# *Trans* FA in Sunflower Oil at Different Steps of Refining

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**ABSTRACT:** The contents of total *trans* FA of sunflower oils at different stages of refining processes were determined by capillary GLC. The contents of 18:1, 18:2, and 18:3 *trans* acids were 0.22 ± 0.03, 2.31 ± 0.23, and 0.03 ± 0.01%, respectively, in physically refined sunflower oils, and 0.05 ± 0.01, 0.69 ± 0.26, and 0.02 ± 0.01%, respectively, in chemically refined sunflower oils. The total *trans* FA contents drastically increased at the end of the physical refining process. The total *trans* FA contents of chemically refined sunflower oils were <1%. Because of the high temperature applied in the last stage of physical refining, the content of total *trans* FA was higher than in chemically refined sunflower oils. The last-stage conditions should be carefully evaluated to reduce the formation of *trans* FA during physical refining.

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**KEY WORDS:** Capillary gas–liquid chromatography, chemical refining, physical refining, sunflower oil, *trans* FA.

Vegetable oils are refined by chemical or physical means. The typical oil-refining process includes degumming, chemical or physical refining, bleaching, and deodorizing (1). The objective of refining edible oils is to remove unacceptable materials with the least possible effect on desirable components and the least possible loss of oil (2). However, chemical or physical refining subjects oils to high temperatures, alkali, and metal processing equipment that can alter their chemical compositions (3). Deodorization/steam distillation is an important operation in the vegetable oil refining process. In both industrial processes, the last stage consists of heating the oil for 1 to 4 h at a high temperature (180–260°C), under low pressure (1–10 mbar), and with steam or nitrogen injection (4). The heating during deodorizing and/or physical refining causes changes in the content of minor glycerol compounds that show hydrolytic, oxidative, or thermal degradation (5). Small amounts of *trans* unsaturated FA are formed during refining, particularly in the last refining stage, i.e., during deodorization (6).

Refining not only eliminates impurities, such as phospholipids, FFA, peroxides, polymers, pigments, and secondary oxidation products, but also minimizes *trans* FA formation and tocopherol loss (7). There is an international trend toward replacing chemical refining with physical refining (2), although some experts remain skeptical. The caustic soda refining system is the technology of choice (1). The aim of this study was to investigate the effects of chemical and physical refining processes that are carried out industrially on the geometrical isomerization of unsaturated FA in sunflower oil.

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## EXPERIMENTAL PROCEDURES

*Samples*. Sunflower oils were obtained from processing lines of factories using chemical (including degumming-neutralizing, bleaching, winterizing, and, finally, deodorizing steps) and physical refining (including degumming, bleaching, winterizing, and, finally, steam distillation steps). Samples were taken before and after each refining step. Samples were taken three times over a 3-mon period. Values are the means ± SD. Dark glass containers were purged with nitrogen gas after filling to prevent oxidation and stored at 4°C until analyzed. FAME standards (99% purity) were purchased from Nu-Chek-Prep Inc. (Elysian, MN).

*Industrial chemical refining process.* Crude oil was degummed by 0.2% phosphoric acid (85%) at 60°C with slow agitation for 30 min. Gums were separated by centrifuging. Degummed oil was mixed with sodium hydroxide solutions at 80–90°C. After being stirred for 10 min at this temperature, the soapstock was separated from the refined oil by decanting and centrifuging. The neutralized oil was washed and dried. In the next step, the oil was bleached at 80°C with vigorous stirring for 25 min using 1% bleaching earth (w/w). The oil was then cooled to 60°C and filtered. Winterization was carried out from 30 to 5°C for 10 h, and the final temperature was maintained for 10 h. After filtering, the winterized oil was deodorized at 230°C for 2 h, and cooled to 45°C.

