to measuring the relative thermooxidative stability of oils is by no means new, but still unique in using extremely small samples, in being fast and in providing good reproducibility of results. Such an analytical method, which is capable of measuring the relative thermooxidative stability, is potentially useful not only in the oil and food industry, but also in cosmetics production, the plastics and petrochemical industries and many others.

REFERENCES

1. Gray, J.I., JAOCS 55:539 (1978).
2. Hadorn, H., and K. Zurcher, Dtsch. Lebensm. Rundschau 70:57 (1974).
3. Wheeler, D.H., Oil and Soap 9:89 (1932).
4. AOCS Official and Tentative Methods, Champaign, IL, 1981, Method Cd 12-57.
5. deMan, J.M., and L. deMan, JAOCS 61:534 (1984).
6. "Petroleum Products and Lubricants," Part 24, Annual Book of Standards, American Society for Testing and Materials, ASTM, Philadelphia, PA, 1972, Method D 2272-67 (Reapproved 1983).
7. Gearhart, W.M., B.N. Stuckey and J.J. Austin, JAOCS 34:427 (1957).
8. Warner, K., and E.N. Frankel, JAOCS 62:100 (1985).
9. Cross, C.K., JAOCS 47:229 (1970).
10. Hassel, R.L., JAOCS 53:179 (1976).
11. Nieschlag, H.J., J.W. Hagemann and J.A. Rothfus, Anal. Chem. 46:2215 (1974).
12. Hagemann, J.W., and J.A. Rothfus, JAOCS 56:629 (1979).
13. Buzás, I., J. Simon and J. Holló, J. Thermal. Anal. 12:397 (1977).
14. Buzás, I., E. Kurucz-Lusztig and J. Holló, Acta Aliment. Acad. Sci. Hung. 7:335 (1978).
15. Buzás, I., E. Kurucz and J. Holló, JAOCS 56:685 (1979).
16. Olcott, H.S., and E. Einset, JAOCS 35:161 (1958).
17. Cassel, B.B., and A.P. Gray, Thermochim. Acta 36:265 (1980).
18. Norem, S.D., M.J. O'Neill and A.P. Gray, Thermochim. Acta 1:29 (1970).
19. Kwon, T.W., H.E. Snyder and H.G. Brown, JAOCS 61:1843 (1984).
20. Going, L.H., JAOCS 45:632 (1968).
21. Rock, S.P., and H. Roth, JAOCS 41:228 (1964).
22. Emanuel, N.M., "The Inhibition of Fat Oxidation Processes," Pergamon Press, Oxford, New York, 1967, pp. 29-33.

♣ Flavor and Oxidative Stability of Continuously Hydrogenated Soybean Oils

K.J. MOULTON SR.*, S. KORITALA and **K. WARNER,**
Northern Regional Research Center, Agricultural Research Service,
U.S. Department of Agriculture, Peoria, IL 61604

ABSTRACT

Soybean oil was partially hydrogenated in a continuous system with copper and nickel catalysts. The hydrogenated products were evaluated for flavor and oxidative stability. Processing conditions were varied to produce oils of linolenate contents between 0.4 and 2.7%, as follows: oil flow, 0.6-2.2 liters/hr; reaction temperature, 180-220 C; hydrogen pressure, 100-525 psig, and catalyst concentration, 0.5-1% copper catalyst or 0.1% nickel catalyst. *Trans* unsaturation varied from 8 to 20% with copper catalyst and from 15.0 to 27% with nickel catalyst. Linolenate selectivity was 9 with copper catalyst and 2 with nickel catalyst. Flavor evaluation of finished oils containing 0.01% citric acid (CA), appraised initially and after accelerated storage at 60 C, showed no significant difference between hydrogenated oils and nonhydrogenated oil. However, peroxide values and oxidative stability showed that hydrogenated oils were more stable than the unhydrogenated oil. CA+TBHQ (tertiary butylhydroquinone) significantly improved the oxidative stability of test oils over oils with CA only, but flavor scores showed no improvement. Dimethylpolysiloxane (MS) had no effect on either flavor or oxidative stability of the oils.

INTRODUCTION

Currently most of the acceptable soybean salad oils and shortening-base stocks having good shelf-life are produced by batch hydrogenation processes. Partial hydrogenations in batch convertors with nickel or copper catlyst are reported to improve flavor and oxidative stability of oils for cooking, frying and baking (1-4). The potential of effective continuous slurry hydrogenation with nickel or copper catalyst has been reported by several authors (5-8); however, the oils produced by these processes were not evaluated for flavor and oxidative stability.

