Preliminary Studies on the Application of Certain Chlorinated Solvents to Soybean Oil Extraction

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CHLORINATED solvents have been investigated for the extraction of vegetable oils from seeds largely because of two characteristics, very good solvent action and low flammability. Being definite compounds they have for practical purposes a third desirable characteristic, definite boiling points (varying only a degree or two because of impurities). Of these solvents trichloroethylene is being used commercially for the extraction of soybean oil (7). Methylene chloride (dichlormethane) extraction of soybean oil has been studied in this laboratory (1, 2). The results of preliminary studies of the characteristics of four other chlorinated solvents as applied to soybean oil extraction are presented in this paper. These four are methyl chloroform (1,1,1-trichloroethane), ethylene dichloride (1,2-dichloroethane), propylene dichloride (1,2-dichloropropane), and 1,2,3-trichloropropane (trichlorohydrin). The physical properties of these solvents, and of trichloroethylene for comparison, are given in Table I.

In the application of any solvent it is desirable to know the relationship between the specific gravity and the percentage of oil in the miscella. This relationship was determined for soybean oil miscellas, using methyl chloroform, ethylene dichloride, and propylene dichloride as solvents. Twelve miscellas of different concentrations for each solvent were made by weighing the constituents on an analytical balance. The specific gravity for each concentration at 25°C.(77°F.) was determined by means of a Westphal balance. These specific gravities and similar data secured in this laboratory on methylene chloride (dichlormethane) miscellas by Breuklander (2) are given in Table II. Specific gravities of 1,2,3-trichloropropane miscellas were not determined but would be expected to be very similar to those of the methyl chloroform miscellas because of the similarity in the specific gravities of the two solvents.

Comparative extraction rate data for the four solvents when used to extract soybean oil were determined by passing the solvent down through batches of 30 g. each of flaked soybeans in a glass tube 28.6 mm. in diameter at the rate of 4 cc. per square centimeter per minute. The tube was fitted with a water jacket through which water at a constant temperature of 30°C. was circulated. The bottom of the tube was closed with a one-hole stopper containing a small glass tube which, together with the constant head of solvent maintained over the flakes, regulated the flow of solvent. The flakes used for the four solvents were all from the same well-mixed batch and averaged 0.010 in. in thickness. The oil content of the flakes was determined in a Soxhlet extractor, using hexane (Skelly solve-B) as a solvent. The miscella (solvent-oil solution) flowing from the tube was collected over definite time intervals. The amount of oil in each increment was calculated from the specific gravity. From these data the residual oil contents shown in Figure 1 were calculated.

TABLE II

Specific Gravities of Soybean Oil-Miscellas at 25°C.

Percent Oil by Weight	Methyl Chloroform	Ethylene Dichloride	Propylene Dichloride	Methylene Chloride(2)
0	1.332	1.247	1.149	1.326
5	1.299	1.223	1.131	1.297
10	1.271	1.199	1.117	1.269
15	1.244	1.175	1.103	1.242
20	1.219	1.154	1.092	1.216
30	1.177	1.116	1.068	1.166
40	1.153	1.085	1.046	1.120
50	1.088	1.054	1.023	1.077
60	1.049	1.025	1.000	1.037
70	1.013	0.996	0.978	1.004
80	0.979	0.970	0.956	0.974
90	0.948	0.945	0.938	0.946
100	0.924	0.924	0.924	0.921

These extraction rate curves, plotted on semilog paper, are typical for solvent extraction of soybean oil. It is difficult to distinguish between the curves during the first five minutes. An examination of the original data shows ethylene dichloride to be a slightly better solvent than propylene dichloride during the first 10 minutes, a trend definitely reversed after 15 minutes. Both dichlorides appear to be somewhat better than methyl chloroform and very definitely better than trichloropropane.