*Industrial physical refining process.* Crude oil was degummed with 2% water (w/w) at 70°C for 30 min. After drying, the oil was submitted to dry degumming with 0.1% citric acid (64%) at 30°C for 30 min. The oil was bleached at 100°C with vigorous stirring for 20 min, using 1% activated earth (w/w). The oil was then cooled to 75°C and filtered. After bleaching, the oil was winterized as in the chemical refining process. Steam refining was carried out at 265°C for 1 h, and the oil was cooled to 50°C.

*Preparation of FAME.* FAME were prepared from the sunflower oils after alkaline hydrolysis, followed by methylating in methanol with 12.5% $BF_3$ catalyst. The final concentration of the FAME was approximately 7 mg/mL in heptane (8).

*Capillary GLC.* Analyses of the FAME by capillary GLC were carried out on a Hewlett-Packard 6890 chromatograph, equipped with an FID on a split injector. A fused-silica capillary column (Chrompack, Middleburg, The Netherlands) was used for the FAME analysis (CP™-Sil 88, 50 m × 0.25 mm i.d., 0.2 μm film). GLC operating conditions were: a temper-

ature program of 130°C for 5 min, increasing at a rate of 2°C/min to 177°C; injector temperature, 250°C; detector temperature, 250°C; and carrier gas, 1 mL/min helium.

## RESULTS AND DISCUSSION

The contents of *trans* FA during the chemical and physical refining processes of sunflower oils are given in Tables 1 and 2. The crude sunflower oils contained no measurable amounts of 18:3 *trans* acid and only very small amounts of 18:2 *trans* acid (from 0.04 ± 0.01 to 0.05 ± 0.01%) and 18:1 *trans* acid (0.01 ± 0.01%). The amount of 18:2 *trans* acid was higher than 18:1 *trans* acid in crude sunflower. *Trans* FA are probably formed by heat treatment of sunflower seed before or during the extraction process. Raw vegetable oils include a negligible amount of *trans* unsaturated FA, ranging between 0.1 and 0.3% of the total FA content (6). Ferrari *et al.* (9) reported that crude corn, soybean, and rapeseed oils contained small amounts of total *trans* unsaturated FA (0.1%). Heating the raw material (oilseed or nuts) may also considerably increase the *trans* FA content of the resulting oils (10). The low-*trans* level for the refined oils was explained by the fact that these oils were cold pressed (11).

In both chemical and physical refining, there were no changes in the contents of geometrical isomerization of unsaturated FA as a result of degumming, neutralizing, and winterizing. The *trans* FA contents remained at their original levels. In contrast, there were minor changes in the contents of 18:2 *trans* acid and 18:1 *trans* acid after bleaching, and no measurable amounts of 18:3 *trans* acid were detected in either of the bleached sunflower oils. The amount of total *trans* unsaturated FA increased from 0.06 ± 0.02 to 0.08 ± 0.01% during bleaching in chemical refining (Table 1). Similar effects were observed for the bleached sunflower oil in physical refining in which the amount of total *trans* unsaturated FA increased from 0.05 ± 0.03 to 0.08 ± 0.03% (Table 2). Ferrari *et al.* (9) reported that bleaching induced *trans* isomerization (from 0.3 to 0.7%) in chemical refining of soybean and rapeseed oils. According to Segers (12), *trans* FA increased sharply when bleaching was carried out at high temperatures. On the other hand, as Schwarz (6) demonstrated in refining on an industrial scale, no *trans* isomerization occurred during hydration (degumming), deacidifying, and bleaching.

