

SCI LECTURE PAPERS SERIES

## **HYDROGENATION: *Quo vadis?***

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### **Hydrogenation: *quo vadis?***

The hockey stick is a favorite tool for illustrating what has happened and predicting what is going to happen, for about anything. For instance, It is a extremely popular in sales forecasts. It usually depicts what sales have been for the past several years



and then projects the Sales Manager's optimistic look into the future.



The hockey stick can also be used to chart what has happened over the past seventy years, related to the amount of vegetable oil hydrogenated in a typical refinery. In this case, the stick is being held aloft, not sitting on the ice. Beginning in the 1930s, the amount of oil being hydrogenated every year was on a steep rise.

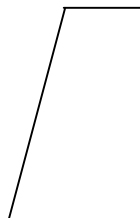


Those steeply rising years reflected several things:

- An expanding population;
- The replacement of meat fats by vegetable oils in shortenings;
- The replacement of butter by margarine; and
- A positive image of hydrogenation.

As an example of the positive image, every can of Crisco, the largest selling shortening in the United States, had the words **All Hydrogenated** prominently and proudly displayed on the label.

However, in the early 1960s, the hockey stick depiction appeared, as sales plateaued.



What caused the early 1960s abrupt plateauing of what had been a 30 year steadily rising curve for hydrogenation?

For some time, the public had become increasingly concerned about the rapidly rising incidence of heart disease, especially among men and particularly among younger and younger men. Coincidentally, extensive statistical evidence was being accumulated and published by nutritionists pointing to increasing levels of cholesterol in the blood. They concluded that this was the heart disease villain and postulated its cause as cholesterol being manufactured in the body from the ingestion of saturated fat in the diet. Hydrogenation was then singled out as a principal source of the saturated fat.

The response of the edible oil industry was to switch their manufacturing practices to a base stock system of formulating margarine and shortening which permitted the incorporation of unhydrogenated oils containing low levels of saturates. In a short time, formulations went from all-hydrogenated to about 50% hydrogenated.

A major reason it was feasible to incorporate so much unhydrogenated oil was the steadily improving quality of refined oils. This made them more resistant to flavor degradation, even while still containing significant amounts of polyunsaturated fatty acid esters, whose removal by hydrogenation had previously been considered essential for adequate shelf life.

The second major reason such formulations were now possible was the availability of highly selective catalyst having excellent uniformity. When using this catalyst, hydrogenators were able to control hardening conditions so as to manipulate up to 80% of the double bonds into a *trans*-isomeric configuration. This *trans* configuration imparted physical properties which, when formulated with unhydrogenated oil, produced a product with melting characteristics ideal for margarine - particularly for tub margarine, which was rapidly gaining consumer favor. Because this switch to base stock formulation came about more gradually than the hockey stick depicts, population growth and the continuing switch from butter to margarine, resulted in the hydrogenation curve plateauing rather than dropping. Catalyst manufacturers were pleased to note their sales at least held constant and that catalyst performance quality had become increasingly important. Customers were convinced they were eating more healthy fats and oils and were pleased that shortenings and margarines looked, tasted and had the same functionality properties as always.

This 1960s plateau was with us for such a long time that the hockey stick seemed to now be laying on its side.



This brings us to the present when many people are predicting the hydrogenation hockey stick curve will make another turn, and this time it will be downward.



Why? Because *trans*-isomers, those previously acclaimed good guys, are now being accused of having the same *in-vivo* cholesterol forming properties as saturates. Further studies may confirm this, they may refute it, or they may confuse the picture more than it is already. Meanwhile, manufacturers of margarine and shortening are searching for responses to the marketplace threat, regardless of whether the accusations ultimately prove to be true or false.

I will not go into detail concerning how manufacturers of a wide array of shortening and margarine products are already, or may in the future, respond to this potential threat. The experts speaking after me will do this. To lay the groundwork for them, I will attempt to outline and illustrate the basic facts, particularly as they apply to margarine formulation. Among my sources is Barbara Haumann's excellent article which appeared in the January issue of *INFORM* (1). It contained a table comparing butter and several margarine products. In Table 1, it has been simplified somewhat for illustrative purposes.

