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LETTER TO THE EDITOR

Selectivities in Partial Hydrogenation

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Dear Sir,

In a recent and most interesting article [1] discussing hydrogenation and *trans* isomer formation using a membrane sputtered with platinum, the authors calculate hydrogenation selectivities by starting from the first-order irreversible reaction scheme shown below:

$$\mathrm{C18{:}3(Ln)} \xrightarrow{k_1} \mathrm{C18{:}2(L)} \xrightarrow{k_2} \mathrm{C18{:}1(O)} \xrightarrow{k_3} \mathrm{C18{:}0(S)}$$

Using the pseudo-first-order rate constants k_1, k_2, and k_3 they list the well-known definitions [2] of linolenate selectivity (S_{Ln}), linoleate selectivity (S_{L}) and oleate selectivity (S_{O}, which equals the product of the other two):

$$S_{\mathrm{Ln}} = \frac{k_1}{k_2} \quad S_{\mathrm{L}} = \frac{k_2}{k_3} \quad S_{\mathrm{O}} = \frac{k_1}{k_3}$$

They also mention AOCS Official Method Tz 1b-79 to calculate the above selectivities.

However, when these selectivity ratios were defined more than 40 years ago, simplifications had to be introduced and assumptions had to be made and it is my impression that nowadays, people are insufficiently aware of these simplifications and assumptions and moreover do not realise that several of them turned out to be incorrect; hence this letter.

The first assumption I want to discuss is the concept of the common fatty acid pool hesitantly suggested by Bailey and Fisher in 1946 [3] as follows: "In the case of a number of different fatty acids existing together in an oil and competing for hydrogen, it appears reasonable to assume that, of an infinitesimal amount of hydrogen absorbed, the fraction going to each acid will depend on the concentration of the acid and a constant expressive of the affinity of the acid for hydrogen under the particular conditions of hydrogenation then obtaining." Do not forget that at that time, GLC had still to be invented and determining a fatty acid composition was laborious, not very accurate and limited to far fewer fatty acids than actually present in hydrogenation samples. It involved the determination of the iodine value, the thiocyanogen number, measuring the UV absorption after alkali isomerisation and the determination of the saturated fatty acid content by oxidation.

At the time the suggestion was made, there was some evidence to the contrary in that Hilditch and Jones [4] had noted that tri-olein is attacked more rapidly than di-oleo-glycerides and the latter somewhat more so than the mono-oleo-glycerides. According to the common pool concept, the di-oleo-glycerides should react twice as fast as the mono-oleo-glycerides and apparently, they did not. So Bailey was correct in postulating a hypothesis but what started as a hypothesis soon became dogma.

So when Schilling [5] studied tri- and mono-linolenate and concluded that these triglycerides reacted at a roughly equal rate and thereby refuted this dogma, his contribution went unnoticed. In 1983, Beyens and Dijkstra [6] reported that linoleic acid present in triglycerides with two or more linoleic acid moieties reacted more slowly than when it was the only linoleic acid moiety present in triglycerides. Finally, deviations from the common pool kinetics, which have been linked to pore diffusion limitations [7, 8], may be at least partially explained by abandoning the common pool concept [9]. Since the definitions of the fatty acid selectivities are based on the common pool concept, their meaningfulness is severely curtailed. That also holds for the great majority of kinetic studies that look at the rates at

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which individual fatty acids react rather than at the rates at which triglycerides react.

This meaningfulness is further curtailed since the definitions assume that the rates of addition of hydrogen to the various unsaturated fatty acids depend, in an identical manner, on the hydrogen concentration in the oil. This assumption has also to be rejected [9] since the hydrogen is not added as a molecule of hydrogen but as a consecutive addition of two hydrogen atoms [10], the first one of which is reversible.

Accordingly, the hydrogenation reaction can be envisaged as follows [11]. Because of the affinity of double bonds for the surface of the catalyst, a triglyceride molecule containing one or more unsaturated fatty acid moieties becomes attached to this surface. This holds for all types of unsaturated fatty acids: polyunsaturated fatty acids, which get saturated, and monounsaturated fatty acids, since they isomerise. The degree of unsaturation and the number of unsaturated fatty acids in the triglyceride molecule only affect the likelihood of attachment, the frequency factor of the rate constant of attachment.

No experimental data are available that permit this factor to be quantified but it should be possible to develop a relatively simple, triglyceride-based system. In such a system, the frequency factor pertaining to a monounsaturated triglyceride such as P_2O or S_2O (P = palmitic acid; O = oleic acid; S = stearic acid) could be arbitrarily set at o. Then triglycerides like PO_2 and SO_2 might show a frequency factor of their rate of attachment equal to $o \times s$, where $1 < s < 2$. For tri-oleate this factor would then be $o \times s^2$. When the triglyceride contains a linoleic acid moiety (L), a further parameter (l) has to be introduced to quantify the frequency factor of the rate of attachment of triglycerides like P_2L and S_2L. Since linoleic acid has twice as many double bonds as oleic acid, it is likely that it becomes more readily attached than oleic acid, which means that $l > s$ but how much larger is not known; according to Schilling [5], all unsaturated triglycerides react equally fast so he concludes $s = 1$ and $s = l$. In practice, the system may well be more complex than the rudimentary system outlined above. Factors may well depend on the lengths of the saturated fatty acids present in the unsaturated triglycerides and their quantification requires well-designed experiments.

