oleate. The amount of alpha linkage is, therefore, not more than 5–10% in the dehydro-oleate dimer ester. In view of this fact, attack at other non-activated methylenes is probably quite small in extent.

ACKNOWLEDGMENTS

GLC analysis by J. Nelson. UV and IR analyses by R. Fisher. Ozonization studies by O. Privett and M. Blank.

REFERENCES

1. Harrison, S. A., and D. H. Wheeler, J. Am. Chem. Soc., *73*, 839 (1951).
2. Harrison, S. A., and D. H. Wheeler, Minnesota Chemist, *4*, (5), 17 (1952).
3. Harrison, S. A., and D. H. Wheeler, J. Am. Chem. Soc., *76*, 2379–82 (1954).
4. Clingman, A. L., and D. A. Sutton, JAOCS, *30*, 53–56 (1953).
5. Harrison, S. A., and K. E. McCaleb (General Mills, Inc.), U.S. 2,731,481 (1956).
6. Paschke, R. F., J. R. Kerns, and D. H. Wheeler, JAOCS, *31*, 5–7 (1954).
7. Cowan, J. C., B. L. F. Falkenberg, and H. Teeter, Ind. Eng. Chem. Anal., *16*, 90–92 (1944).
8. Paschke, R. F., and D. H. Wheeler, JAOCS, *26*, 278–83 (1949).
9. Rusoff, I. I., J. R. Platt, H. B. Klevens, and G. O. Burr, J. Am. Chem. Soc., *67*, 673–78 (1945).
10. Cason, J., J. S. Fessendon, and C. L. Agre, Tetrahedron, *7*, 289–298 (1959).
11. Peterson, L. E., Anal. Chem. *34*, 1850–1 (1962).
12. Ryhage, R., and E. Stenhagen, J. Lipid Res., *1*, 361–390 (1960).

[Received May 6, 1963—Accepted July 2, 1963]

Cyclic Fatty Acids from Linolenic Acid[1]

R. A. EISENHAUER, R. E. BEAL, and E. L. GRIFFIN, Northern Regional Research Laboratory,[2] Peoria, Illinois

Abstract

Linolenic acid of 95% purity was heated with excess alkali in ethylene glycol to produce cyclic fatty acids. Reaction variables, which are associated with the cyclization reaction and which were investigated, included solvent-to-fatty-acid ratio, catalyst concentration, and reaction temperature, headspace gas (N_2 or C_2H_4), and headspace gas pressure.

Yields of cyclic acids were improved by increasing solvent ratio (1.5–6 wt basis), reaction temperature (225–295C), and catalyst concentration (10–100% excess). With nitrogen the optimum catalyst concentration was about 100% excess, but when ethylene was used, no increase was obtained beyond 50% excess catalyst. Yields of polymeric acids produced in the reaction generally decreased as cyclic acid yields increased, except in one instance.

Higher yields of cyclic fatty acids were obtained with ethylene than with nitrogen under all comparable conditions, and increasing the ethylene pressure to as high as 500 psi improved the yield. Ethylene adds to the conjugated double bonds and is believed to give C_{20} fatty acids having a 1,4-disubstituted monoene ring in the chain. The maximum yield of monomeric cyclic acids from 95% linolenic acid was 84.6%, the balance being polymeric and unreacted monomeric acids. Monomeric acids from this test contained 95% cyclic acids.

Introduction

IN A PREVIOUS PAPER (4) it was demonstrated that the linolenic acid fraction of linseed oil can be converted to a cyclized structure under proper reaction conditions. Linolenic acid of 95% purity, prepared at this laboratory from linseed fatty acids by liquid-liquid extraction as reported by Beal et al. (2), was cyclized with ethylene glycol as the solvent and sodium hydroxide as the catalyst. These reactions were conducted with either nitrogen or ethylene under various pressures in the reactor headspace. Increased yields of cyclic acids have been reported by conducting the cyclization reaction with linseed oil in the presence of ethylene (1). Ethylene enters into the reaction to form a cyclized C_{20} fatty acid. In the present studies, undertaken to determine optimum conditions for producing cyclic acids from linolenic acid, substantially increased yields were again obtained with ethylene.

Reaction conditions, such as solvent ratio, catalyst concentration, temperature, reactor headspace gas, and gas pressure, were varied to determine their effects on the yield of cyclic fatty acids.