**Table 1. Comparison of butter and margarine products (based on a tablespoon serving)**

Product	Calories	Total fat (G)	Saturated fat (G)	<i>Trans</i> fat (G)	Cholesterol (mg)
Butter	100	11	7	0.5	30
Trad. Marg. (stick)	100	11	2	3	0
40% Spread (tub)	50	5.5	1	1.5	0
0% Spread (tub)	0	0	0	0	0
Liq. Marg. (bottle)	100	11	2	0	0

I have not included formulations utilizing tropical tree oils, which are currently being marketed in Europe and Canada. These oils are acceptable many places in the world but not in the United States, where there is a prejudice against them.

A great advantage of the free enterprise system is its fostering of experimentation in the marketplace. Much experimentation is presently happening, using a wide variety of approaches, as

is detailed in the cited *INFORM* article. Some of these approaches are what Americans call "far out". They include utilization of such things as tall oil and animal fat stripped of cholesterol. Lipton (Unilever), is marketing a full line of so-called zero *trans* margarines and spreads in the United States. Some formulations, especially those containing tropical fats, utilize interesterification - either exclusively or in combination with hydrogenation. One thing all of these formulations have in common is a higher price than standard supermarket margarines and spreads. How successful they will eventually be is an open question at this time. So far their sales have been disappointing. While a high percentage of the public endorse the use of foods with the highest possible nutritional value, it has been repeatedly demonstrated that they do not follow through when making purchasing decisions in the supermarket if the decision includes paying a higher price.

In the United States, much attention is currently focused on a report being finalized by Joseph Judd of the USDA/ARS Human Research Center in Beltsville, Maryland. It expected to be released during April. Assuming Dr Judd's findings show *trans* acids to act similarly to saturated fats in the body's production of serum cholesterol, attention will then shift to the U. S. Food and Drug Administration (FDA) and their action in proposing new labeling regulations related to *trans* fatty acid content in foods for which claims are made.

In addition to doing nothing, the FDA may propose new labeling regulations. They could require separate *trans* labeling; or require inclusion of *trans* fat in a saturated fat category; or allow voluntary *trans* fat disclosure.

Consensus of the industry is they will choose the option of allowing voluntary *trans* disclosure. If it is, the very likely result will be an eruption of advertising claims by different brands of margarine, attempting to secure business by frightening the public concerning the life-threatening properties of competing products. Depending on the particular formulation being touted, advertisements will infer that **SATURATED FAT** or **TRANS-ISOMERS** or just **HYDROGENATION** is a health hazard similar to smoking.

What effect these scare tactics will have on sales of particular products and on margarine in general, no one knows. Tongue in cheek, I offer several factors which will have some influence. They are:

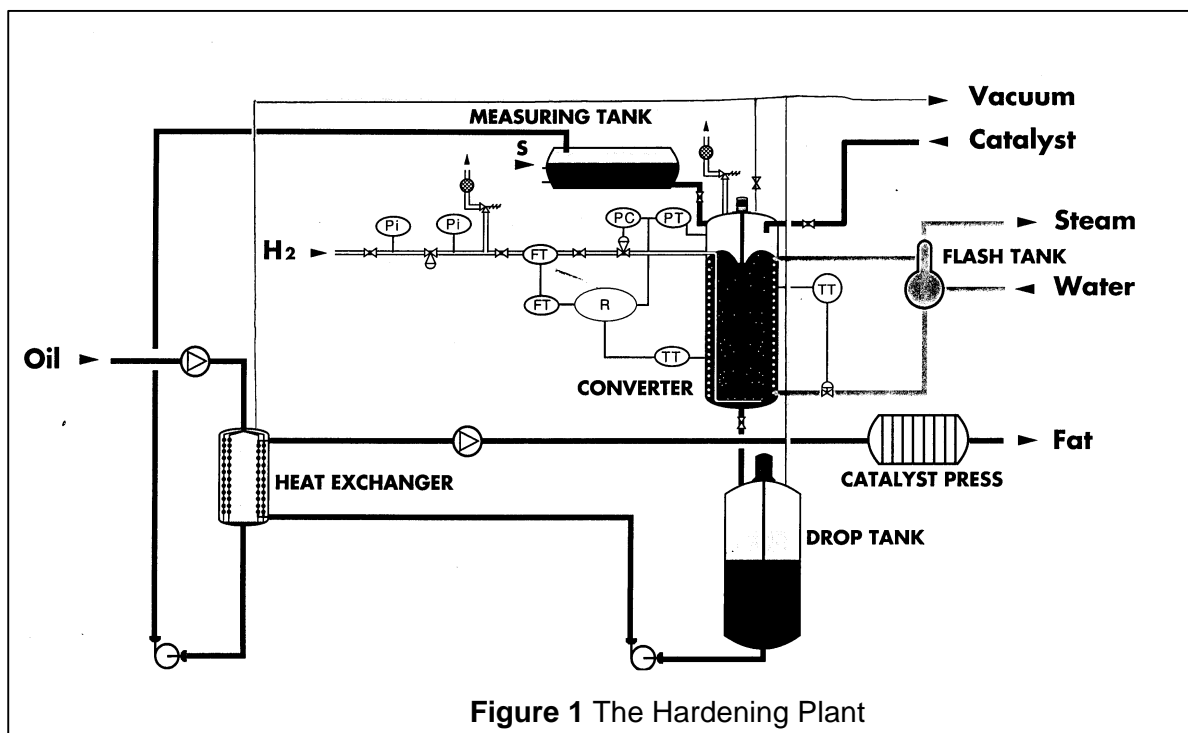
- Margarine (spread) manufacturers, being well aware that water is cheaper than oil, will always prefer to sell low-fat products, particularly if they can do it at a premium price.
- Research scientists, always on the lookout for grants to fund their investigations, will continue to write and present learned papers pointing out the need for more research.
- Catalyst manufacturers, being aware that discontinuing hydrogenation threatens their very existence, will spend a lot of time and money attempting to invent new or modified catalysts which hydrogenate oils into fats having good functionality but with few saturates or *trans*-isomers.

