experiments. Only two experiments have been carried out, and the results are given in Table III.

In the case of polymerized sunflower seed oil the agreement is satisfactory. The linseed oil was highly polymerized, and the calculations become inaccurate because of the unknown magnitude of association in solution caused by free acid groups present in large molecules. This effect can be very great if the weight average molecular weight is high, and an attempt has been made to correct for it by using equations which have been solved (15). The calculated values given have also been corrected for intramolecular reaction by assuming the same amount of intramolecular reaction as in the case of an esterification reaction between glycerol and dimeric acids (7).

Conclusion

In the case of slowly polymerizing oils it should now be possible to follow the changes in molecular weight distribution as polymerization proceeds and to study the relationship between this distribution and the viscosity.

Whether or not Flory's theory can be applied to rapidly polymerizing oils depends largely upon the fatty acid distribution over the glycerol molecules in any particular oil. It is probable that an approximation to a random state exists so that the polycondensation theory will be approximately followed.

The application of the theory is not limited to the thermal polymerization of oils. Provided that a random state exists, the theory can also be applied to the drying of oil films which is a catalytic polymerization. It would appear to be very attractive to investigate film properties as a function of the molecular weight distribution.

Summary

Flory's polymerization theory can be applied to polymerized oils, provided that the different acids are randomly esterified with the alcohol groups of glycerol. This state is attained when the oils are heated at 300°C. for long periods. The calculated amounts of monomeric triglycerides in polymerized linseed oils are compared with experimental results, and calculated and measured weight average molecular weights are also compared.

Acknowledgment

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A Rapid Dielectric Method for Determining the Oil Content of Safflower and Sunflower Seed[1]

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THE ECONOMIC IMPORTANCE of safflower seed in this country has increased in recent years, especially in the Pacific Northwest, Northern Great Plains area, and in certain sections of the Far Western and Southwestern States where the crop has possibilities as an irrigated or as a dryland winter crop. The most important characteristic of safflower seed oil is that it is the most economical source of linoleic acid available commercially. This factor makes the oil highly desirable for the manufacture of oil-modified alkyd resins and similar products (3). Sunflower seed in this country is primarily grown in the North Central States. In Canada sunflower seed production has been encouraged by the introduction of improved varieties, especially in the province of Manitoba. The most important characteristics of sunflower seed oil are its mild taste, pleasant odor, and resistance to the development of rancidity. In the United States both safflower and sunflower are grown primarily for the oil contained in the seed. The commercial products obtained from safflower and sunflower seeds are oil and oilseed or meal. Safflower seed contains from 26% to 40% oil; sunflower seed from 22% to 36%. Oil quantity therefore is an important factor governing the intrinsic commercial value of these oil-bearing seeds.

Two previous papers (1, 2) covered in detail the theory and procedure for determining rapidly the oil content of both soybeans and flaxseed by the dielectric method. The primary purpose of the work described in this paper was to modify the procedure previously adopted, to adapt the dielectric method to the determination of oil content in safflower and sunflower seeds, and to develop conversion charts for these oilseeds.

Since there are no well-established methods for determining either the oil content or moisture content in safflower and sunflower seeds, it became necessary to develop a standard procedure for determining these

[1] The study on which these findings are based was made under authority of the Agricultural Marketing Act of 1946 (RMA, Title II). Presented at fall meeting, American Oil Chemists' Society, Philadelphia, Pa., Oct. 10–12, 1955.

factors before proceeding with the modifications of the rapid dielectric method already established for soybeans and flaxseed. The current methods of analysis for oil content of oleaginous seeds are generally tedious and time-consuming, especially in the preparation of the ground sample.

The structure and composition of sunflower seed presents certain problems in analysis for oil content. The moisture level in the hull is generally higher than in the meat (4). The hull constitutes approximately 40–50% of the whole seed weight and contains somewhat more than 50% of the total moisture in the seed, but it contains only about 1% of the total fat. Safflower seed likewise presents a problem in obtaining a representative ground sample since approximately 45% of the whole seed weight consists of hull.

Finding the proper mill to grind oil-bearing seeds has been a special problem for each type of seed. Mills such as the Allis-Chalmers experimental roller type of mill described by Zeleny and Coleman (5), the Bauer mill, the Labconco mill, and the Henry nut slicer were employed in preparing ground samples for extraction. In addition, a new model of the Stein mill (Figure 1) previously employed in the dielectric method for oil content was investigated and found suitable as a means of reducing most oil-bearing seeds to a fine consistency in a minimum of time for the preparation of ground samples for use in the standard procedure. The ground samples were extracted in a Soxhlet extractor for 16 hrs., using Skellysolve F [2] and then the solvent was evaporated and the residue was weighed. This was adopted as the standard procedure against which the results obtained by the more rapid dielectric method were calibrated.

