Solvent Effects on the Products of Soybean Oil Extraction

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IN processing soybeans, although the effect of the solvent on the principal products, oil and meal, is of considerable importance, it has received less systematic study than commonly supposed. As a matter of fact, the solvents *"per se"* probably do not alter the oil or protein significantly yet the effect of the solvent will appear because of dissolution of minor constituents which accompany the oil or conversely are left in the meal to interfere with purification of the protein.

The importance of edible soybean oil has inspired numerous researches toward improving its organoleptic and color properties. On the contrary, the meal, having been originally developed for livestock feed, has been slower to attract this type of research. The recent great demand for protein foods, resulting from the war, and the increasing demand for industrial proteins is now focusing attention on the protein problem. A light-colored protein is essential for important industrial applications such as paper coatings and textile fibers as well as for many food uses.

Experience (4) has demonstrated that certain minor constituents of soybean meal are carried along with the protein in its isolation, especially when the industrial method of alkali extraction and acid precipitation is used. Some of these minor constituents are responsible for the various shades of color of the isolated protein, ranging from brown to yellow.

The present investigation was started to survey the effects of various oil solvents on the color and taste of soybean meal and on the color of the isolated protein. It was deemed equally important, from the standpoint of practical results, to compare the properties of the crude oils obtained in the extraction. Any deleterious effects on the oil, resulting from action of the solvent, would for practical purposes nullify improvements obtained in the meal and isolated protein.

The solvents used in this study were carbon tetrachloride, trichloroethylene, ethylene dichloride, isobutyl alcohol, isopropyl alcohol, ethyl alcohol, and hexane (b.p. range 30° to 60°C.).

Hexane, its immediately higher homologues, and the chlorinated hydrocarbons are noted for their excellent oil-solvent properties. The chlorinated solvents have the additional advantage of nonflammability and the disadvantage of corrosiveness. The alcohols are less favorable as oil solvents and must be used at elevated temperatures to be completely miscible with soybean oil. In fact, methanol is too low in oil-solvent properties to be of practical interest and, for this reason, was not included in the study. The alcohols are in the intermediate range as hazardous solvents; although they are flammable, their vapor pressures are low enough to forestall dangerous concentrations in the atmosphere at room temperature.

The Japanese (1) have reported the use of ethanol as a solvent for the batch extraction of soybeans in a plant at Darien, Manchuria. They have published data on the miscibility of soybean oil in various ethanol-water ratios. Their data for 99.52% and 95.92% ethanol are shown graphically in Figure 1.

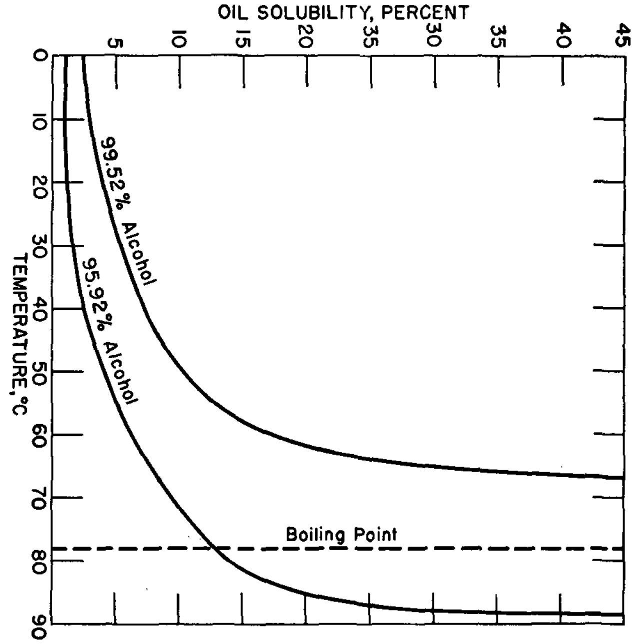

FIG. 1.

These data show that near absolute ethanol (99.52%) is miscible in all proportions with soybean oil above 67.3°C. At the lower alcohol concentration (95.92%) the oil solubility is greatly reduced, and complete miscibility is not attained at the boiling point. However, the solvent properties of the 95% alcohol may be brought into a practical solvent range by operating under sufficient pressure to bring the temperature to 90°C.