- Engineering companies, knowing that new or modified manufacturing techniques would be a great boon to plant modification and equipment sales, will eagerly anticipate changes of any type.
- Organizations, such as SCI and AOCS, will be pleased to present ever more conferences and symposiums to discuss these issues.
- Persons like us will always be happy for the opportunity to get together with our old friends and exchange views on such matters.

Let me now discard my cynicism and loudly acclaim the advances made in the relatively few years since the connection between nutrition and health has been accepted as fact. While there is always more to learn, to a very great extent we now understand the benefits of, and have the means to chose, a diet which will provide the best health and greatest longevity our genes will permit. The greatest problem with food in developed countries is not knowing what to eat, it is eating too much. Obesity contributes to about every health malady known.

While the hydrogenated portion of margarine and shortening formulations may drop off somewhat in the future, I definitely do not believe the hockey stick curve of total oil hydrogenated will take the abrupt turn downward some persons are predicting. While many valid reasons can be cited to back up my opinion, by far the most convincing one comes from the industry itself. Edible oil processing in the United States is currently undergoing its greatest modernization and expansion in history. In not one single case is hydrogenation capacity being built or planned at a level less than would be expected. I believe the old advice of "follow the money" is still the best predictor of the future.

While hydrogenation capacity is not being downsized, it is being utilized more effectively. Instead of using a converter as a heating vessel, a cooling tank and a filter press supply tank, contemporary Hardening Plants are designed to use converters only for hydrogenation. Through drop tanks, hot oil tanks and properly designed and sized heat exchangers, pipes and valves, the batch mode is approaching a continual (not continuous) operation. Computerized control of the batch cycle makes this possible. As a result, instead of 5 or 6 batches a day through a converter, the better designed plants now harden at least 10 or 12. Within 5 years, as many as 24 may become routine. This means that 2 x 30 ton converters, the current standard size in the United States, even at only 10 batches per day, can readily hydrogenate 600 tons in 24 hours - adequate for a typical 1000 tons per day edible oil refinery. Figure 1 (2) depicts the equipment and oil flow through a contemporary Hardening Plant of this type and Table 2 (3) depicts what the converter cycle could be in a properly designed and computer controlled Hardening Plant.