The affinity for the catalyst surface decreases when a hydrogen atom is added to the double bond and a half-hydrogenated intermediate is formed. This permits rotation around the former double bond. If this half-hydrogenated fatty acid originated from linoleic or linolenic acid, it will still have a double bond left and this may cause it to remain attached to the catalyst surface. On the other hand, if the half-hydrogenated intermediate was formed from an oleic acid moiety, it would be less firmly attached to the catalyst surface and could leave this surface after dissociation. So whereas Coenen and Boerma [12] concluded that monounsaturated fatty acids only isomerise when some of them become saturated, it is clear that isomerisation without saturation is possible when the second addition of a hydrogen atom is suppressed by maintaining a low hydrogen concentration.

In standard, nickel-catalysed industrial hydrogenation reactions, such a low hydrogen concentration automatically arises in the early stages of the batch process after the catalyst has been activated and has not yet been poisoned, and the reaction mixture is still highly unsaturated. Since a low hydrogen concentration in the oil will cause the hydrogen concentration on the catalyst surface to be low as well, polyunsaturated fatty acids will become partially saturated since they remain attached to the catalyst surface for a sufficiently long time for the second hydrogen to react. Monounsaturated fatty acids on the other hand, may well have left the catalyst surface before this second hydrogen atom has had a chance to react and form a saturated fatty acid. Accordingly, the rate of formation of partially hydrogenated polyunsaturated fatty acids is proportional to the concentration of the hydrogen atoms on the catalyst surface whereas the rate of formation of fully saturated fatty acids is proportional to the square of this concentration [13]. The assumption that the rates of hydrogenation of polyunsaturated fatty acids and monounsaturated fatty acids depend in an identical manner on the hydrogen concentration is therefore untenable.

Above, the fatty acid selectivities were defined as the ratio of two rate constants and the assumption that the hydrogen concentration did not play any role allowed this ratio of rate constants to be calculated as the ratio of two rates of formation. However, the rate of formation of the saturated fatty acids depends more strongly on the hydrogen concentration than the rate of the partial saturation of polyunsaturated fatty acids, which means that the linoleic acid selectivity as calculated decreases when the hydrogen concentration increases. This is exactly what is observed [9, 14]: the ratio of two rate constants (*sic*) is itself not a constant but decreases in the course of a batch hydrogenation.

Another assumption that underlies the definition of the fatty acid selectivities is that fatty acid isomers react at equal rate. This assumption is also untenable, as demonstrated by the hydrogenation of a mixture of methyl linoleate and alkali-conjugated methyl linoleate, i.e. two linoleic acid isomers. When using a nickel catalyst, the rate of reaction of the conjugated isomer was found to be 13.0 times as fast as the rate of reaction of the methylene interrupted isomer [15]. In other words, fatty acid isomers can react at widely different rates. Some 20 years earlier, Thompson hydrogenated a mixture of linseed oil and tung oil and thus compared the rates of reaction of methylene interrupted linolenic acid and conjugated linolenic acid (eleostearic acid); he also found that the conjugated isomer reacts much faster than the non-conjugated isomer [16]. However, in practice when comparing similar oils, the impact of this assumption being wrong is minimal.

So after all these years, we continue to use the fatty acid selectivity concept, despite the fact that most of the assumptions on which this concept is based have turned out to be false and the present meaning of this concept has deviated from its original definition. So when catalyst manufacturers report improvements in the selectivity of their catalysts, does this mean that these catalysts are more active and thus maintain a low hydrogen concentration for a longer period of time? When people talk about "selective process conditions", they unwittingly concede that the ratio of rate constants, which should itself be a constant, depends on process conditions after all.

Accordingly, the concept of fatty acid selectivity fulfils a need. This raises the question of whether a better, i.e. scientifically sound definition can be put forward. In theory, this should be possible. It should be possible to characterise hydrogenation catalysts by the actual rate constants of the various reactions involved in hydrogenating edible oils. Describing the likelihood that the catalyst adsorbs a particular triglyceride may be difficult but with sufficient insight, some simplifications may well be introduced into this description. Quantifying rate constants is more difficult especially since at the moment, no suitable equipment to measure the concentration of the hydrogen concentration in the oil is available; the sensor that is commercially available (http://www.fugatron.com) only operates within a temperature range of 20–200 °C.

But would it not be nice and informative if catalyst manufacturers were to describe their products by adsorption constants, rate constants and equilibrium constants? Then we would be in a position to compare different catalysts and choose the most suitable one on an objective basis. Sadly enough, the current *trans* scare and the notion that academic research should be socially relevant make it unlikely that any progress in this direction will be made.

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