To obtain a better concept of what was happening in the early critical minutes of extraction before the curve levelled out to a slow rate, extraction rate data were determined for the two dichlorides at three different temperatures, 30°C., 50°C., and 70°C., for a period of eight minutes. Data were also obtained with trichloroethylene for comparative purposes. The rate of extraction was slowed to obtain a better comparison of the solvent rates so that these data (Figure 2) are not strictly comparable with the data in Figure 1.

These data indicate that, while ethylene dichloride is more effective at the end of eight minutes of ex-

TABLE I

Physical Properties of the Solvents

	Methyl Chloroform (3)	1,2,3-trichloropropane(6)	Ethylene Dichloride(5)	Propylene Dichloride(5)	Trichloroethylene(5)
Molecular weight	133.42	147.40	98.97	112.99	131.40
Specific gravity of liquid d 20°C./4°C.	1.325	1.388	1.253	1.155	1.464
Boiling point °C.	74.1	156.2	83.5	96.4	86.9
Steam distillation point (1 atm.)°C.	....	....	71.4	78.2	73.2
Heat of vaporization (at boil. pt.) cal. per gram	....	65.7	77.3	72.3	57.2
Viscosity of liquid at 20°C., centipoises	....	....	0.84	0.80	0.58
Solubility of solvent in water, g. per 100 g.	0	0.3(20°C.)	0.84(25°C.)	0.27(20°C.)	0.11(25°C.)
Flash point, °F.	None	165.0	53.4	70.0	None

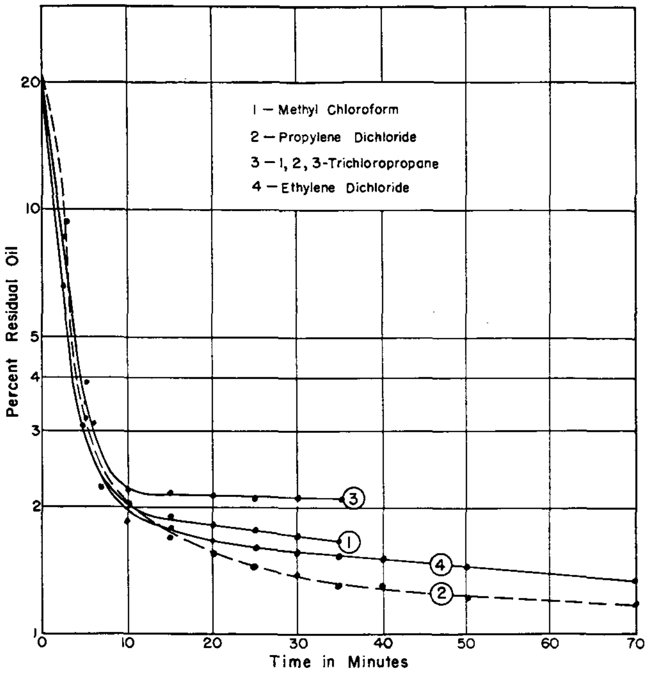

FIG. 1. Extraction rate curves for soybean oil using methyl chloroform, propylene dichloride, 1,2,3-trichloropropane, and ethylene dichloride as solvents.

traction at both 30°C. and 50°C. than propylene dichloride, the relationship is reversed at 70°C. Both dichlorides have considerably slower extraction rates than trichloroethylene at all three temperatures.

As a further check on the extraction properties of the two dichlorides a two-hour continuous extraction run was made with each in the pilot plant previously used in developing the process of extracting soybeans with trichloroethylene (7). The pilot plant consisted essentially of a continuous inverted trapezoidal loop of 5- by 4½-inch Redler conveyor casing, through which the flaked soybeans were moved by a continuous Redler chain. The solvent passed through the extractor countercurrent to the flakes. The extraction time was 17 minutes. The miscella was concentrated in a rising film evaporator, and the oil was stripped of solvent in a packed column. The pilot plant data (Table III) show a high residual oil in the meals compared with the usual 1% or less obtained with miscella concentrations of 20% when trichloroethylene is used. While the propylene chloride apparently shows poorer extraction than ethylene dichloride, actually, when consideration is given to the respective miscella concentrations, it is equal to or better than ethylene dichloride. This agrees with the data in Figure 1. The color of the oil produced by both solvents was inferior to that usually produced with trichloroethylene.