**Table 2 Converter cycle**

Load converter from hot oil tank	5 – 7	minutes
Hardening time	40 – 46	minutes
Empty converter to drop tank	5 – 7	minutes
<b>TOTAL TIME</b>	<b>50 – 60</b>	<b>minutes</b>

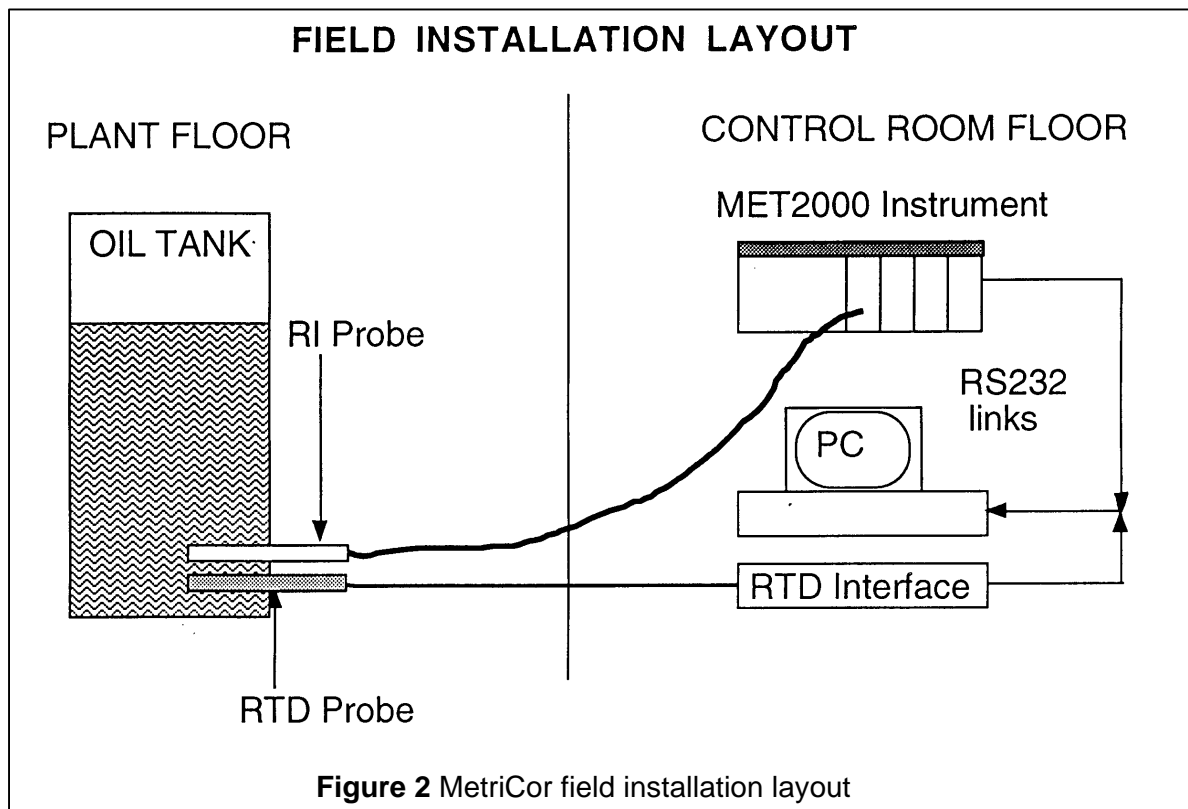
The base system of formulation has simplified Hardening Plant operation. When several converter batches are scheduled in succession, control adjustments can be made during the run which insure the attainment of desired melting points and melting curves. The best current technique for doing this is by metering hydrogen consumption. Combining this technique with high purity feedstock, uniform quality catalyst, and close control of pressure and mixing, hydrogenated base stocks can be produced which have quite predictable melting characteristics. The weakest link in this practiced is measuring degree of hardening by the metering of hydrogen.

It appears this weakest link is about to be strengthened considerably through utilization of an instrument which will measure refractive index *in situ*. Two papers on this subject were presented at the 1997 AOCS Annual Meeting. One was by Charles Cole of Cole Engineering Co. in Little Rock, Arkansas (4). The other was by Francois Desforges *et al* of the MetriCor Division of Photonetics, Inc. in Wakefield, Massachusetts (5).

While their specific techniques are different, both Cole Engineering and Photonetics utilize fiber optic technology to measure refractive index. Very importantly, readings can be made of oil which contains catalyst - thus surmounting the principal problem of previous *in situ* approaches.

In Dr Cole's system a slip-stream circulates the oil/catalyst mixture through a heat exchanger, reducing its temperature to a standard 50.0°C, and then measuring its refractive index. With the

MetriCor instrument, a probe in the converter measures refractive index directly. A second probe, located very close to the refractometer probe, measures the temperature. Signals from the two probes are tied into an instrument containing software which converts the refractive index to a constant temperature - again, about 50° C. Figure 2 is a sketch of the layout.



