Triglyceride Composition of a Partially Randomized Reaction Mixture

Sir:

In their paper "Monitoring chemical interesterification" (1), the authors claim that "partially interesterified products have unique functional properties (melting point and solid fat index/content) compared to the physical and randomized blends." I disagree with this claim because I expect that the triglyceride composition of a partially randomized reaction mixture can also be attained by mixing the fully randomized product with the raw materials used in the interesterification process.

Allow me to substantiate this expectation by considering a very simple system consisting of fatty acid esters of ethylene glycol and comprising only two different fatty acids, A and B. If the starting materials are then denoted by AA and BB, they form AB and BA on randomization, and their mole fractions can be calculated from the molar ratio of A to B. If we assume the mole fraction of AA in the starting mixture to be a, then the mole fraction of BB equals $(1 - a)$. After complete randomization, the mole fractions of the three components are:

$$\mathrm{AA} = a^2;\quad \mathrm{BB} = (1-a)^2;\quad \mathrm{AB}+\mathrm{BA} = 2a(1-a) \qquad [1]$$

If we then assume that by partial randomization a mole fraction $2p$ of the compounds (AB + BA) is formed, the composition of the partially randomized mixture is:

$$\mathrm{AA} = a - p;\quad \mathrm{BB} = 1 - a - p;\quad \mathrm{AB}+\mathrm{BA} = 2p \qquad [2]$$

Part of the AA in this partially randomized mixture is unreacted AA since the randomization is partial, and the remainder corresponds to its concentration in the randomization product. The unreacted part can thus be calculated by deducting the randomization-linked amount of AA from the total amount $[a - p]$ of AA. This randomization-linked amount is expressed on a *pro rata* basis by multiplying the actual mole fraction $[2p]$ of (AB + BA) in the partially randomized mixture with the mole fraction $[a^2]$ of AA in the fully randomized product and then dividing by the mole fraction $[2a(1 - a)]$ of (AB + BA) in the fully randomized product:

$$\begin{aligned}\mathrm{AA}_{\text{unreacted}} &= a - p - \frac{2pa^2}{2a(1-a)}\\ &= a - p - \frac{pa}{1-a}\\ &= \frac{a(1-a) - p(1-a) - pa}{1-a}\\ &= \frac{a - a^2 - p}{1-a}\end{aligned} \qquad [3]$$

Similarly, the mole fraction of BB in the partially randomized mixture can be calculated as:

$$\begin{aligned}\mathrm{BB}_{\text{unreacted}} &= 1 - a - p - \frac{2p(1-a)^2}{2a(1-a)}\\ &= 1 - a - p - \frac{p(1-a)}{a}\\ &= \frac{a - a^2 - ap - p(1-a)}{a}\\ &= \frac{a - a^2 - p}{a}\end{aligned} \qquad [4]$$

The two final expressions for $\mathrm{AA}_{\text{unreacted}}$ and $\mathrm{BB}_{\text{unreacted}}$ show that their ratio equals $a/(1 - a)$ and is the same as in the starting mixture. In other words, in the case of ethylene glycol and only two different fatty acids, a partially randomized reaction mixture consists of fully randomized product and the raw materials, whereby these raw materials are present in the same ratio as in the original starting mixture.

This finding has been derived for a simple system in order to simplify the mathematics concerned, but what about the randomization of triglycerides? They contain many different fatty acid moieties that are bound to glycerol instead of to ethylene glycol. However, (i) since interesterification occurs at the ester bond, (ii) since fatty acids in commonly processed oils have a long chain, and (iii) any double bonds are far removed from the ester bond, an effect of chain length or unsaturation on the reactivity of fatty acids is not to be expected. Since intraesterification has been found to be fast in comparison with interesterification, positional selectivity can also be ruled out so that it is highly likely that the above finding is also valid for the partial randomization of triglycerides.

Therefore, the products obtained by partial interesterification (1) can be arrived at more easily and cheaply by blending the fully randomized product with the starting materials used to produce it.

REFERENCE

1. Liu, L., and D. Lampert, Monitoring Chemical Interesterification, *J. Am. Oil Chem. Soc. 76*:783–787 (1999).

Albert J. Dijkstra
Albijn Van den Abeelelaan 2
B-8500 Kortrijk, Belgium
E-mail: dijkstra-tucker@technologist.com

Paper no. J9408 in *JAOCS 77*, 333 (March 2000).

[Received September 23, 1999; accepted November 29, 1999]

Copyright © 2000 by AOCS Press