Determination of the Extent of Rancidity of Soybean Oil by Gas Chromatography Compared With Peroxide Value

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ABSTRACT

The development of rancidity in soybean oil has been studied by gas chromatography (GC), peroxide value (PV) and sensory evaluation. The GC method has been adapted from previous methodology and another type of column packing has been used for the purpose. The GC peaks have been treated as one whole group, and and oxidation value (OV) has been computed by means of an internal standard (*n*-octanol). The OV's have been correlated with the PV's. The flavor of soybean oil and a blend of 50% soybean oil and 50% hydrogenated soybean oil, both kept at 60 C for varying lengths of time, was evaluated by a panel and the results have been presented in a new graphical form. A relationship between the OV and the flavor of the fat has been demonstrated. The merits of the method are discussed.

INTRODUCTION

Organoleptic flavor evaluations of fats and oils are subjective and an objective instrumental technique would be very useful. Gas chromatography (GC) has been previously used to analyze volatile compounds from heated fats (1-4). Decomposition products of hydroperoxides, which are formed when the oil containing them is injected directly into a GC column, have also been studied (5-7). However, the quantitative relationship between the hydroperoxides in an oil and their decomposition products have not been fully investigated. In this study an attempt has been made to correlate organoleptic results with peroxide values (PV) and oxidation values (OV) which have been

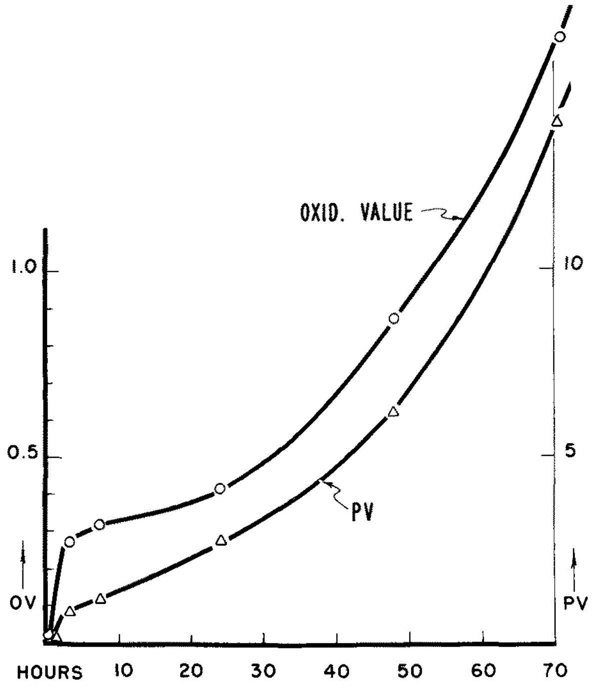

FIG. 2. The development of rancidity in soybean oil measured by gas chromatography (OV) and peroxide value (PV) held in dark at 60 C.

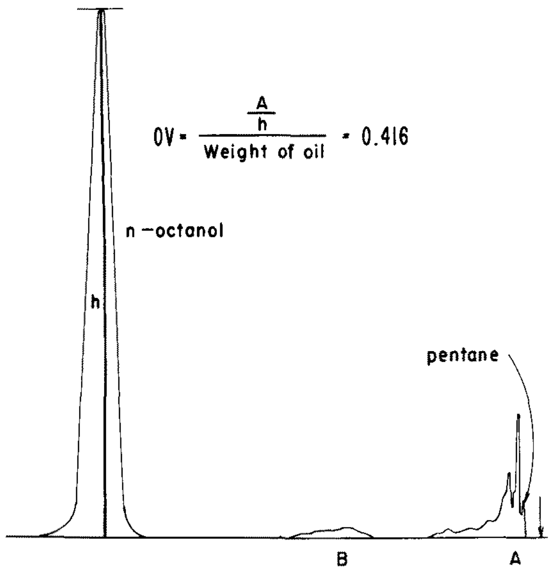

FIG. 1. Gas chromatogram of soybean oil, aged 24 hr at 60 C. Oil injected directly into the column.

