inexpensive, healthy, semisolid fat is not out of the question, either. Partial hydrogenation creates trans fatty acids, but full hydrogenation, in which all of the double bonds are broken, does not—with no double bonds left, there can’t be any in the trans configuration. Fully hydrogenated oils have a consistency said to resemble candle wax, but they can be blended with liquid oils to create a more pleasant texture with no trans fat and a low saturated fatty acid content, attributes useful for shortenings, margarines, and icings.

One way to blend solid fats with liquid oils is a process known as interesterification. Triglycerides are an ester, so “interesterification” refers to rearranging the fatty acids between or among esters. “What you end up with is a whole mixture of different triglycerides,” Matlock says. “Some of them will have one saturated fatty acid, some will have two, and some will have none, and they will have enough different melting points that you begin to get a change in the solid fat profile.”

Chemical interesterification has been popular for some time in Europe, but it has two disadvantages. The movement of fatty acids is random, so a second step is needed to isolate the desired triglycerides from the

mixture. Chemical interesterification also creates wastewater that is difficult to treat.

Another approach solves both problems. Enzymes known as lipases can rearrange fatty acids in a targeted manner without creating wastewater issues. Enzymes have been cost-prohibitive for commercial applications, but ADM and the Danish company Novozyme recently developed a method to immobilize lipases for repeated use that makes them more affordable. In 2005, the companies were jointly awarded the U.S. Environmental Protection Agency's Presidential Green Chemistry Challenge Award for the process.

In practice, ADM completely hydrogenates soybean oil, which yields about 90% stearic acid, a saturated fat. "Then we would take, say, 20% of this solid fat and 80% of a non-hydrogenated, high polyunsaturated fatty acid soybean oil, melt them and blend them together and then run them through an immobilized enzyme column," Matlock says. "Out the other end would come this interesterified fat with all the characteristics we were looking for. And it had no waste issues."

The saturated fat content might raise some eyebrows, but Matlock said two factors ameliorate that concern. First, most of the product consists of fatty acids from liquid soybean oil, so the concentration of saturated fatty acids is relatively low. Second, not all saturated fats are created equal, and some evidence suggests that stearic acid might be neutral in terms of cholesterol levels.

Consumers will soon see interesterified soybean or canola oil showing up on ingredient lists for crackers and margarines, for example. "The product has been quite successful," Matlock says. "We have two plants that are producing it, and we've had to scale it up multiple times since we started."

Stender and Willett are guardedly optimistic about the health effects of interesterified fats. "We have very good documentation for a harmful effect of trans fat, and we have no documentation for a harmful effect of interesterified fatty acids, so in my opinion, there's a lot to gain, even if we replace trans fatty acid with interestified fat," Stender says. "But we may 50 years from now learn that we should have replaced it with saturated fat from coconuts, because they have been around for hundreds of thousands of years together with humans and we may have adapted to that fat."

One reason that Stender remains cautious is evidence from animal studies that moving fatty acids around in the three positions on the glycerol molecule can affect how the body handles them. "It shouldn't matter whether you have linoleic acid or palmitic acid in the 1 or 2 position [on the glycerol molecule] because it's hydrolyzed and it's absorbed," Stender says. "But it seems to make a difference in cholesterol metabolism in certain animal models."

Willett also comments on the lack of knowledge about the long-term effects of interesterification and full hydrogenation. "Although there is no evidence of problems with interesterification, my preference would be to keep the application low as we don't have long-term human experience with this and we can't be as confident about safety," he wrote. "I also would prefer to avoid full hydrogenation, although in small amounts this is probably OK; there is evidence that higher amounts of stearic acid will increase inflammatory markers that are related to heart disease and diabetes, and again we don't have long-term human experience with large amounts of fully hydrogenated fats."

Using multiple processes, such as full hydrogenation followed by interesterification, can get expensive. Some researchers are working on ways to make partial hydrogenation by itself part of the trans fat solution. By modifying the reaction conditions, it may be possible to partially hydrogenate oils without forming trans isomers.

"Hydrogenation is simpler to operate and cheaper to produce the fat products," wrote Mun Yhung Jung, a professor of lipid chemistry in the Department of Food Science and Technology at Woosuk University in Korea. "Thus, hydrogenation is still a viable choice for the food manufacturer if trans fatty acids can be substantially reduced during the hydrogenation."

One option is electrocatalytic hydrogenation. The application of an electrical current to the reaction allows it to take place at lower temperatures, thereby preventing the formation of trans isomers. Work is under way to make this process cost-effective.

Another way to reduce the formation of trans isomers is to use precious metals as catalysts, as opposed to the nickel commonly used in conventional hydrogenation. Precious metals also allow the reaction to take place at a lower temperature. To be economically viable, however, chemists will need to develop methods to retrieve and reuse the metal catalysts.

Among the precious metals, platinum-based catalysts demonstrate the most promising results for reducing the production of trans fatty acids. However, platinum also produces relatively high levels of saturated fats, and Jung says that research continues on a second generation of platinum-based technology that can suppress the formation of both trans isomers and saturated fats during the hydrogenation of edible oils.

A third method theoretically could improve hydrogenation. Supercritical-fluid-state hydrogenation uses carbon dioxide or propane in a supercritical state, which speeds up the reaction by increasing mass transfer of hydrogen to the catalyst and thereby decreases the formation of trans isomers. However, Jung wrote that supercritical-fluid-state hydrogenation requires a reaction vessel that can tolerate extremely high pressures. Thus, this method is not currently considered practical.

As new ways of working with fats are developed, nutritionists have one solid recommendation: "Some alternatives are likely to be better than others, but trans fats are so bad that almost anything will be better," Willett says. 🍷

Writer Barbara Maynard prefers a fat blend of equal parts stearic and oleic acids, a little less palmitic acid, with just a pinch of linoleic thrown in. Conveniently, this is the fat mixture found in cocoa butter.

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