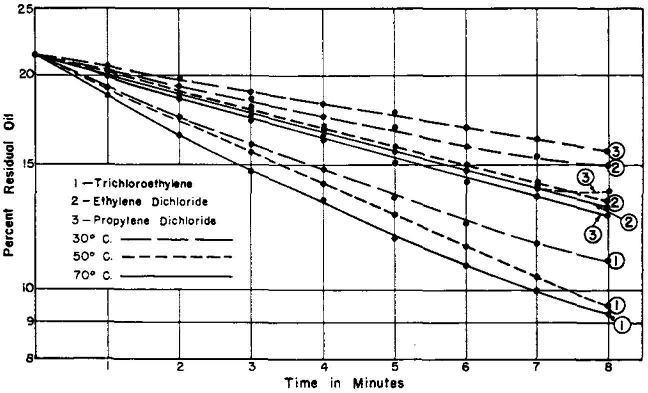

FIG. 2. Extraction rate curves at three temperatures for soybean oil using trichloroethylene, ethylene dichloride, and propylene dichloride as solvents.

TABLE III
Results of Pilot Plant Extractions of Soybean Oil

	Ethylene Dichloride	Propylene Dichloride
Flake thickness, in.	0.010	0.010
Oil content of beans, %	21.6	20.2
Moisture content of beans, %	6.0	7.0
Residual oil in meal, %	2.39	2.63
Miscella from extractor, % oil	11.5	21.6
Lovibond color		
Refined oil	70Y-21R	70Y-12R
Refined and bleached oil	70Y-9.5R	18Y-2.0R

While the performance data on these solvents are limited, a preliminary evaluation of the four solvents may be made. The ethylene and propylene dichlorides showed the best extraction rates. Of the two it seems probable that the propylene dichloride could be used at a higher extraction temperature, at which superior results should be obtainable. The color of the oil was better than that produced with the ethylene dichloride and perhaps could be improved by using vacuum stripping. However it is doubtful if propylene dichloride would prove equal to trichloroethylene on the basis of either the extraction rate or the oil quality.

No attempt was made to obtain operating costs experimentally with the dichlorides, but a general comparison of some cost factors can be made using the data in Table I. The higher boiling point of the propylene dichloride will tend to reduce cooling water requirements somewhat, at the same time reducing the heat transfer rate in the desolventizers. The slightly lower heat of vaporization is lower than that of hexane and is higher than that of trichloroethylene. The viscosity, which affects the load of solvent to the meal desolventizers, shows the same general relationship. Propylene chloride on the weight basis is cheaper in cost than either ethylene dichloride or methyl chloroform and is about the same as the 1,2,3-trichloropropane. The initial cost of a solvent is not nearly as important as the solvent loss, which varies with characteristics of the solvent such as volatility, stability, and solubility in water as well as with the design and operation of the equipment in which it is used. Propylene dichloride would be expected to be cheaper in the overall cost than ethylene dichloride and possibly slightly less than trichloroethylene.

From the fire safety angle propylene dichloride with a moderate flammability rating and a flash point of 70°F. has a slight advantage over ethylene dichloride with a flash point of 53.6°F. Trichloroethylene, classed as nonflammable, is superior to both.

On the basis of the data presented it may be concluded that, of the four solvents investigated for the extraction of soybean oil, propylene dichloride shows the greatest promise but that it is inferior to trichloroethylene. It should be pointed out however that these conclusions do not apply necessarily to fats other than soybean oil and may be subject to revision with determination of more complete experimental data. Further study of methyl chloroform may be desirable, especially if it should reach a more favorable price in relation to the other solvents. The cost data used were those of June, 1952, and obviously may vary with time. No evaluation of either the oil or the meal, other than the oil color data in Table III, was made.