_____
*To whom correspondence should be addressed.

This study extends our previous work (8) and considers the relationship of flavor scores and oxidative stability of test oils to the operating conditions for continuous production of partially hydrogenated oils.

EXPERIMENTAL

Materials

Commercial alkali refined and bleached soybean oil (SBO) from Central Soya Inc., Ft. Wayne, Indiana, was used as base and control oil. Commercially hydrogenated and processed oil (Ni-4.6) was included for comparison purposes in the sensory testing program. Analyses of SBO and commercial oils are shown in Table I.

Hydrogenation catalysts, Cu1106P (39% CuO, 43.5% Cr_2O_3, 10% BaO), Nysel (25% nickel in tristearin) and Super-filtrol bleaching earth were obtained from Harshaw/Filtrol Partnership, Cleveland, Ohio.

Additives in deodorized test oils, added during the cooling stage, included: citric acid (CA) (J.T. Baker Chemical Co., Phillipsburg, New Jersey) dissolved in distilled water; tertiary butylhydroquinone (TBHQ) (Eastman Chemical Products, Inc., Kingsport, Tennessee) dissolved in ethyl alcohol, and dimethylpolysiloxane (MS) (Dow Corning Corp., Midland, Michigan).

Analytical Methods

Methyl esters of fatty acids were prepared by transesterification of the sample oil with sodium methoxide in methanol (9). Fatty acid compositions were determined by gas liquid chromatography (GLC) of methyl esters on a column packed with

EGSS-X. Iodine values (IV) were calculated from the GLC analyses. Percent trans-isomers were determined by infrared adsorption of the methyl esters at 966 cm⁻— with methyl elaidate standard. Linolenate selectivities (K_{Ln}/K_{Lo}) were determined according to AOCS method Tz 1b-79 (10). Specific trans isomerization for an oil was calculated by dividing trans value by the decrease in IV (trans/ΔIV). Peroxide value was determined by AOCS method Cd 8-53 (10). Induction period of oils was determined by a modified weight method of Olcott et al. (11) with 10 g oil (in 100 ml uncovered beaker) aged at 60 C in a forced-draft oven. The induction period is defined as the day the test oil shows a rapid change in slope in the time-weight gain plot. Induction period is the time an oil resists formation of oxidation products.

TABLE I

Fatty Acid Composition of Test Oils

Test oil[a]	Fatty acid composition, %				Calc IV[c]	trans %
	St[b]	M	D	T		
SBO	4.3	22.7	54.2	8.7	136	--
Ni-4.6 (w)[d]	3.5	37.8	42.9	4.6	119	17
Ni-2.7	7.1	49.3	30.7	2.7	103	15
Cu-2.4	4.2	30.4	52.7	2.4	124	8
Cu-0.5 (w)	4.0	41.9	44.0	0.5	114	19
Cu-0.4	4.4	42.2	42.4	0.4	111	20
Ni-0.4	16.4	62.8	10.2	0.4	73	27

[a]SBO, Soybean oil; Ni, nickel catalyst; Cu, copper catalyst; w, winterized oil; numerical values indicate linolenate content in the hydrogenated oil, i.e., Ni-4.6 (w) = soybean oil hydrogenated with nickel catalyst to linolenate content of 4.6% and winterized.

[b]St, stearate; M, monoene; D, diene; T, triene.

[c]Calculated from GLC data.

[d]Commercially hydrogenated and winterized (w).

Hydrogenation

The continuous hydrogenation system for this study, shown in Figure 1, was similar to a previously reported system (7) with the receiving section modified to discharge the product continuously without upsetting the system equilibrium. The apparatus consisted of an oil/catalyst charge reservoir, reciprocating pump, preheater, heated tube reactor and a degassing receiver. Oil/catalyst slurry of desired catalyst concentration was pumped at a predetermined rate (0.5 to 2.2 liters/hr) through the preheater to the reactor. The slurry, heated to 180-200 C in the reactor, was contacted with hydrogen (1 liter/min) near the entrance of the reactor. After the oil was hydrogenated, the oil/catalyst/hydrogen continued to the receiver where the oil/catalyst slurry was separated from the excess hydrogen and discharged continuously under a liquid oil seal. By use of external valves, connected to each port, the desired discharge point in the reactor could be chosen to obtain a pre-determined residence (reaction) time of the oil/catalyst/hydrogen mixture. The reaction temperature was measured by thermocouples at each port. A back-pressure regulator in the vent line controlled the system pressure (100-525 psig) within present limits. Hydrogenation conditions were adjusted to produce oils with varied compositions for taste panel evaluation (Table I).