Steam-distilled sunflower oils had higher total *trans* FA content (2.56 ± 0.25%) than did the deodorized sunflower oils (0.76 ± 0.27%). The 18:2 *trans* acid was the major *trans* group at the end of physical and chemical refining. The 18:2 *trans* acid contents of the steam-distilled sunflower oils (2.31 ± 0.23%) were higher than the contents (0.69 ± 0.26%) of deodorized sunflower oils. The 18:1 *trans* acid contents of the steam-distilled sunflower oils were 0.22 ± 0.03%, whereas those of deodorized sunflower oils were 0.05 ± 0.01%. In contrast to deodorization, the 18:1 *trans* acid content of sunflower oil significantly increased during steam distillation. The starting crude sunflower oils contained no measurable amount of 18:3 *trans* acid, but the oils from both physical and chemical refining contained very small amounts of 18:3 *trans* acid. The 18:3 *trans* acid contents of the physically and chemically refined oils were very similar. Total *trans* FA, 18:1 *trans* acid, and 18:2 *trans* acid contents were higher in physically refined oil compared to chemically refined oil. Because of the higher steam-distillation temperature applied in physical refining,

**TABLE 1**
**FA Compositions and *trans* FA Contents of Sunflower Oil After Different Processing Steps of Chemical Refining[a]**

| FA | Crude[b] | Degummed-neutralized | Bleached | Winterized | Deodorized |
|---|---|---|---|---|---|
| 14:0 | 0.08 ± 0.01 | 0.08 ± 0.01 | 0.07 ± 0.01 | 0.06 ± 0.01 | 0.06 ± 0.01 |
| 16:0 | 5.73 ± 0.11 | 5.80 ± 0.08 | 5.71 ± 0.12 | 5.41 ± 0.31 | 5.39 ± 0.32 |
| 16:1 | 0.14 ± 0.01 | 0.14 ± 0.01 | 0.14 ± 0.01 | 0.14 ± 0.01 | 0.14 ± 0.01 |
| 18:0 | 3.70 ± 0.09 | 3.87 ± 0.12 | 3.70 ± 0.11 | 3.39 ± 0.27 | 3.49 ± 0.19 |
| 18:1 *trans* | 0.01 ± 0.01 | 0.01 ± 0.01 | 0.02 ± 0.01 | 0.02 ± 0.01 | 0.05 ± 0.01 |
| 18:1 *cis* | 26.81 ± 0.96 | 26.48 ± 0.81 | 26.74 ± 0.99 | 26.81 ± 0.97 | 26.84 ± 0.99 |
| 18:2 *trans* | 0.05 ± 0.01 | 0.05 ± 0.01 | 0.06 ± 0.01 | 0.06 ± 0.01 | 0.69 ± 0.26 |
| 18:2 *cis* | 62.09 ± 1.08 | 62.16 ± 0.98 | 62.14 ± 1.07 | 62.70 ± 0.96 | 61.93 ± 1.01 |
| 18:3 *trans* | —[c] | — | — | — | 0.02 ± 0.01 |
| 18:3 *cis* | 0.08 ± 0.01 | 0.08 ± 0.01 | 0.09 ± 0.01 | 0.09 ± 0.01 | 0.07 ± 0.01 |
| 20:0 | 0.26 ± 0.02 | 0.26 ± 0.02 | 0.26 ± 0.02 | 0.26 ± 0.02 | 0.26 ± 0.02 |
| 20:1 | 0.14 ± 0.01 | 0.15 ± 0.02 | 0.15 ± 0.02 | 0.15 ± 0.02 | 0.15 ± 0.02 |
| 22:0 | 0.69 ± 0.02 | 0.69 ± 0.01 | 0.69 ± 0.01 | 0.69 ± 0.01 | 0.69 ± 0.01 |
| 24:0 | 0.22 ± 0.02 | 0.23 ± 0.01 | 0.23 ± 0.01 | 0.22 ± 0.01 | 0.22 ± 0.01 |
| Total saturated | 10.68 ± 0.21 | 10.93 ± 0.15 | 10.66 ± 0.21 | 10.03 ± 0.58 | 10.11 ± 0.51 |
| Total monounsaturated | 27.10 ± 0.97 | 26.78 ± 0.82 | 27.05 ± 1.01 | 27.12 ± 0.98 | 27.18 ± 1.02 |
| Total polyunsaturated | 62.22 ± 1.06 | 62.29 ± 0.97 | 62.29 ± 1.06 | 62.85 ± 0.96 | 62.71 ± 1.03 |
| Total *trans* | 0.06 ± 0.02 | 0.06 ± 0.02 | 0.08 ± 0.01 | 0.08 ± 0.01 | 0.76 ± 0.27 |
| Total unsaturated | 89.32 ± 0.21 | 89.07 ± 0.15 | 89.34 ± 0.21 | 89.97 ± 0.58 | 89.89 ± 0.51 |
| Total unsaturated/ total saturated | 8.36 ± 0.18 | 8.15 ± 0.12 | 8.38 ± 0.19 | 8.97 ± 0.59 | 8.89 ± 0.50 |