Accuracy for both instruments of plus or minus 1.0 iodine value is claimed.

Dr Cole's instrument is being evaluated at Riceland Foods' plant in Stuttgart, Arkansas. The Photonetics instrument is being evaluated at Bunge Foods' refinery in Fort Worth, Texas and is also planned at Owensboro Grain's refinery in Owensboro, Kentucky. Dr Allan Hodgson of Bunge has been monitoring the testing in Fort Worth. Allan is in the audience today and has indicated his willingness to discuss his experience with the Photonetics instrument.

Photonetics recently announced that their MetriCor 2000 instrument will be priced in the \$40,000–\$50,000 range. It has the capability of monitoring up to 4 converters simultaneously.

While catalyst manufacturers will no doubt continue their evolutionary development of slurry type nickel catalysts, I do not expect any huge advances. With achievable catalyst usage approaching 0.025% nickel, the economic payback from further activity enhancement is minimal. Catalysts forming less *trans*-isomers will no doubt receive more market emphasis. However, catalysts with this characteristic have been on-the-shelf for a long time. When used in combination with hardening conditions of high pressure and low temperature, they are definitely effective in reducing

*trans*-isomer formation. However, since they also form more saturates, exactly how these stocks can be utilized in finished product formulations is another question. I will say more on this subject later.

Uniformity is also an important catalyst quality. However, since most catalyst manufacturers now use ISO manufacturing practices, uniformity is so good that further improvement is no longer a significant priority.

Looking beyond the conventional batch/slurry reactor, the fixed bed mode is attractive. In addition to being significantly easier to control on an ongoing basis, it is superior in achieving product uniformity, especially with contemporary instrumentation and computerization techniques.

The fixed bed mode would be very adaptable to precious metal catalysts. Platinum and palladium have selectivity characteristics, both preferential and *trans*-isomer, quite different from nickel. These characteristics have the potential of being useful in producing base stocks for margarines and shortenings. Being reactive at much lower temperatures than nickel, e.g., 50° – 80°C compared to the 150° – 200°C range of nickel, they offer a significant energy conservation advantage.

Two additional factors make precious metals more attractive currently than they were previously. One is the greatly improved, and still improving, quality of vegetable oil hydrogenation feedstock. This extends the productive life of catalyst. The other factor is the reasonably recent availability of facilities for reclaiming precious metals from organic material containing spent catalyst. Because of their price, it is essential to reclaim essentially all of the metal from these catalysts.

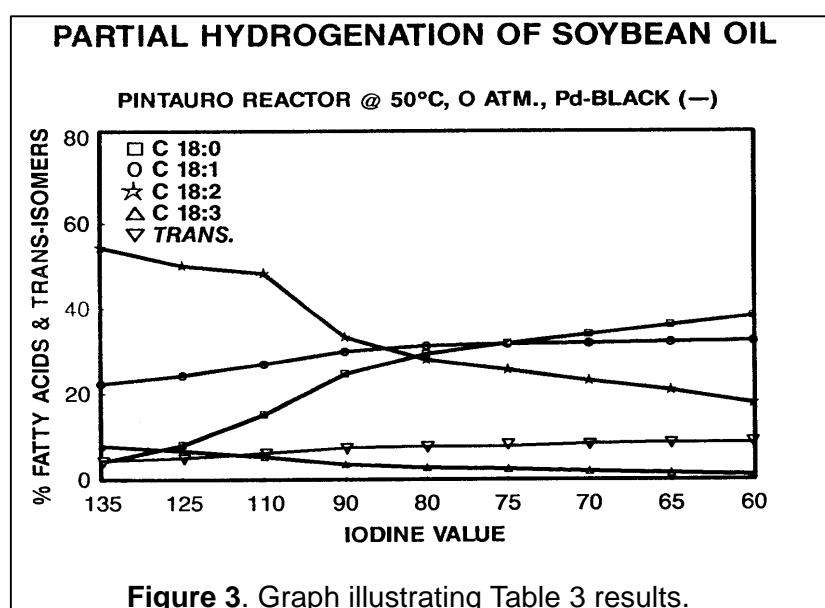
Several papers, proposing more radical approaches to hydrogenation, were presented at last year's AOCS Annual Meeting in Seattle.