Experimental

A 2-liter Parr autoclave equipped with stirrer and sample tube was used for all reactions. Figure 1 is a flowsheet (of the method used) for determining percentage of cyclic and polymeric ester yields. The autoclave was charged with ethylene glycol, NaOH, and linolenic acid. The headspace was evacuated and filled with either nitrogen or ethylene gas. Solvent ratios of 6,3, and 1.5 to 1 (wt basis); temperatures of 225,250,275, and 295C; ethylene gas pressures of 150,300, and 500 psi (before heating); and excess

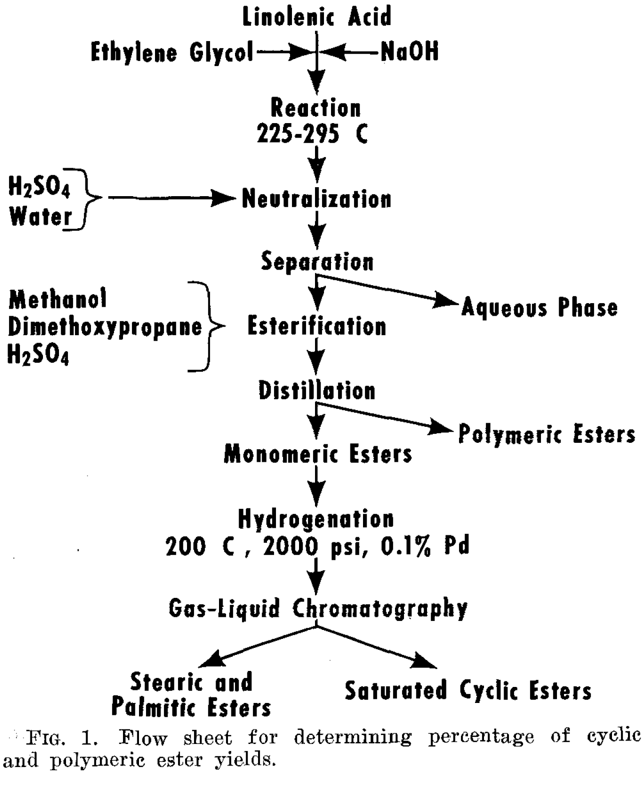

FIG. 1. Flow sheet for determining percentage of cyclic and polymeric ester yields.

---

[1] Presented at AOCS meeting, New Orleans, 1962.

[2] No. Utiliz. Res. & Dev. Div., ARS, U.S.D.A.

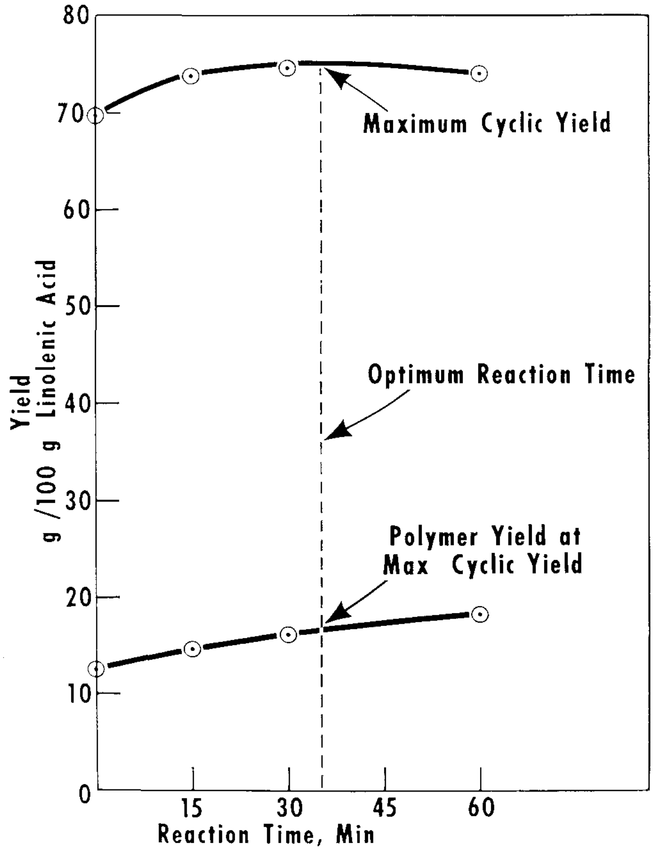

FIG. 2. Method of determining optimum reaction time and maximum cyclic acid yield.

catalyst concentrations of 10,50,80, and 100% were studied. Excess catalyst concentration is defined as the amount of NaOH in excess of that required to saponify the fatty acids.