[a]Each value is an average of three determinations, mean ± SD, and is expressed as a weight percentage of total FAME.
[b]Equal amounts of pressed oil and extracted oil (by hexane extraction of oilcake) were mixed to prepare the crude sunflower oils.
[c]—, not detected (<0.01%).

**TABLE 2**
**FA Compositions and *trans* FA Contents of Sunflower Oils After Different Processing Steps of Physical Refining[a]**

| FA | Crude[b] | Degummed | Bleached | Winterized | Steam distillated |
|---|---|---|---|---|---|
| 14:0 | 0.06 ± 0.01 | 0.07 ± 0.01 | 0.07 ± 0.01 | 0.06 ± 0.01 | 0.06 ± 0.01 |
| 16:0 | 5.88 ± 0.12 | 5.89 ± 0.12 | 5.88 ± 0.12 | 5.31 ± 0.34 | 5.30 ± 0.35 |
| 16:1 | 0.15 ± 0.01 | 0.15 ± 0.01 | 0.15 ± 0.01 | 0.15 ± 0.01 | 0.15 ± 0.01 |
| 18:0 | 3.78 ± 0.07 | 3.79 ± 0.08 | 3.83 ± 0.12 | 3.40 ± 0.10 | 3.70 ± 0.10 |
| 18:1 *trans* | 0.01 ± 0.01 | 0.01 ± 0.01 | 0.02 ± 0.01 | 0.02 ± 0.01 | 0.22 ± 0.03 |
| 18:1 *cis* | 25.89 ± 1.67 | 25.82 ± 1.72 | 25.94 ± 1.73 | 25.98 ± 1.74 | 26.08 ± 1.76 |
| 18:2 *trans* | 0.04 ± 0.01 | 0.04 ± 0.02 | 0.06 ± 0.02 | 0.06 ± 0.02 | 2.31 ± 0.23 |
| 18:2 *cis* | 62.81 ± 1.57 | 62.85 ± 1.62 | 62.63 ± 1.60 | 63.62 ± 1.56 | 60.79 ± 1.63 |
| 18:3 *trans* | —[c] | — | — | — | 0.03 ± 0.01 |
| 18:3 *cis* | 0.07 ± 0.01 | 0.07 ± 0.01 | 0.08 ± 0.01 | 0.08 ± 0.01 | 0.04 ± 0.01 |
| 20:0 | 0.27 ± 0.02 | 0.26 ± 0.01 | 0.27 ± 0.02 | 0.27 ± 0.02 | 0.27 ± 0.02 |
| 20:1 | 0.14 ± 0.01 | 0.15 ± 0.01 | 0.15 ± 0.01 | 0.15 ± 0.01 | 0.14 ± 0.01 |
| 22:0 | 0.70 ± 0.01 | 0.70 ± 0.01 | 0.71 ± 0.01 | 0.70 ± 0.02 | 0.71 ± 0.02 |
| 24:0 | 0.20 ± 0.01 | 0.20 ± 0.01 | 0.21 ± 0.01 | 0.20 ± 0.01 | 0.20 ± 0.01 |
| Total saturated | 10.89 ± 0.12 | 10.91 ± 0.12 | 10.97 ± 0.17 | 9.94 ± 0.43 | 10.24 ± 0.34 |
| Total monounsaturated | 26.19 ± 1.69 | 26.13 ± 1.73 | 26.26 ± 1.74 | 26.30 ± 1.74 | 26.59 ± 1.78 |
| Total polyunsaturated | 62.92 ± 1.57 | 62.96 ± 1.61 | 62.77 ± 1.59 | 63.76 ± 1.55 | 63.17 ± 1.56 |
| Total *trans* | 0.05 ± 0.03 | 0.05 ± 0.03 | 0.08 ± 0.03 | 0.08 ± 0.03 | 2.56 ± 0.25 |
| Total unsaturated | 89.11 ± 0.12 | 89.09 ± 0.12 | 89.03 ± 0.17 | 90.06 ± 0.43 | 89.76 ± 0.34 |
| Total unsaturated/ total saturated | 8.18 ± 0.10 | 8.17 ± 0.11 | 8.12 ± 0.14 | 9.06 ± 0.42 | 8.77 ± 0.31 |