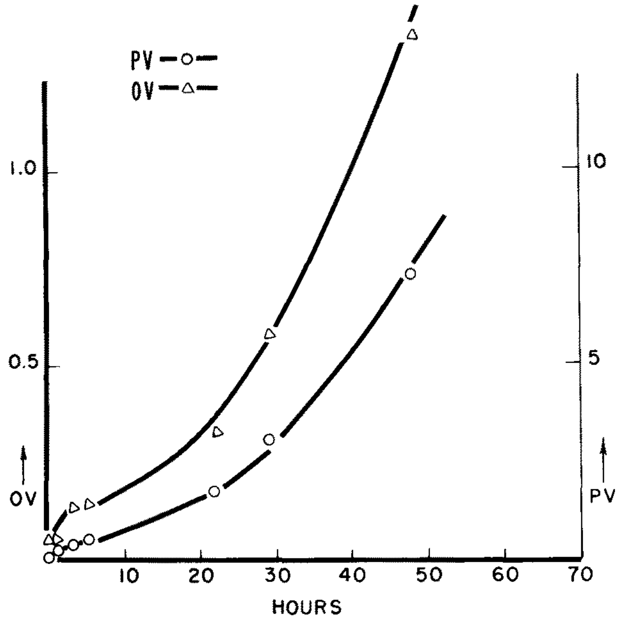

FIG. 3. The development of rancidity in a blend of soybean oil and hydrogenated soybean oil measured by gas chromatography (OV) and peroxide value (PV) held in dark at 60 C.

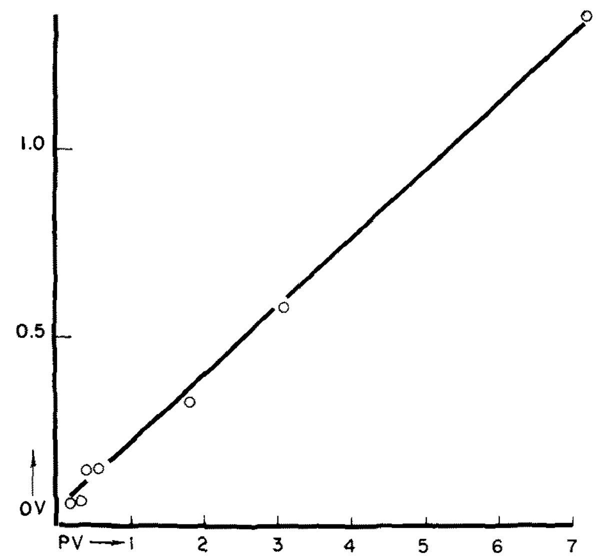

FIG. 4. Soybean oil plus hydrogenated soybean oil. Peroxide value (PV) plotted against gas chromatographic oxidation value (OV). Held in dark at 60 C.

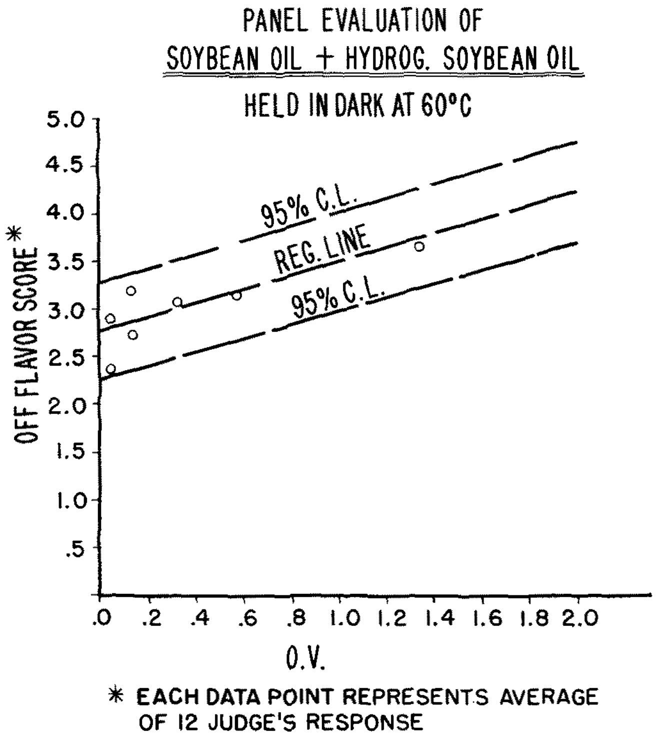

FIG. 5. The regression line of off flavor score vs. oxidation value (OV) of a blend of soybean oil and hydrogenated soybean oil. Simple rated score. The confidence limits (CL) have been marked.

TABLE I

Mean Off Flavor Scores for 50% Soybean Oil and 50% Hydrogenated Soybean Oil

Sample (class) no.	Off flavor score[a]	Ranking average
0	2.37	0.83
1	2.91	2.08
2	3.20	3.16
3	2.73	2.50
4	3.08	3.75
5	3.18	3.83
6	3.69	4.82

[a] The range is from 1.0, no off flavor to 6.0, very much off flavor. The average is 12.