The miscibility of the alcohols with water complicates their use as oil solvents. Practical methods for dealing with this problem will be present in the next report. In the present study the alcohols were maintained in the concentration range of 95.0% to 99.5% alcohol.

Extraction Procedure

The cracked and dehulled soybeans were flaked to a thickness range of 0.005 to 0.010 inch on cold rolls at a moisture content of about 15%. The moisture was immediately reduced to 6% to 8% at room temperature, in a forced-draft oven. When a lower moisture value was required, the oven temperature was raised to about 50°C.

A laboratory-model extractor, built for countercurrent and continuous operation, was used in extracting the flaked soybeans. The extractor and its operation has been described in another report (2). With the alcohols the extractions were carried out at their boiling point and for other solvents at room temperature.

For the alcohols (essentially absolute) a solvent to flake ratio of 2.5 to 1.0 was used; for the other sol-

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vents, the ratio was 2 to 1 or slightly less. The ethanol-extracted flakes contained 37.5% ethanol on a wet basis while the hexane-extracted flakes held 30% on the same basis. Data were not taken for the other solvents. All flakes were extracted to below 1% oil content.

The oils were recovered from the alcoholic miscella, after cooling to room temperature, by phase separation. The heavier, or "oil phase," contained 6% to 8% alcohol and was not further refined while the lighter, or "alcohol phase," contained 1% to 4% oil as well as the phospholipids, sugars, and much of the other alcohol-soluble materials of the soybean. The oils were recovered from the non-alcoholic solvents by vacuum evaporation of the solvent and nitrogen stripping. It is apparent that for the hydrocarbons and chlorinated solvents whatever is extracted from the flakes is left in the oil; whereas for the alcohol solvents the greater portion of the nonoil constituents of the bean are in the alcohol phase and are partially removed from the system in the solid phase when cooled or are left with the solvent on the flakes.

After the flakes were extracted, a portion was used for isolating the protein by the method of water extraction and acid precipitation (5). The water extraction and precipitation method was used because it gave the most consistent results although a similar result can be obtained by alkali extraction.

The effect of the solvent on the reflectance of the soybean meal and isolated protein is given in Table 1. The reflectance measurements were made on a Hunter reflectometer with a blue filter. A porcelain plate furnished with the instrument was used as a reflectance standard. The reflectance measurements are on a comparative basis since the method of preparing the sample has a marked influence on the results.

TABLE 1

Reflectance as Determined on a Hunter Reflectometer of Soybean Flakes and Isolated Protein Resulting From Removal of the Oil With Various Solvents

Solvent	Reflectance	
	Meal	Isolated Protein
1. Carbon tetrachloride	84.4	71.1
2. Trichloroethylene	84.6	73.5
3. Dichloroethylene	85.6	73.3
4. Isobutanol	83.0	68.6
5. Isopropanol	......	75.0
6. Ethyl alcohol	87.4	79.6[1]
7. Ethyl alcohol	87.4	79.1[2]
8. Ethyl alcohol	87.4	75.9[3]
9. Casein	......	80.5
10. Commercial flakes (Hexane)	83.8	72.4
Protein From Pilot Plant Operation		
11. Ethanol ext. flakes } Water ext. protein }	......	79.6
12. Ethanol ext. flakes, protein ext'd with 0.3% sulfite	......	79.1
13. Commercial hexane flakes } Water ext. protein }	......	66.4
14. Commercial hexane flakes, protein ext'd with 0.3% sulfite	......	71.7

[1] Water ext'd. [2] Na_2SO_3 ext'd. [3] 0.05% NaOH ext'd.