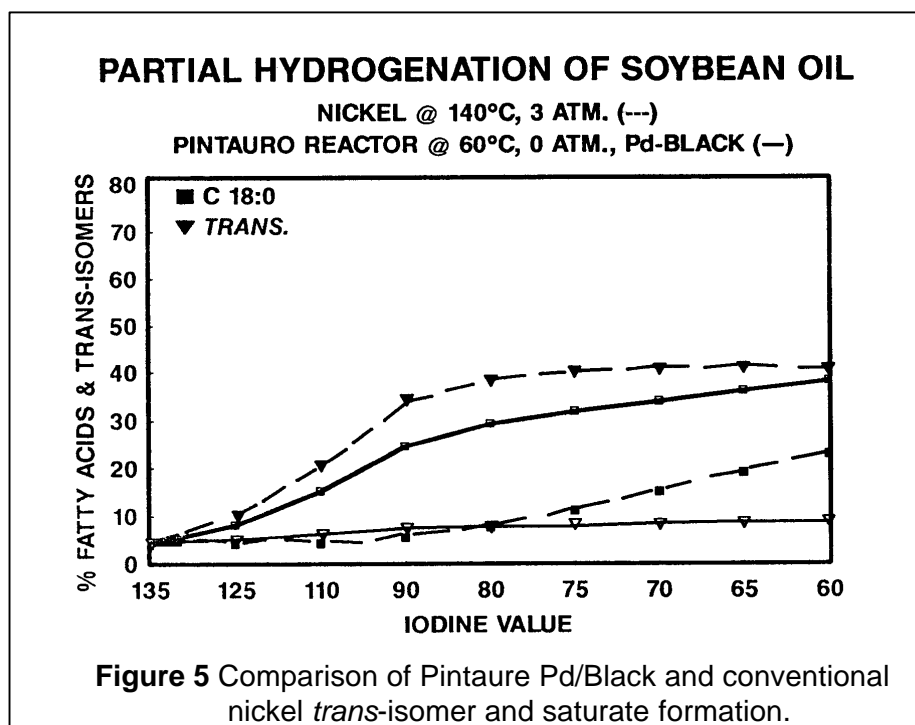
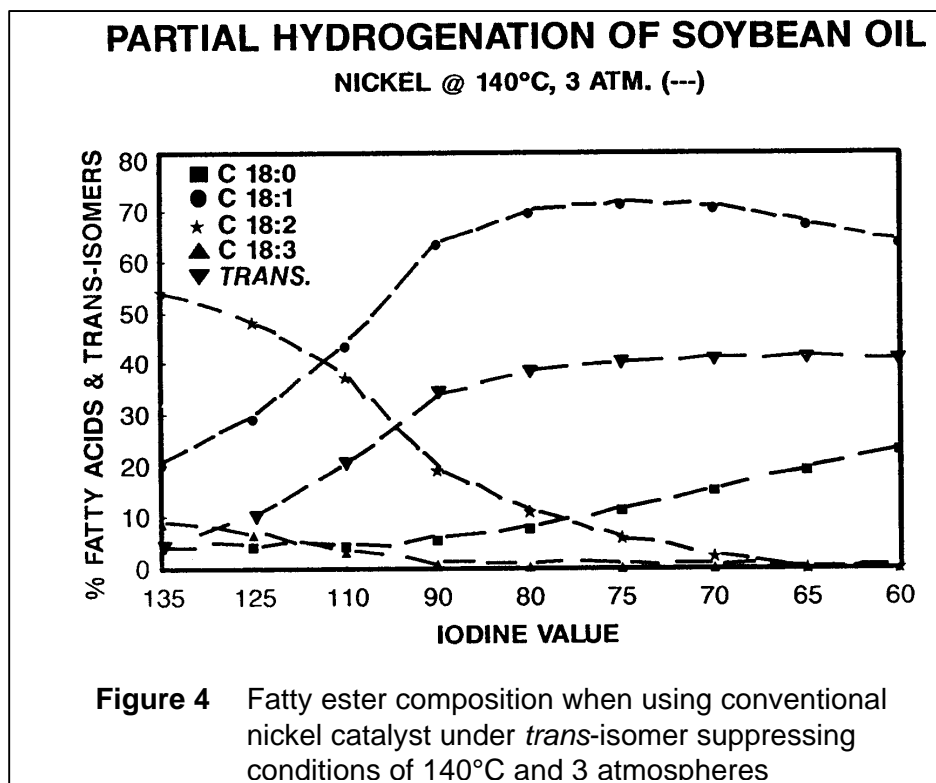
Peter Pintauro and his colleagues at Tulane University, in cooperation with Kathy Warner and her associates at the USDA/ARS laboratory in Peoria, Illinois, presented two papers (6)(7). The first illustrated the design and use of a solid polymer electrolyte reactor similar to that used in H<sub>2</sub>/O<sub>2</sub> fuel cells, with water as the source of hydrogen - very interesting of itself. The catalyst was Pd-black powder which had been hot-pressed onto a membrane. Fatty acid profile results are listed in Table 3 and depicted in Figure 3. Figure 4 depicts the fatty acid profile when using a commercial nickel catalyst under *trans*-isomer suppressing conditions of 140°C and 3 atm. Figure 5 is a side-by-side comparison of the saturates and *trans*-isomers. Table 4 reflects this comparison in Dropping Point and percent *trans* at about 90 Iodine Value.