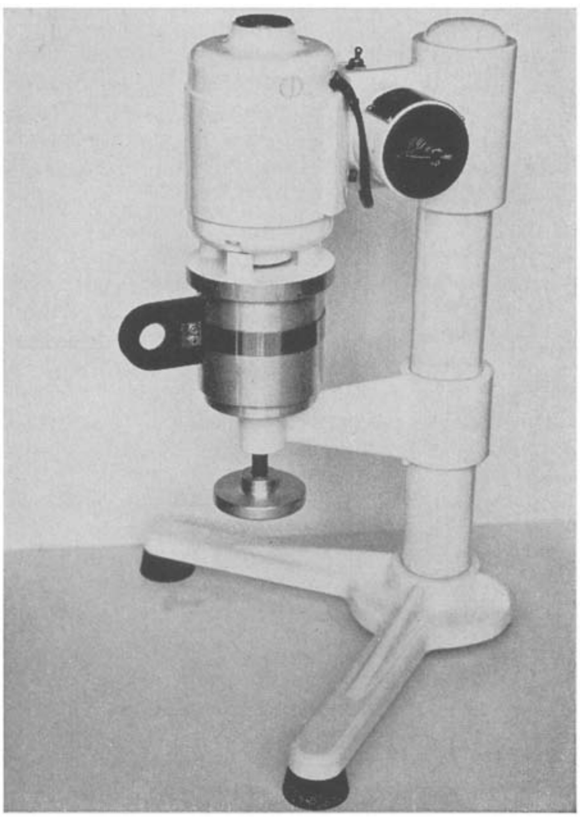

FIG. 1. Stein Mill (Model M1)

Reference Procedure for Determining Oil Content

The standard procedure for grinding safflower seed is as follows:

1. Reduce the size of a dockage-free sample to approximately 50–75 g. by use of a mechanical device, such as the Boerner Divider or by hand-quartering.
2. Place the sample in the cup of the Stein Mill, and grind for 15 seconds.
3. Scrape the ground material from the sides and bottom of the cup with a spatula, and grind again for 15 seconds.
4. Transfer the ground sample to a closed sample jar, and mix thoroughly.
5. Samples should be weighed and extraction begun immediately after grinding to insure reproducible results. Weigh duplicate 10.00-g. portions, transfer quantitatively to the extraction thimbles, and cover with wads of fat-free cotton.
6. Extract with Skellysolve F in a Soxhlet extractor for at least 16 hrs.
7. Completely evaporate the solvent on a steam bath by agitating the oil-solvent mixture with a stream of air while under reduced pressure. Cool to room temperature and weigh.

Sunflower seed, which is larger than safflower seed, cannot be ground fine enough in the Stein mill; therefore the Labconco Mill was used. Otherwise the procedure for analyzing sunflower seed for oil content after grinding is the same as for safflower seed (step 4).

As is shown in Table 1, when samples of safflower seed are ground as suggested, usually less than 0.2% of additional extract is obtained by regrinding the samples after 16 hrs. of extraction and again extracting for 16 hrs. Also there is evidence that this additional extract is made up in part at least of material other than oil. In view of the small amount of additional extract obtained after regrinding, it is evident that the Stein Mill is an efficient mill for grinding such oil-bearing seeds as safflower seed, flaxseed, and soybeans.

TABLE I

Efficiency of Grinding and Soxhlet Extraction Procedure for Safflower Seed

Oil Content, %	
16-hr. extraction	Reground—16 hrs. additional extraction
37.1	.12
36.9	.10
37.0	.10
38.5	.16
38.1	.17
35.8	.15
37.9	.07
37.8	.08
36.3	.01
38.4	.04

Procedure for Determining Moisture Content

Since there are no established or official methods for the determination of moisture content of safflower or sunflower seeds, a practical oven method was investigated and developed. The Brabender Forced-Draft Oven [2] was used for this study primarily because samples could be weighed periodically without removing them from the oven. It was observed that ground samples of both safflower and sunflower seeds when heated at 130°C. apparently oxidize before reaching constant weight, as was indicated by an in-

[2] The mention of firm names or trade products does not imply that they are endorsed or recommended by the Department of Agriculture over other firms or similar products not mentioned.