TABLE 2

The Color, Acid Number, and Break Value of Soybean Oil Samples Extracted With Various Solvents

Solvent	Lovibond Color		Acid Number	Break
	Yellow	*Red*	*Per cent*	*Per cent*
Dichloroethylene	70	14.4	0.52	......
Trichloroethylene	70	10.3	1.04	1.00
Carbon tetrachloride	70	10.3	.44	.06
Isopropyl alcohol	70	12.8	.95	.86
Ethanol	70	2.9	.06	.00
Ethanol—residue	70	5.6	.24	.02
Hexane (b.p. 30°-60°C.)	70	7.0	.50	.50

The samples were prepared by grinding in a mortar, then screen grading for particle size. In making up the sample discs, the material used was that which passed through a 100-mesh but was retained on a 200-mesh screen. The samples were placed in a humidified room for 48 hours at 70°F. and 50% relative humidity to bring all of them to an equal moisture level. The discs were formed at room temperature in an hydraulic press, using a hardened steel mold. The relatively low moisture content of the protein and low temperature of pressing forestalled plastic flow. The discs thus formed had only enough strength for careful handling. For making the reflectance tests a disc was placed in a holder which exposed a surface 1½ inches in diameter. Five readings were taken with frequent rechecking of the instrument against the standard reflectance disc. A series of readings usually checked within ±0.2 units, with extreme variation of 0.4 units. Visual observation was used to check the results of the instrument. A difference of one unit between two samples is a definite visual color difference.

The results of the reflectance tests of the soybean meal extracted with various solvents show that the meal extracted with ethanol has the highest reflectance. The ethanol flakes have a reflectance of 87.4 compared to 83.8 for commercial hexane flakes. Likewise, the isolated protein from the ethanol-extracted flakes has the highest reflectance, 79.1 and 79.6, and it approaches very close to 80.5 for the light-colored casein.

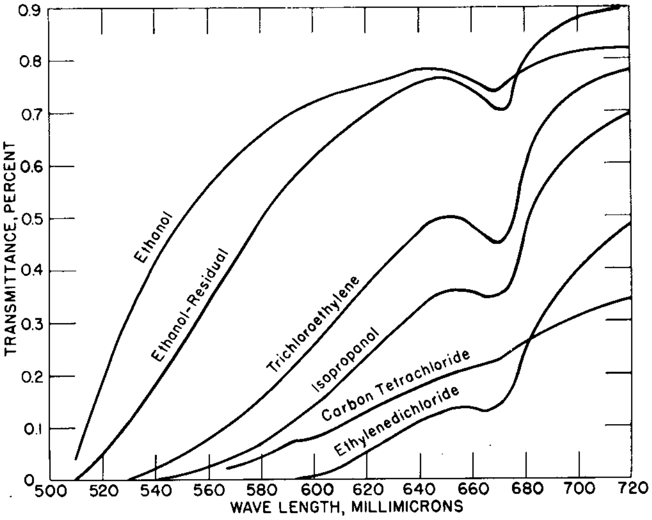

FIG. 2.

The constituents of the soybean responsible for the brown color of the protein isolated from the hexane-extracted flakes have not been identified. In extracting with ethanol it was observed that the miscella was brown whereas the hexane miscella was a golden yellow. In a series of extractions with a Soxhlet extractor it was noted that the presence of water, either in the flakes or in the alcohol, hastened the extraction of the brown color. These results suggest the possibility that the improved color of the ethanol-extracted flakes is due in part to a removal of phosphatides.

Fortunately, the ethanol had another desirable effect on the flakes, namely, the extraction of the bitter principle and much of the beany flavor (3).

The taste of the ethanol-extracted flakes approaches very close to blandness. Although it is not possible at this time to report any systematic organoleptic tests on the above soybean meals, it has been the observation of many tasters, nevertheless, that soybean flakes from ethanol extraction have a more agreeable flavor than ordinary steam debittered soybean flakes.

The effect of solvent on the nature of the crude oil is as marked as its effect on the meal. The Lovibond color, acid number, break, spectral transmittance, and solvent removal of the crude oils was examined on a comparative basis to obtain a preview of their relative condition at this stage of processing. Table 2 shows the first three of these values and Figure 2 the spectral transmittance curves for wave lengths between 550 and 720 millimicrons as determined in a Beckman spectrophotometer.