**Table 3.** Fatty ester constituents when using Pd-black powder catalyst in an electrolyte reactor

IV	Fatty acid profile				% Trans
	C18:0	C18:1	C18:2	C18:3	
134	4.0	22.5	54.6	7.7	
91	23.8	28.9	32.5	3.6	6.5
80	28.1	31.7	26.2	2.7	
66	37.4	26.9	22.2	1.7	7.4
62	37.4	32.3	17.9	1.0	8.0





**Table 4. *Trans*-isomer and Dropping Point comparisons in the 90 - 95 IV range between Pintauro/Pd-Black and conventional nickel catalyst**

Catalyst	IV	% <i>Trans</i>	Dropping point
Ni	94	35.0	22.3
Pd	90	6.5	56.9

While Dr Pintauro's technique is unique and intriguing, the preferential and *trans*-isomer selectivity results are similar to those reported by other investigators employing precious metal catalysts.

Paul Muller and Magnus Harrod presented a paper in Seattle (8) which offered an even more radical approach to hydrogenation. It utilizes the supercritical approach of dissolving hydrogen and oil in a mutual solvent - in their case, propane. This technique eliminates the conventional rate-dominating transport resistance of limited hydrogen availability at the catalyst surface. Using precious metal catalyst, at or near supercritical conditions, Muller and Magnus report an activity rate increase of more than 1000 times and a *trans*-isomer formation decrease of about 90%. DeGussa is also investigating supercritical hydrogenation and have a patent on the process. In their case, carbon dioxide is the preferred solvent. No fatty ester profiles nor physical measurements have been presented by either Muller and Harrod or DeGussa.

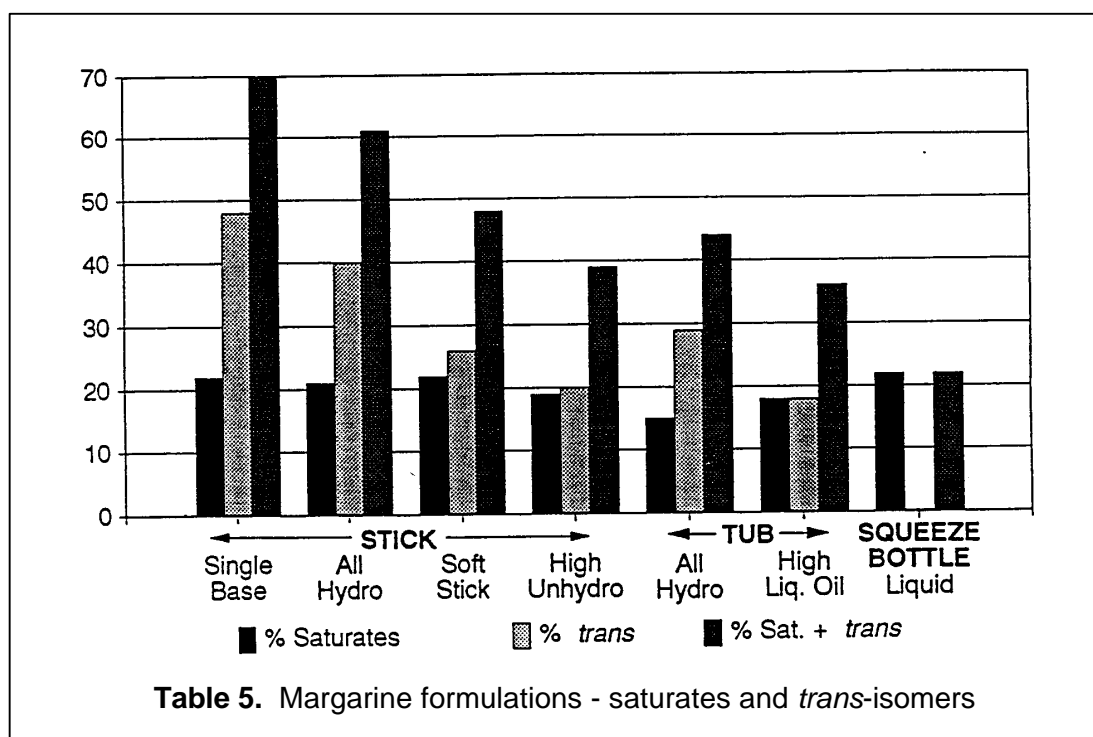
J. P. Cuperus, O. M. Ilinitich and J. T. P. Derksen, of The Netherlands and Russia, also presented a paper in Seattle (9) offering a novel approach to hydrogenation. It proposed the use of a catalyst prepared by plating a porous polymeric membrane with palladium in a highly dispersed manner. The reactor is in a fixed bed mode. They also reported low *trans*-isomer formation but, again, without any supporting chemical or physical data.