An earlier publication (2) reported that small amounts of nickel catalyst tend to remain in a converter and lower the selectivity when copper is the catalyst in the next hydrogenation in the converter. We observed the same effect for continuous slurry reactions in a tube reactor. It was necessary to wash the reactor with acid, followed by several water rinses and complete drying, to remove the last traces of nickel catalyst from the system prior to hydrogenating with a copper catalyst. Ideally, one reactor should be dedicated for copper and another for nickel hydrogenation.

Post-refining processing treatments given each tested oil included hydrogenation, bleaching, winterization (when required) and deodorization. Selected partially hydrogenated and post-bleached oils were winterized in 1-gal wide-mouth
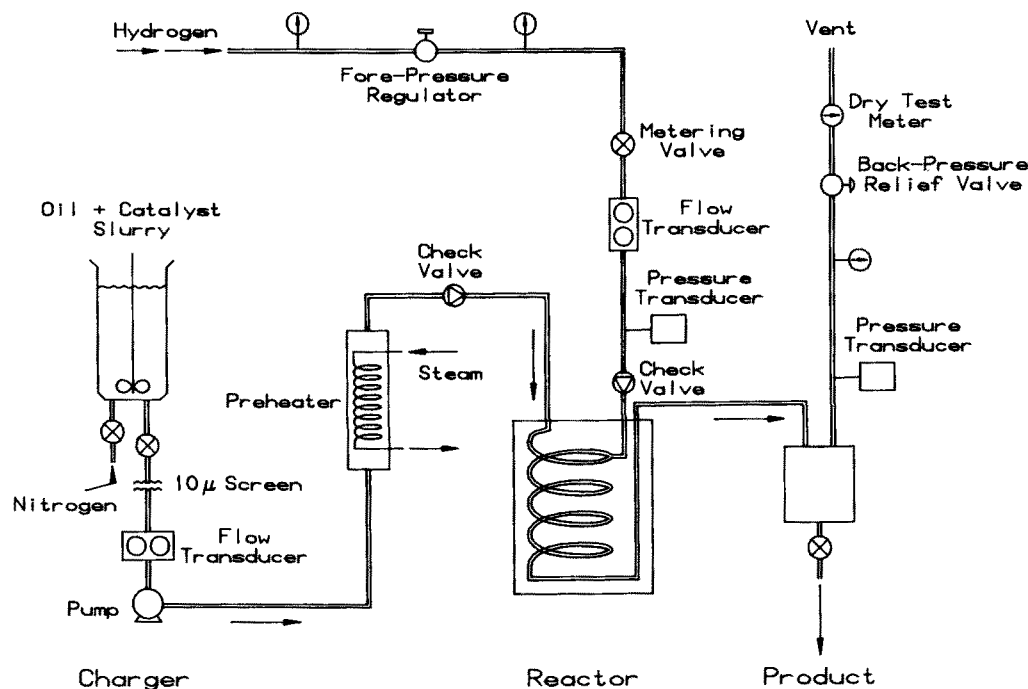

FIG. 1. Continuous slurry hydrogenation system.

jars at 4 C for 40 hr, then vacuum filtered through filter disks faced with gauze. Commercially hydrogenated/winterized oil and test oils were deodorized in the laboratory with an all-glass 4-flask apparatus (12) for 3 hr at 220 C, at less than 1 mm (Hg) with 5% steam. Citric acid (0.01%), TBHQ (0.02%) and MS (8 ppm) were added to the deodorized oils on the cooling cycle. Deodorized and stabilized oils were blanketed with nitrogen and stored at 0-5 C until testing.

Sensory Evaluation

A 15-member taste panel, trained to discriminate and identify oil flavors, evaluated oils using a flavor intensity scale ranging from 0 (strong) to 10 (bland) (13,14). Deodorized oils were evaluated initially (0-time) and after accelerated storage (8 days at 60 C). Significance of flavor scores was statistically computed by analysis of variances.