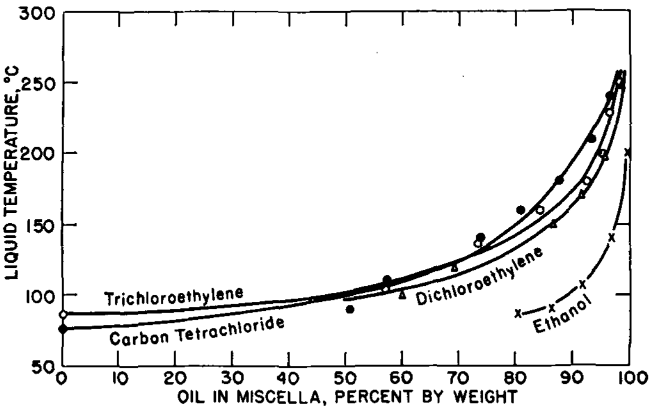

FIG. 3.

The sample designated "residue" was recovered from the "alcohol phase" which contained about 4% oil at 25°C. To recover the "residual oil" the alcoholic phase was reduced to about one-fourth its original volume by evaporation, thus concentrating the oil and obtaining a second phase separation.

In comparing the crude oils recovered from the various solvents, the oil from ethanol extraction is lowest in color, fatty acids, and break. The low break value and other qualitative tests are evidence that the phosphatides, sugars, a considerable portion of the coloring matter, and perhaps other alcohol- soluble constituents of the soybean have remained in the alcohol phase.

The spectral transmittance values for the oils show the two ethanol samples to have the highest percentage of spectral transmittance. The transmittance values confirm the color measurements made with the Lovibond colorimeter.

The separation of a solvent from oil depends upon a number of intermolecular forces, few of which are known for the present systems. Accordingly, comparative experiments were carried out on solvent removal, starting with equal parts by weight of solvent and oil. The quantitative loss of solvent was determined by successively heating the solvent-oil systems at atmospheric pressure to a convenient temperature, cooling the system and weighing it. This procedure was then repeated by heating to a higher temperature. The difference in weight represented the loss of solvent within the temperature range under consideration. The results are shown in Figures 3 and 4. From these results it is apparent that ethanol can be removed from soybean oil at a lower temperature than can the higher alcohols, hexane, or the chlorinated hydrocarbons.

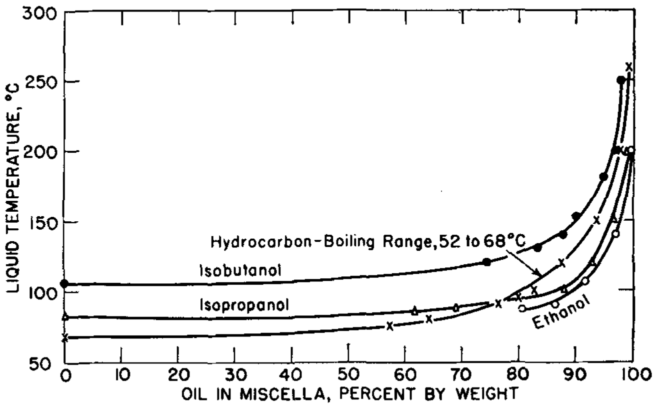

FIG. 4.

Summary

Ethanol, isopropanol, isobutanol, ethylene dichloride, trichloroethylene, carbon tetrachloride, and hexane (b.p. range 30° to 60°C.) were used as solvents for the extraction of soybean oil and the comparative effect of the solvent on the color and other properties of the oil, meal, and isolated protein was measured. Ethanol extraction gave the best results with respect to the color of oil, meal, and protein, and it also served as a debittering agent for the soybean meal.

Acknowledgment

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REFERENCES

1. Okatomo, Sajiro, Contemporary Manchuria *1* (3), 83-101 (1937).
2. Beckel, A. C., Belter, P. A., and Smith, A. K., Ind. Eng. Chem., Anal. Ed., *18*, 56-58 (1946).
3. Beckel, A. C., and Smith, A. K., Food Indust. *16*, 614 and 664 (Aug., 1944).
4. Smiley, William G., and Smith, A. K., Cereal Chem. *23*, 288 (1946).
5. Smith, A. K., and Circle, S. J., Ind. Eng. Chem. *31*, 1284-88 (1939).