

rounded off to four digits. To illustrate, Relation I for the combined data:

$$I. \text{ No.} = 8626.877 \frac{25}{D} - 12,575.226,$$

becomes

$$I. \text{ No.} = 8627. \left( \frac{25}{D} - 1.45768 \right).$$

A constant effort is made by the U. S. Regional Soybean Industrial Products Laboratory to find and use methods which will furnish additional information about the many unique soybean varieties analyzed in connection with the agronomic program. As a means of finding soybean oils whose properties are different from those obtained from the usual commercial

varieties, and at the same time reducing the analytical work necessary, only one determination each has been made, in the past few months, of the iodine number and the refractive index on oil obtained in the course of routine analysis. In case these values did not check with the equation, the sample was subjected to further examination. Of some 400 samples of soybeans, embracing 185 varieties, so far examined, only 3 have given oils whose iodine number and index of refraction did not conform statistically to the relationships given above. These samples are being studied in greater detail.

Conclusions

The iodine number of soybean oil can be determined by calculation from the measurement of refractive index with an accuracy comparable to any chemical method, provided that the instrument used is sufficiently accurate, the measurements are carefully made, and, for any given crop year, a correlation curve is established.

LITERATURE CITED

- (1) Hopper, T. H., and Nesbitt, L. L. Oil and Soap, 14, 34-36 (1937).
- (2) Pickering, G. F., and Cowlshaw, G. E. J. Soc. Chem. Ind., 41, 74-77T (1922).
- (3) Yule, G. U., and Kendall, M. G. An Introduction to the Theory of Statistics, Chapter 17, Charles Griffin and Co., Ltd., London (1937).
- (4) Zeleny, L., and Coleman, D. A. U. S. Dept. Agr. Tech. Bull. 554 (1937).

# Molecular Distillation of Soybean and Corn Oils\*

By HERBERT W. RAWLINGS  
DISTILLATION PRODUCTS, INC., ROCHESTER, NEW YORK

THE process of molecular distillation is now well known through its application in concentrating vitamins A and D from certain fish liver oils (1). In the present paper, data obtained from a study of two American vegetable oils, soybean and corn, are presented.

A batch of 1000 gallons of alkali refined soybean oil was molecularly distilled at an average absolute pressure of 0.002 mm. of Hg. and at a rate of 7 to 8 gallons per hour. The oil was passed through 4 still units operating at temperatures shown in Table 1. The residue was redistilled at a higher temperature range, but since no fraction distilled from the first unit only three fractions and a

final residue were obtained. The nine fractions and the original refined oil were analyzed with the results given in Table 1.

A batch of 700 gallons of corn oil was distilled in substantially the same way except that the residue was not redistilled. The five fractions and the original refined oil were analyzed with the results given in Table 2.

Methods of Analysis

The free fatty acid and saponification values were determined by the official A.O.C.S. methods and the iodine value determinations were carried out by the Wijs method. The thiocyanogen value determinations and the calculation of the percentage of the unsaturated acid constituents were made in ac-

cordance with the method of Kaufmann and co-workers as described by Jamieson (2) in the case of the corn oil and by the A.O.C.S. procedure in the case of the soybean oil.

The determination of unsaponifiable matter was carried out in accordance with the procedure often used for vitamin extraction in the laboratories of Distillation Products, Inc. This method employs a five-fold ethyl ether extraction of the saponified sample following which the fractions are combined and washed twice with water, once with N/4 KOH, and twice more with water. The ethereal extract was then evaporated and the residue dried to constant weight in a tared flask. The data given in the

TABLE 1  
MOLECULARLY DISTILLED SOYBEAN OIL

CHARACTERISTIC	Orig. Oil Refined	Frac. 1	Frac. 2	Frac. 3	Frac. 4	Res.	Frac. R <sub>2</sub>	Frac. R <sub>3</sub>	Frac. R <sub>4</sub>	Final Residue
Per cent Distilled		0.02	3.4	4.4	4.4		23.2	20.4	28.4	
Distill'n Temp.		170-8°C.	255-65	265-70	275		280	295	295	
Color — Evelyn L4400	1.35		too dark	1.28	1.28	1.22	1.10	0.33	0.40	1.28
Color — Evelyn L5200	.716		too dark	0.328	0.172	0.301	0.059	0.019	0.023	0.810
Lovibond — Yellow	70a			35b	35b	130b	25b	18b	20b	95c
Lovibond — Red	14.1a			11.2b	6.2b	10.9b	3.0b	1.6b	1.7b	66c
Free Fatty Acid (Oleic), percent	0.04	5.0	0.5	0.2	0.15	0.03	0.10	0.06	0.04	0.09
Unsaponified Matter, percent	0.8	74.2	10.7	1.5	0.7	0.04	0.28	—	—	—
Saponification Number	193	50	175	193	193.5	194	193	193	194	193
Sap. Number of Glycerides	194	194	196	196	195	194	194	193	194	193
Refractive Index 40°C.	1.4682			1.4673	1.4672	1.4680	1.4673	1.4676	1.4674	1.4682
Iodine Val. (Wij's)	134.5	150.8	131.2	127.2	127.8	134.4	129.9	131.2	132.0	137.6
Thiocyan. Value	83.7			79.7	79.2	83.8	82.3	85.0	80.6	87.1
Iod. Val. of Fatty Acids	139.2		136.3	134.7	132.8	140.1	136.8	136.8	137.0	143.2
Thiocyan. Val. of Fatty Acids	86.8		81.3	85.1	82.8	87.3	85.8	86.3	85.8	90.1
Solid Fatty Acids, percent	12.5		16.0	14.9	15.8	11.5	12.9	12.6	12.2	11.0
Unsaturated (by difference), percent	87.5		84.0	85.1	84.2	88.5	87.1	87.4	87.8	89.0
Oleic Acid, percent	29.7		23.2	28.2	29.2	30.1	30.9	31.7	31.3	30.4
Linoleic Acid, percent	49.4		54.8	50.1	47.7	50.4	48.4	47.7	49.4	48.0
Linolenic Acid, percent	8.4		6.0	6.8	7.3	8.0	7.8	8.0	7.1	10.6

a — 2.5 inch column.

b — 5.25 inch column.

c — 1 inch column.