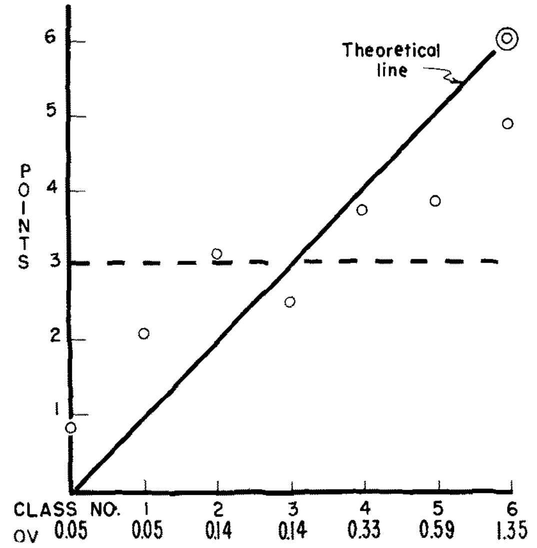

FIG. 6. Off flavor evaluation of a blend of soybean oil and hydrogenated soybean oil. Held in dark at 60 C. The marked straight line indicates perfect scoring. The horizontal dashed line represents a statistical average if no correlation is found.

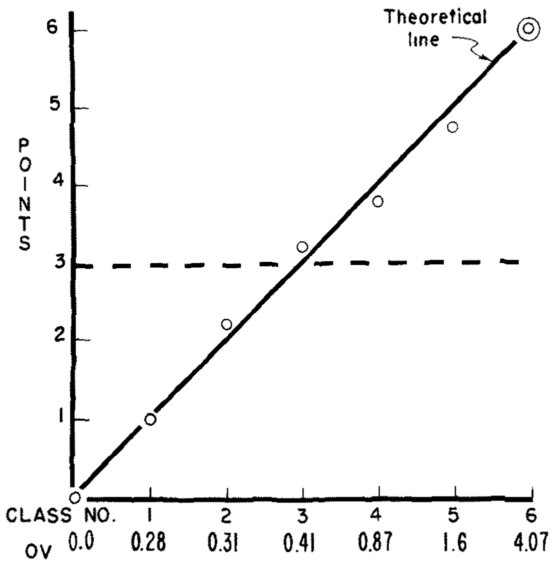

FIG. 7. Off flavor evaluation of soybean oil by the ranking method. Held in dark at 60 C. The marked straight line indicates perfect scoring. The horizontal dashed line represents a statistical average if no correlation is found.

obtained by an improved GC method. An improvement of the sensory evaluation of the samples for off flavor was attempted by using a ranking procedure.

EXPERIMENTAL PROCEDURES

Materials

100% Soybean oil was freshly deodorized in glass apparatus for 4 hr at 230 C, 0.5 mm Hg. Subsequently, it was stored at 60 C in darkness in closed jars for varying lengths of time. A plant-deodorized blend of 50% soybean oil and 50% hydrogenated soybean oil with a final iodine value (IV) of 95 was obtained from a refinery storage tank and also stored as above.

Analyses

N-Pentane and *n*-octanol were obtained from Fisher Scientific Company, and found to be pure by GC. A

TABLE II

Results From Ranking a Blend of 50% Soybean Oil and 50% Hydrogenated Soybean Oil

	0[a]	1	2	3	4	5	6
Length of treatment	0	40 Min	2 Hr 25 Min	5 Hr	22 Hr	29 Hr 35 Min	48 Hr
PV	0.1	0.3	0.4	0.5	1.8	3.1	7.4
OV	0.05	0.05	0.14	0.14	0.33	0.59	1.35
Order of ranking							
Judge 1[b]			4		2	5	6
	3			5		0	6
			4		2	5	6
Judge 2	0			3		5	6
		3		1	4	5	
		1		3	4	5	
Judge 3	0	1			4		6
			5		4	2	6
	3			0		5	6
Judge 4	1	0	5			2	
	1	5	0			2	
	0	1	2			5	
Judge 5		2	3	6			1
		3	6	1			2
	0		3	2	4		
Judge 6	2		0	4	3		
	0	1			4		6
	0	4			6		1
Judge 7		3		1	4	5	
	0		3	2	4		
		1	3	2			6
Total	10	25	38	30	45	46	58
Average	0.83	2.08	3.16	2.5	3.75	3.83	4.82

[a] Class number.

[b] Four samples were given each time to each judge.

Packard modular gas chromatograph was used including the following: Model 871 Proportional Temperature Controller; Model 840 Electrometer (reconditioned to increase stability and sensitivity); Model 835 Power Supply; Model 811 Hydrogen Flame Ionization Detector; Column 10 ft 0.25 in. O.D., glass. A 15% (w/w) Varian Aerograph FFAP stationary phase, on 90-100 Mesh Anakrom AB, was used for packing.

In the analyses, 5 ml of oil were pipetted into a 10 ml flask and weighed accurately. Then 1.0 μliter of *n*-octanol was added and mixed thoroughly. After this, 0.8 μliters of sample were injected, using a 10 μliter Hamilton syringe, directly into the column. The instrument conditions were injection port 245 C, column 125-128 C and carrier gas N_2 at 20 psi.