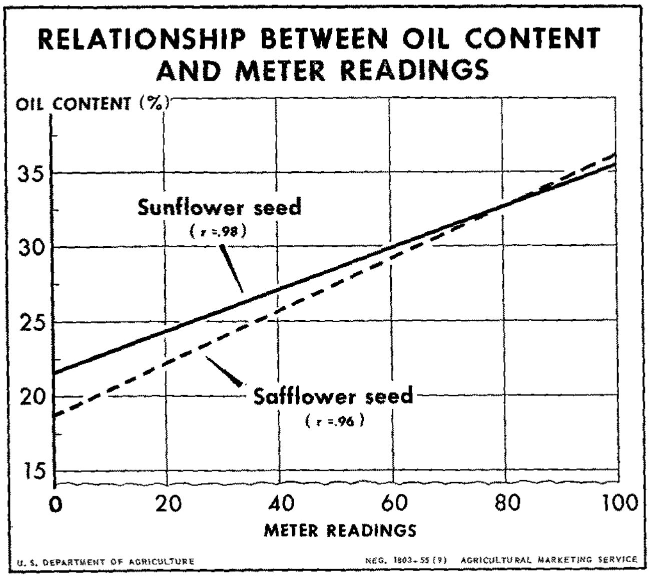

FIG. 2. The relationship between the oil content of safflower seed and sunflower seed and respective meter readings.

crease instead of a decrease in weight after the first hour.

Samples of whole safflower and sunflower seed were placed in a Brabender oven at 130°C. and weighed after 1-, 3-, 6-, and 16-hr. periods. The moisture losses were compared with the moisture values obtained by the Karl Fischer methods. Results are shown in Table II.

TABLE II
Comparison of Oven Method with Karl Fischer Method for Moisture Determination

Moisture Content, %				
Karl Fischer	Brabender Oven—130°C. whole seed			
	1 hr.	3 hrs.	6 hrs.	16 hrs.
Safflower Seed				
4.85	4.75	5.05	5.10	5.25
4.36	4.30	4.60	4.60	4.78
4.03	4.25	4.55	4.58	4.75
4.03	4.20	4.40	4.40	4.60
3.80	3.95	4.20	4.20	4.40
4.38	4.22	4.40	4.40	4.55
Sunflower Seed				
5.82	5.60	5.75	5.80	6.00
4.99	4.90	5.10	5.15	5.25
5.98	5.95	6.10	6.15	6.35
6.12	6.00	6.15	6.22	6.45
6.43	6.05	6.30	6.35	6.60
6.67	6.45	6.70	6.75	7.05

Methods involving heating 10 g. of whole safflower seed for 1 hr. and whole sunflower seed for 3 hrs. at 130°C. in an air oven were adopted as practical routine methods for determining moisture content of these seeds.

Experimental Data and Results

The rapid dielectric method employing the Steinlite LOS Unit is being used in this country and abroad for determining the oil content of soybeans and flaxseed. With certain modifications in technique, namely, by grinding-extracting 80 g. of the sample with 120 ml. of orthodichlorobenzene, this method is also applicable to other oil-bearing seeds, such as safflower and sunflower seeds.

Seventy-six samples of safflower seed and 81 samples of sunflower seed, representing two crop years, were analyzed for oil content by both the standard and dielectric methods. Duplicate determinations were made by each method. Two Steinlite LOS Units were used for reading each filtrate under varying room temperatures. The meter readings corrected to 85°F. were graphically plotted against the oil content determined by the overnight extraction procedure.

Figure 2 shows the relationship between oil content and respective meter readings for both safflower seed and sunflower seed.

The regression lines are plotted from the following regression equations, derived statistically from the data:

Safflower seed $y = 32.5287 + 0.1616x$
Sunflower seed $y = 21.5700 + 0.1430x$

where y = oil content (%) ("as is" moisture basis)
x = meter readings (corrected to 85°F.)

Conversion charts for converting meter readings to oil content percentages were prepared from the regression equations for each oilseed. The standard error of estimate in determining oil content by the rapid dielectric method was found to be 0.27 in terms of percentage of oil for safflower seed and 0.34% for sunflower seed. The coefficient of determination ($r^2 \times 100$) for safflower seed is 92.0 and for sunflower seed is 96.0, that is, 92% of the variance in oil content is concomitant with variation in meter readings in the case of safflower seed and 96% of the variance in oil content is concomitant with variation in meter readings in the case of sunflower seed.

Discussion

The rapid dielectric method for determining oil content in oleaginous seeds is equally applicable to sunflower and safflower seeds as it is for soybeans and flaxseed. The method is simple, accurate, and practical. Tests can be made by non-chemists after brief training with the degree of accuracy indicated in the report. Results on a single sample can be obtained in about 20 min., depending on the rate of filtration. When run sequentially, only about 10 min. are required per sample.

A rapid, practical test of this type should readily lend itself to application in those areas where these oilseeds are grown and marketed. The test could be used in the trading of oilseeds on the basis of the principal factor affecting their intrinsic value, the oil content.

Acknowledgment

The dielectric LOS unit and improved mill were built for this project by the Fred Stein Laboratories, Atchison, Kans., who have worked closely with the United States Department of Agriculture in redesigning the equipment, when necessary, to meet the needs of the work.

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