[a]Each value is an average of three determinations, mean ± SD, and expressed as a weight percentage of total FAME.
[b]Equal amounts of pressed oil and extracted oil (by hexane extraction of oilcake) were mixed to prepare the crude sunflower oils.
[c]—, not detected (<0.01%).

the content of total *trans* FA was higher than in chemically refined oils. The appearance of 18:2 *trans* acid and 18:3 *trans* acid in vegetable oils is linked to deodorizing or physical refining (13). Ackman and Hooper (14) showed that geometrical isomerization of 18:2 and 18:3 acids occurs during deodorization, even under normal industry conditions. According to Čmolik *et al.* (15), the concentration of isomeric PUFA in physically refined rapeseed oil was slightly higher than in chemically refined rapeseed oil. Ferrari *et al.* (9) also reported that the levels of *trans* FA of corn, soybean, and rapeseed oils increased substantially (1–4%) in the industrial refining processes. Greyt *et al.* (16) found that the *trans* FA contents of the commercial sunflower oils ranged from 0.2 to 1.8%.

Clearly, the physical and chemical refining processes induce geometrical isomerization of unsaturated FA. Deodorization/steam distillation is the principal step in oil refining that increases the content of *trans* FA. The major factors affecting the formation of *trans* FA are temperature, heating time, pressure, and stripping steam dosage (11,17). A deodorization temperature of 220–230°C seems to be the critical point above which 18:3 acid isomerization substantially increases. The critical temperature is higher for 18:2 acid, over 240°C (18). Kellens (7) reported that chemical refining should be done at 230–235°C and physical refining at 235–240°C to obtain deodorized oils with low levels of *trans* FA (<1%). Bruggen *et al.* (17) reported that the rate of conversion also depends on the level of unsaturation of the FA molecule: trienoic FA isomerize more easily than dienoic FA. The lowest conversion rate is observed for the monoenoic FA. The distribution of the 18:1, 18:2, and 18:3 FA in the starting oils is quite different. Consequently, the amounts of detectable *trans* isomers formed during refining are different.

For the formation of geometrical isomers of FA to be avoided during deodorization, the temperature in the deodorizer should be relatively low and the heating time sufficiently short to minimize isomerization (19). The severity of the deodorizing conditions should be reduced to obtain *trans* FA contents below 0.5% for sunflower oil (7). In European countries the quality parameters for refined edible oils include low levels of *trans* FA (<1%) (20).

This study indicates a drastic increases in the total *trans* FA content at the end of the physical refining process. Isomerization during the physical refining process exceeded that of chemical refining. The mean *trans* FA content of the chemically refined sunflower oils was less than 1%. The last stage was the principal stage of refining of sunflower oils that contributed to increases in the content of *trans* FA. Adjustments in the temperature used in the last stage of physical refining are recommended to attain international quality standards with respect to the *trans* FA content.

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