Summary

Data for specific-gravity concentration curves were determined for soybean oil miscellas, using methyl chloroform, ethylene dichloride, and propylene dichloride as solvents. Extraction rates of five solvents extracting soybean oil were found to increase in the following order: 1,2,3-trichloropropane, methyl chloroform, ethylene dichloride, propylene dichloride, and trichloroethylene. As the result of pilot plant runs on ethylene and propylene dichlorides and consideration of other data the preliminary conclusion was reached that propylene dichloride could be used at a higher temperature where it would be more satisfactory than ethylene dichloride but less so than trichloroethylene.

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Loss of Oil in Hulling Tung Fruit in the Field and at the Mill

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FOR a number of years the tung oil industry has been interested in the possibility of hulling tung fruit on the farm, provided it can be done economically. The hull fraction constitutes about 55% of the air-dry weight of tung fruit. Hulling in the field would therefore decrease by 55% the weight of material hauled to the mill, leave the hulls on the farm for use as mulch, and relieve the mill of the problem of disposing of the hulls.

The disc huller used in tung mills in this country removes the hulls and breaks or removes a large proportion of the shells. It also damages some of the kernels. From previous experience with other oilseeds it might be expected that a rapid increase in free fatty acids would result through break-down of the oil unless the broken seeds were dried or expressed immediately. This was found to be the case also with tung. The moist broken seed developed free fatty acids rapidly and heated spontaneously unless forced ventilation was used for drying. However, investigations by Holmes, Pack, and Gilbert (1) showed that the hulled nuts can be safely stored and processed efficiently after drying to 10% moisture at temperatures below 175°F. Mills have installed well-designed seed dryers (2), in which nuts previously hulled in the field or at the mill can be successfully dried prior to storage and processing.

The disc huller used at domestic mills can be mounted on a tractor and used in the orchard to hull fruit. This huller operates most efficiently on fruit containing 15-20% moisture (3). Farmers hesitated, at first, to hull fruit in the field because they thought excessive loss of oil might result from this type of operation. A number of growers were willing to hull fruit in the field if they could be assured that no excessive loss of oil occurred.

Tests made at the mills have shown that loss of oil occurs during hulling and as a result of inability to press all the oil from the ground seeds and kernels (3). Laboratory examination of samples of commercial hulls revealed that the loss of oil during hulling resulted from the presence of pieces of kernels and appreciable quantities of oil in the fine portion of the hull material. Microscopic examination of the latter material showed the presence of fine kernel particles which were very oily. The shell and hull particles however contained no oil (3). Data are available which show that the mills recover about 85.5% of the oil in the fruit. In the case of tung nuts hulled in the field the recovery of oil based on the amount of oil in the hulled nuts should be higher, simply because that part of the loss caused by hulling has taken place before the nuts are delivered to the mill.

Materials and Methods

In the hulling operation the partly dried fruit is passed through decorticators and separators to remove the thick hull and the loose shells from the hulled nuts. The hulled nuts are subsequently ground to a meal and pressed to express the oil.

The hulls and shells are aspirated from the seeds and kernels at the mills, and samples of hulls are collected from the bottom of the cyclone. Collecting representative samples of hulls during hulling in the field was more difficult because the hulls aspirated from the separator pass through a long horizontal pipe supported some 20 feet above ground level and are then discharged to the ground. The sampler used during the first season consisted of a large burlap sack supported by a hoop attached to a pole. During the second season the sampler consisted of a long cylindrically-shaped piece of burlap with one opening attached to a large hoop fastened to a pole and the other end open. A cord was attached at the open end so that it could be quickly closed. In collecting a sample, the hoop was placed over the discharge end of the horizontal separator pipe and the other end of the burlap cylinder was closed by drawing the cord.