Oxidation values were calculated from the chromatograms (Fig. 1) using the formula:

$$OV = A/h/\text{weight of oil (in grams)} \qquad [1]$$

in which, A is the area A in square inches multiplied by 100, and h is the height of the *n*-octanol peak in centimeters.

The PV's were obtained by the AOCS method (5).

Sensory Evaluation

The sensory evaluation of the aged blended oil samples (50% soybean oil and 50% hydrogenated soybean oil) was done by scoring four samples at the same time (scale 1 to 5, in which 5 represents the most off flavor) by seven judges. However, to obtain more information from the panel the judges were also requested to rank the same four samples at the same time by placing them in order according to increasing off flavor (method of sample inversion (9), see Table I where class numer equals sample number).

TABLE III

Results From Ranking 100% Soybean Oil

	0[a]	1	2	3	4	5	6
Length of Treatment, hr	0	3	7	24	48	72	144
PV	0.1	0.8	1.2	2.8	6.2	14.0	32.0
OV	0.0	0.28	0.31	0.41	0.87	1.60	4.07
Order of Ranking							
Judge 1[b]	0	1	2	3	4	5	6
Judge 2	0	1	2	4	3	5	6
Judge 3	0	1	2	3	5	4	6
Judge 4	0	1	3	2	4	5	6
Judge 5	0	1	2	4	3	5	6
Judge 6	0	1	2	3	4	5	6
Total	0	6	13	19	23	29	36
Average	0	1	2.18	3.16	3.84	4.83	6.0

[a] Class number.

[b] Seven samples were given at one time to each judge.

The 100% soybean oil was evaluated organoleptically by six judges, who simply ranked, without scoring, all seven samples at the same time and placed them in order according to increasing off flavor.

RESULTS AND DISCUSSIONS

A gas chromatogram of an aged soybean oil is presented in Figure 1. The pentane peak was difficult to distinguish at the low PV's and could not be used for reliable evaluations, therefore, the entire area A was utilized. Area B in Figure 1 was omitted in the computation of the OV. The analytical procedure had to be followed precisely to obtain reproducible results.

The development of rancidity as measured by OV and PV is presented in Figures 2 and 3. The close relationship between the OV and PV is graphically demonstrated for 50% soybean oil and 50% hydrogenated soybean oil in Figure 4. The corresponding equation is

$$OV = -0.037 + 0.177\ (PV) \pm 0.07 \qquad [2]$$

with 95% confidence limits (correlation coefficient 0.99).

In Figure 5 the off flavor scores (Table I) of the blend of 50% hydrogenated soybean oil and 50% soybean oil have been plotted against the OV. It is apparent that the judges have satisfactorily detected a general deterioration of the flavor. Linear regression analyses show a relationship expressed with the equation

$$\text{off flavor score} = 2.747 + 0.728\ (OV) \pm 0.67 \qquad [3]$$

with 95% confidence limits (correlation coefficient, 0.82), between the flavor score and the OV. Both regression line and 95% confidence limits are indicated in Figure 5.

The application of the ranking method (rankings obtained simultaneously with the scores) is presented in Table II. The sample numbers 0-6 were used as point values for the classes. From individual points the total and average were computed for each class. These are graphically presented in Figure 6.

Theoretically, when the class numbers are plotted against the point values (Fig. 6,7) a straight line should result if perfect correlation exists between the results of analyses and the judges. When less correlation is detected the points will be deflected in the direction of the dashed horizontal line at the level of 3.

Figure 7 presents the results of an experiment with 100% soybean oil. The results of the ranking (Table III) were very good, i.e., the deviation of the points from the theoretical straight line was small. However, the differences between the samples were more pronounced than in the case of the previously described experiment with the oil blend. Sample No. 1 was held only 3 hr at 60 C. Sample No. 2 was estimated to be still acceptable by the refinery standard (7.5 in a 1-to-10 scale). Samples taken later (OV > 0.3) had already developed a stronger flavor and the off flavor of samples 5 and 6 exceeded that which would be found under practical conditions.

Comparison of Figures 6 and 7 to Figure 5 shows that the judges' ability to discriminate accurately between the samples was reflected in greater detail by the ranking method than by the straight rated scores, which are neccesarily more subjective. It would appear that starting from the OV of 0.15 the off flavor becomes noticeable and reaches the limit of acceptability (7.5 in the 1-to-10 scale) at the OV of 0.3.

In the study described in this paper the oils were kept in darkness at 60 C. Under other conditions and with other oils the results might be different. Investigations in this area and to clarify the theoretical background are continuing. The conditions used in these experiments approximate those inside a refinery tank, and the results may provide useful data, e.g., for planning and designing automated control of refinery operations. For this purpose the impulse obtainable from the GC instrument is better suited than the PV measurement. Also, very small amounts of hydroperoxides, too small to be detected by the PV analysis and too small for OV computations, can be visually detected by the GC method.

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