RESULTS AND DISCUSSION

Preliminary hydrogenation runs were conducted to select the proper temperature, pressure and slurry flow rate necessary to produce partially hydrogenated oils of desired fatty acid composition for salad or cooking uses. Because the slurry pump had a minimum practical rate of 0.5 liter/hr and the length of the reactor was fixed, it was necessary when using the less active copper catalyst to make multiple consecutive passes through the reactor to produce an oil low in linolenate. For example, to produce Cu-0.4 (soybean oil, hydrogenated with copper catalyst to 0.4% linolenate) it was necessary first to hydrogenate with 1% Cu catalyst at 200 C, 525 psig and oil flow-rate of 0.5 liter/hr and then hydrogenate again, without adding fresh catalyst, at the same temperature and pressure, but at an oil flow-rate of 1.5 liter/hr. With the more active nickel catalyst, only one pass was necessary at 181 C, 110 psig and an oil flow-rate of 0.6 liter/hr to reduce linolenate to 0.4% (Ni-0.4). At the other extreme, to produce hydrogenated oils with 2.4-2.7% linolenate (Cu-2.4 and Ni-2.7), an oil flow-rate of 2.2 liter/hr was found to be sufficient. For this study all oils traveled the entire length of the reactor and were discharged from port 9. Characteristics of the test oils are summarized in Table II. After winterization (w) the oil yield was 84% for Cu-0.5 (w). Both oils had cold tests exceeding 20 hr. Winterization was not necessary for SBO and Cu-2.4 because the cold test of these oils exceeded 36 hr.

A multifactorial statistical design was developed for sensory evaluation, to test the effect of hydrogenation with nickel and copper catalysts, each at three levels of linolenate and with two types of additives. The hydrogenated oils and control (SBO) were found to have good initial quality with flavor scores ranging from 7.3 to 8.5 (Table III) and PV (0). The effect of hydrogenation on flavor stability can be evaluated by comparing oils with CA only. After storage at 60 C, Ni-2.7 was rated significantly lower than Cu-2.4 or Ni-0.4. Ni-2.7 was described as rancid and "hydrogenated" (tallowy), whereas the other oils were judged predominantly buttery. The aged SBO was the least oxidatively stable with the highest PV (8.7) and shortest induction period (6 days). In contrast, Ni-0.4 was the most oxidatively stable, with the lowest PV (0.6) and longest induction period (25 days).

Evaluation of oils containing CA + MS showed a similar pattern except that the score for Ni-2.7 was slightly higher in the CA + MS series than in the CA series. In the presence of CA + MS, no significant differences were noted between the SBO and hydrogenated oils. Previous work (15) also showed little change in flavor stability and volatile headspace induction period for SBO containing CA + MS compared to SBO + CA only.

In the presence of CA + TBHQ, Ni-0.4 and Cu-2.4 aged oils had the highest flavor scores and were described by the panel as buttery, with a few "off flavor" descriptions. The effect of hydrogenation on peroxide value was obscured by the addition of TBHQ, but Ni-0.4 still had the lowest and SBO control the highest PV. The induction periods followed the same pattern as the corresponding PV, but with a much wider range of values. Addition of TBHQ to the oils did not improve the flavor stability of hydrogenated or nonhydrogenated oils when compared to the same oil treated with CA only. These results agree with previous work (4) showing that flavor stability of hydrogenated and nonhydrogenated oils was not significantly enhanced by addition of TBHQ. However, oxidative stability was significantly improved with TBHQ. With test oils containing CA + TBHQ + MS, some effects of hydrogenation were noted. Flavor stability of aged Ni-4.6 (w) and Cu-2.4 was greater than either the SBO or Ni-0.4. The lower score for the aged Ni-0.4 is unusual and could not be explained. Oxidative stability of oils containing CA + TBHQ + MS was not significantly different from oils with CA + TBHQ.

Results of this work agree with previous research (4) in showing little agreement between flavor scores and chemical measurements of oxidative stability. Factors that promote

TABLE II

Characteristics of Continuous Hydrogenated Test Oils

Oil	Hydrogenation conditions			Calc IV	trans %	SR, Ln	Cold test, hr	Winterization yield, %
	Temp. C	Press, psig	Oil rate, liter/hr					
SBO	---	---	---	136	0	-	36	100
Ni-4.6 (w)	---	Commercial	---	119	17	-	14	---
Cu-2.4[a]	200	520	2.2	124	8	9	36	100
Ni-2.7[b]	180	100	2.2	103	15	2		
Cu-0.5 (w)[a]	200	525	0.8	114	19	9	24	84
	200	525	1.5					
Cu-0.4[a]	200	525	0.8	111	20	9		
	200	525	1.5					
Ni-0.4[b]	181	110	0.6	73	27	2		

[a]1% Copper chromite catalyst.

[b]0.1% Nickel catalyst (25% Ni in tristearin).