These radical approaches to hydrogenation all seem to offer tremendously high activity, very low formation of *trans*-isomers and, because of their complete lack of preferential selectivity, very high formation of saturates. I will not attempt to delve into the scientific reasons why this is true. Suffice to say, it seems to be "the nature of the beast".

While this high activity might be useful for complete hydrogenation, how could it be controlled for partial hardening? Even assuming it could be controlled, the poor selectivity makes its usefulness very dubious for partial hydrogenation intended to produce stocks having nutritional attractiveness based on a *trans* + saturate content.

These new techniques, particularly the supercritical approach, is certainly intriguing in that it completely bypasses the technology we have been employing for more than 50 years of controlling both the rate and selectivity of the hydrogenation reaction based on the amount of hydrogen solubilized in the oil. The problem in evaluating all of these new techniques is compounded by the limited knowledge of the edible oil industry evidenced by research workers investigating such things as supercritical hydrogenation. It will be interesting to follow this work in the future when persons with greater knowledge about nutrition and a reasonable understanding of the edible oil industry become involved in it.

Returning to the present, the base system of formulating has allowed astute technologists to play a lot of tricks using certain facts of nature, such as the blending of a low melting point fat with a high melting point fat, resulting in a product with a higher melting point and better functionality than would be calculated arithmetically. This technique has been widely employed since 1960 and Table No. 5 (10) illustrates how the combined total of saturates and *trans*-isomers has been reduced by more than 50% during that time. The shift from stick to tub has helped. A further shift to a squeeze bottle would help further. I remind you that butterfat is nearly 65% saturated.



In summary, my predictions about "whither goest thou" hydrogenation, are:

- The percentage of hydrogenated oil in margarine and shortening formulations will decrease somewhat.
- The total amount of vegetable oil hydrogenated will remain about the same.
- Nickel will remain the catalyst of choice but its consumption will remain flat due to continually improving feedstock quality and better control of the hydrogenation process through new instrumentation and computerization.
- Precious metal catalysts will become commercial over the medium to long term.
- Fixed bed hydrogenation will become commercial over the long term.

- While average refinery size will increase, converter size has plateaued at 30 tons.
- Nutrition will continue to dominate the discussion of edible oils and fats.

In 1981, I presented a paper at a Dietary Fats and Health conference in Chicago. The title of the paper was "HYDROGENATION: A Tool, Not an Epithet". The title has stood the test of time very well. I will conclude this presentation with the same words I used to conclude that paper 17 years ago. "Enjoyment of eating is one of the few pleasures left to humankind. We certainly have a responsibility to cooperate in keeping it from becoming another neurotic experience in our hectic world."

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"*Quo vadis?*" was written by Henryk Sienkiewicz in 1896, the same year Sabatier discovered vapor phase hydrogenation. Both the book and the process are still popular a century later, and are predicted to remain so.

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