Samples taken during the reaction were dissolved in a large excess of water (15–20:1 vol ratio) and acidified with 25% sulfuric acid to recover the fatty acids. Large quantities of water minimized ester formation between ethylene glycol and fatty acids. After the fatty acids were extracted with hexane, the aqueous phase was removed in a separatory funnel. The hexane layer was water washed twice, dried over sodium sulfate, and filtered. Fatty acids were esterified in the hexane solution by using 0.6 ml dimethoxypropane, 0.2 ml methanol, and 0.008 ml sulfuric acid per g of fatty acid. Solution was allowed to stand overnight at room temp; then the fatty esters were recovered by washing with dilute potassium carbonate in excess of amount required to neutralize acidity, and by water washing to remove the last traces of alkali. The esters were dried over sodium sulfate and filtered. Hexane was removed by bubbling nitrogen into the sample on a steam bath. Distillation of the fatty esters at 0.25 mm Hg pressure to a pot temp of 225C produced a distillate monomer fraction and a polymer residue.

Ca. 3-g samples of the monomeric esters were hydrogenated with 0.1% Pd in the form of 10% Pd on carbon at 2,000 psi hydrogen pressure and 200C for 15 min. The hydrogenated monomer esters were diluted with acetone and filtered. After filtration, the acetone, used as a wash to remove the catalyst from the esters, was evaporated. Iodine values of less than three were obtained for all samples. The hydrogenated esters were analyzed by GLC to determine the percentage of cyclic fatty acid esters. This method of analysis has been reported by Black et al. (3).

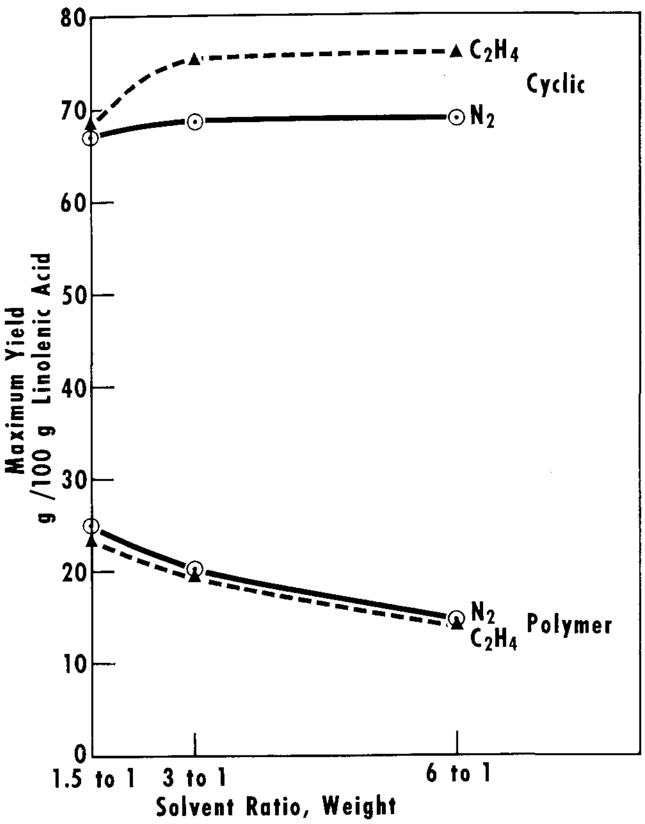

FIG. 3. Effect of solvent ratio on cyclic and polymer acid yields.

Results and Discussion

Four samples were removed from the autoclave during each run, through a stainless steel water-cooled condenser under an inert atmosphere, and were analyzed for cyclic and polymeric acid yields. A graph such as Figure 2 was prepared for each run, plotting yields in grams per 100 g of linolenic acid versus reaction time in minutes. The cyclic acid yield increases to a maximum and then declines, whereas polymer acid yield increases continuously. From the graph the maximum cyclic acid yield, the corresponding polymeric acid yield, and the time required for maximum cyclization to occur were determined. Maximum yields determined in this manner were used to prepare subsequent graphs.

Figure 3 shows the effect of solvent ratio on cyclic and polymeric fatty acid yields per 100 g of the original linolenic acid. Reaction temp was 295C and excess catalyst concentration was 50% in these tests. All yields hereafter are given in grams per 100 g of the original linolenic acid. When nitrogen was used in the reactor headspace and the solvent ratio was increased from 1.5–6, cyclic acid yield increased from 67.0–69.0 and polymer yield decreased from 25.0–14.7. However, when ethylene under 500 psi pressure was in the reactor headspace, the cyclic acid yield increased from 68.5–75.7 while polymer yield again decreased from 23.2–14.0 as the solvent ratio increased. The yield of cyclic acid increased 7.2 g with ethylene as the solvent ratio increased, but the increase in yield with nitrogen was only 2 g.