TABLE III

Flavor and Oxidative Stability of Test Oils

Oil type/additive	Flavor scores[a]		Oxidative stability	
	Initial	8 Days @ 60 C	PV,[b] meq/kg	IP,[c] days
CA				
SBO	8.0	6.6	8.7	6
Ni-4.6 (w)	8.0	6.4	2.5	8
Ni-2.7	7.7	5.9	2.4	8
Cu-2.4	8.4	6.8	4.0	9
Cu-0.5 (w)	8.3	6.3	3.3	17
Cu-0.4	8.5	6.4	2.1	11
Ni-0.4	8.0	6.8	0.6	25
CA + MS				
SBO	8.3	6.3	6.4	5
Ni-4.6 (w)	7.7	6.8	1.5	8
Ni-2.7	7.7	6.3	2.2	8
Cu-2.4	7.9	6.6	2.9	9
Cu-0.5 (w)	---	---	---	---
Cu-0.4	8.3	6.7	2.1	9
Ni-0.4	8.2	6.8	0.3	25
CA + TBHQ				
SBO	8.5	6.2	1.5	47
Ni-4.6 (w)	8.0	6.0	0.9	68
Ni-2.7	7.7	6.6	0.4	81
Cu-2.4	8.2	6.9	0.4	67
Cu-0.5 (w)	8.0	6.1	1.0	>61
Cu-0.4	7.5	6.2	0.5	78
Ni-0.4	7.9	7.0	0.3	121
CA + TBHQ + MS				
SBO	7.6	6.0	1.5	45
Ni-4.6 (w)	8.2	7.6	0.7	68
Ni-2.7	7.3	6.6	0.4	79
Cu-2.4	7.8	7.2	0.6	73
Cu-0.5 (w)	---	---	---	---
Cu-0.4	7.7	6.6	0.5	78
Ni-0.4	7.9	6.1	0.3	113

[a]LSD = 0.8.

[b]PV = Peroxide Value of aged oils (8 days @ 60 C) at time of tasting.

[c]IP = Induction Period.

decomposition of peroxides in the oils have been discussed by Mounts (4) and Frankel (16). Other factors may account for this discrepancy, including higher sensitivity of human testers and their ability to integrate all quality aspects of an oil into a rating rather than just one parameter such as peroxide level. Flavors not related to oxidation, such as "hydrogenated," also affect flavor scores and are not detected by tests such as peroxide analyses.

This work showed that good quality hydrogenated oil can be made continuously in a slurry tube reactor. The flavor stability of continuously hydrogenated soybean oil in this study was not significantly better than the control oil; however, a similar observation was reported previously (4) for batch hydrogenated oil and control.

REFERENCES

1. Cowan, J.C., C.D. Evans, H.A. Moser, G.R. List, S. Koritala, K.J. Moulton and H.J. Dutton, JAOCS 47:470 (1970).
2. List, G.R., C.D. Evans, R.E. Beal, L.T. Black, K.J. Moulton and J.C. Cowan, JAOCS 51:239 (1974).
3. Moulton, K.J., R.E. Beal, K.A. Warner and B.K. Boundy, JAOCS 52:469 (1975).
4. Mounts, T.L., K. Warner and G.R. List, JAOCS 58:792 (1981).
5. Coombes, W.A., R.A. Zavada, J.E. Hansen, W.A. Singleton and R.R. King, U.S. Patent 3,792,067 (1974).
6. Snyder, J.M., T.L. Mounts, C.R. Scholfield and H.J. Dutton, JAOCS 59:19 (1982).
7. Koritala, S., K.J. Moulton Sr., J.P. Friedrich, E.N. Frankel and W.F. Kwolek, JAOCS 61:909 (1984).
8. Koritala, S., K.J. Moulton Sr. and E.N. Frankel, JAOCS 61:1470 (1984).
9. Bitner, E., T.L. Mounts and H.J. Dutton, JAOCS 57:209 (1980).
10. AOCS Official and Tentative Methods, Third Edition, Champaign, IL, 1981.
11. Olcott, H.S., and E. Einst, JAOCS 35:161 (1958).
12. Schwab, A.W., and H.J. Dutton, JAOCS 25:57 (1948).
13. Mounts, T.L., K.A. Warner, G.R. List, J.P. Friedrich and S. Koritala, JAOCS 55:345 (1978).
14. Mounts, T.L., and K. Warner, in "Handbook of Soybean Processing and Utilization," edited by D.R. Erickson, E.H. Pryde, O. Brekke, T.L. Mounts and R.A. Falb, American Oil Chemists' Society, Champaign, IL, 1980, pp. 245-266.
15. Warner, K., and E.N. Frankel, JAOCS 62:100 (1985).
16. Frankel, E.N., in "Handbook of Soybean Processing and Utilization," edited by D.R. Erickson, E.H. Pryde, O. Brekke, T.L. Mounts and R.A. Falb, American Oil Chemists' Society, Champaign, IL, 1980, pp. 229-244.