\*Communication No. 9 from the Laboratories of Distillation Products, Inc., Rochester, New York.

TABLE 2  
 MOLECULARLY DISTILLED CORN OIL

Characteristic	Original Oil (Refined)	Fract. 1	Fract. 2	Fract. 3	Fract. 4	Residue
Percent Distilled .....		0.01	2.58	2.73	5.05	
Distillation Temperature .....		180°C	245-55	257	280	
Color — Evelyn L4400 .....	1.40			1.28	1.00	0.85
Color — Evelyn L5200 .....	0.23			0.242	0.085	0.201
Lovibond — yellow .....				35a	35a	50a
Lovibond — Red .....				10.6a	4.3a	11.2a
Free Fatty Acid (Oleic), percent .....	0.033	10.6	0.95	0.20	0.10	0.02
Unsaponified Matter, percent .....	1.6	64.2	15.0	5.0	2.7	0.8
Refractive Index 40°C .....	1.4678			1.4682	1.4674	1.4672
Iodine Value (Wij's) .....	127.0	151.4	125.7	121.3	123.6	127.6
Iodine Value fatty acids .....		115.6	121.9			
Thiocyanogen Value .....	79.4			74.6	76.8	80.3
Thiocyanogen Value of fatty acids .....		79.8	77.2			
Saponification Value .....	190.	70	165	184	188	192
Sapon. Val. of glycerides .....	193.	196	194	194	193	193
Sat. Fatty Acids, percent .....	7.3	(11.4)b	(14.5)			
		0.4	12.3	8.0	7.8	5.9
Oleic Acid, percent .....	35.4	(49.0)	(36.2)	31.1	33.4	36.8
		17.5	30.7			
Linoleic Acid, percent .....	54.4	(39.6)	(49.3)			
		14.2	41.8	51.6	51.8	52.2

a — 5.25 inch column. b — Values in brackets are percent composition of fatty acid portion.

column marked "Saponification Value of Glycerides" (Table 1) is a tabulation of the saponification values corrected to zero per cent unsaponifiable material.

In the case of the soybean oil, the determination of the saturated fatty acids was carried out by the A.O.C.S. modified Twitchell separation.

Of the corn oil distillate, the first and second fractions contained a very considerable proportion of unsaponifiable material which rendered impossible an accurate calculation of the unsaturated acid content of these fractions from the iodine and thiocyanogen values. In this case the fatty acids were separated and kept under an atmosphere of nitrogen to prevent oxidation until their iodine and thiocyanogen values could be determined.

The color values represent measurements of the apparent optical density at  $\lambda 4400$  and  $\lambda 5200$  as obtained with an Evelyn (4) photo-

electric colorimeter using chloroform as the blank for comparison. The color comparisons of the various fractions are given as apparent optical densities obtained by measuring the per cent transmission at  $\lambda 4400$  (yellow) and  $\lambda 5200$  (red) bands. Lovibond readings are also included.

The flavors of the distillates were examined. Each successive fraction was found to be increasingly bland and the last fraction proved to be almost as tasteless as oil deodorized by the conventional steam-vacuum distillation process.

Although no great fractionation of the glyceride constituents occurred, it is interesting to note that the unsaponifiable portion of the oil was almost completely present in the first two fractions. Thus it is possible by molecular distillation to remove almost completely the unsaponifiable matter from soybean and corn oils without resorting to saponification and extraction, or otherwise altering the phys-

ical or chemical properties of the glycerides. It is interesting to note also that the coloring matter and odorous constituents volatilize readily and therefore separate almost completely from the oil, so that the later fractions consist of fairly pure glycerides which are nearly as light in color and as bland as bleached and steam deodorized oils.

The author wishes to thank the technical staff of Distillation Products, Inc., for their assistance in this work, and R. A. Nagel of Spencer-Kellog & Sons, Inc. for supplying the Lovibond color readings.

#### REFERENCES

- Hickman, K. C. D., *Ind. Eng. Chem.*, **29**, 968-75, 1107-11 (1937).  
Burch, C. R. and Van Dijk, W. J. D., *J. Soc. Chem. Ind.*, **58**, 39-42 (1939).  
Fawcett, E. W. M., *Ibid.*, **58**, 43-50 (1939).  
Burrows, G., *Ibid.*, **58**, 50-56 (1939).  
Jewell, W., Mead, T. H., and Phipps, J. W., *Ibid.*, **58**, 56-64 (1939).
- Jamieson, G. S., *Vegetable Fats & Oils*, American Chem. Soc. Monograph Series, Chemical Catalog Co., New York, 1932, p. 345.
- Jamieson, G. S., *Ibid.*, p. 360.
- Evelyn, K. A., *J. Biol. Chem.*, **115**, 63 (1936).



Corner of Control  
Laboratory of  
Bennett-Clark Co.  
Nacogdoches Plant.