The effect of reaction temperature on cyclic acid yield is shown in Figure 4. A solvent ratio of 3:1 and a 50% excess catalyst concentration were used for these runs. With nitrogen in the reactor headspace, cyclic acid yield increased to a maximum of 68.8, and polymer yield increased continuously to a

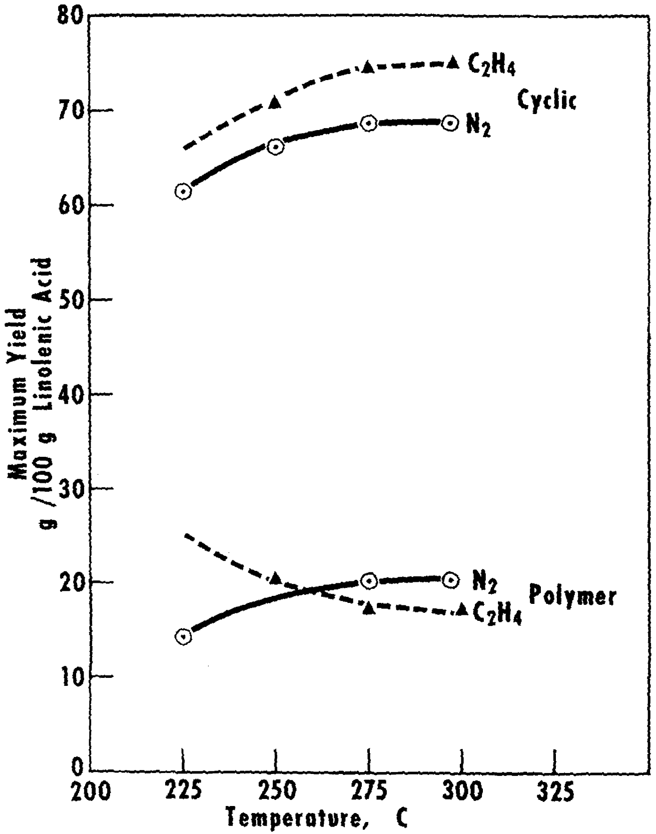

FIG. 4. Effect of temperature on cyclic and polymer acid yields.

maximum of 20.5 as the reaction temp was increased from 225–295C. When ethylene replaced nitrogen, cyclic acid yields increased to a maximum of 75.0 (at 295C) while polymer yields decreased, exactly opposite to the polymer curve obtained with nitrogen. The ethylene runs made at 225 and 250C were not continued long enough to obtain maximum cyclic acid yields, but extrapolating the 250C ethylene curve indicates a maximum yield of 71 would be expected.

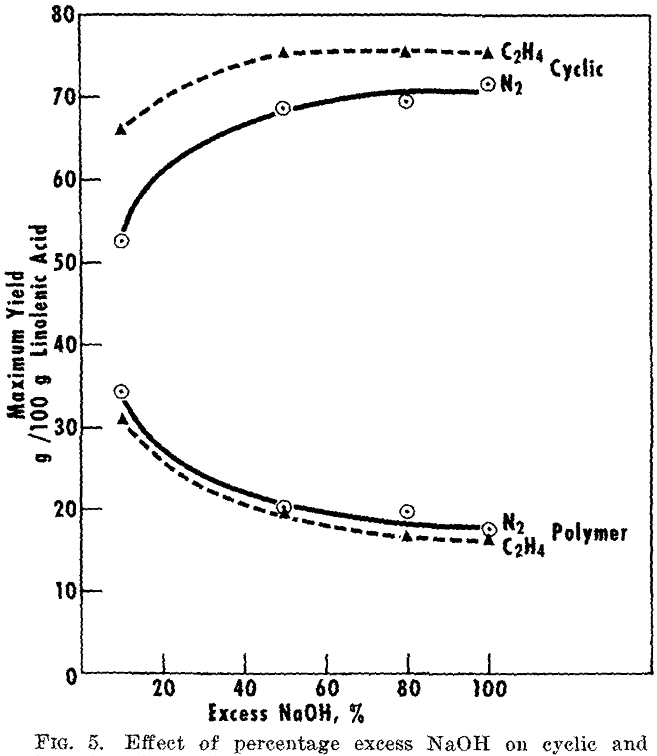

FIG. 5. Effect of percentage excess NaOH on cyclic and polymeric acid yields.

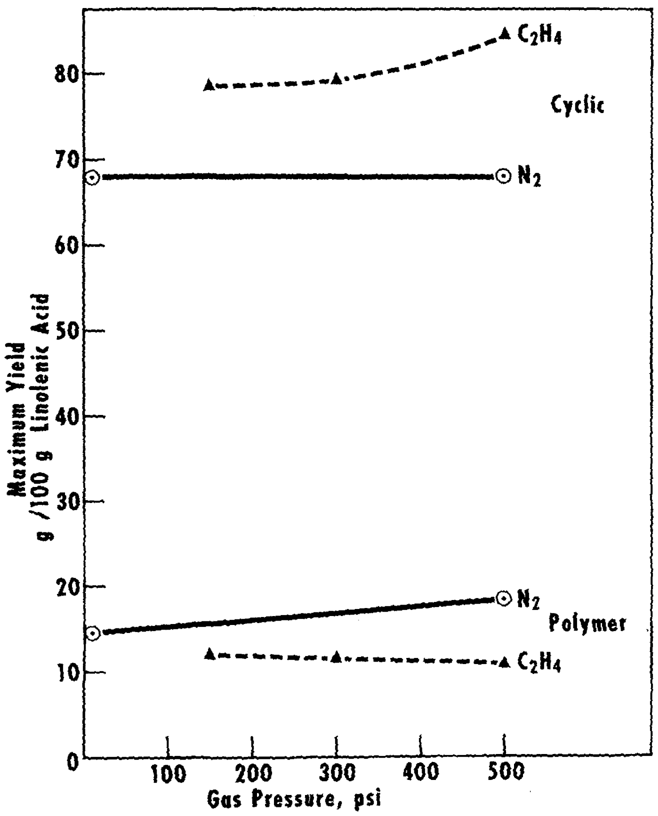

FIG. 6. Effect of gas pressure on cyclic and polymeric acid yields.

A maximum yield could not be determined from the 225C ethylene curve. Higher temperatures favor cyclization and reduce polymerization if ethylene is in the reactor headspace. As the reaction temp was increased from 225–295C, the time required for maximum cyclization to occur decreased from 6 hr to 15 min with ethylene in the reactor headspace and from 4 hr to 30 min with nitrogen.

Figure 5 shows the effect of excess catalyst concentration on cyclic and polymer acid yields. Temp was constant at 295C; the solvent ratio, at 3:1. With either nitrogen or ethylene in the reactor headspace, cyclic acid yield increased and polymeric acid yield decreased as the percentages of excess NaOH increased. If ethylene was used, there was a constant maximum cyclic acid yield of 75.3 at catalyst concentrations above 50%. Evidently, above this concentration, no increase in yield can be obtained. If nitrogen was used, the yield curve approaches a maximum in the 100% excess catalyst concentration area. The polymer yield curves for nitrogen and ethylene parallel each other although the ethylene curve shows about 2% less polymer at all catalyst concentrations studied.

The effect of gas pressure on cyclic and polymeric acid yields is shown in Figure 6. All pressures indicated are initial pressures before any heat is applied. In this series solvent ratio of 6:1, 100% excess catalyst concentration, and 295C temp was used to compare ethylene and nitrogen at low and high pressures. There was no variation of cyclic acid yield with increased nitrogen pressure, but polymer yield increased about 4% when pressure was increased from 10–500 psi. At 10 psi, the maximum yield of cyclic acids was attained in 1¼ hr when reaction temp of 295C was reached. At 500 psi, maximum yield did not occur until after 1 hr at 295C, which again took 1¼ hr to reach. Increased nitrogen pressure evidently inhibits the cyclization reaction, and a longer time is required to obtain maximum cyclization. In contrast, ethylene enters into the reaction and adds to the conjugated fatty acids forming a cyclized C_{20} molecule (5). Increasing ethylene pressure increases cyclic acid yield to 84.6 and decreases polymer yield slightly.

The highest cyclic acid yield, 84.6 g per 100 g linolenic acid, was obtained with 6:1 solvent ratio, 100% excess catalyst concentration, 295C, and 500 psi ethylene pressure. The cyclic acid content of the monomer from this test was 95%.

ACKNOWLEDGMENTS

Laboratory assistance from Sheldon Smith. Hydrogenating of samples by Robert Reichert. GLC determinations by Lynn T. Black.

REFERENCES

1. Beal, R. E. (Secretary of Agriculture), U.S. 3,005,840 (1961).
2. Beal, R. E., V. E. Sohns, R. A. Eisenhauer, and E. L. Griffin, JAOCS, *38*, 524–27 (1961).
3. Black, L. T., and R. A. Eisenhauer, Abstr. Papers, AOCS meeting, New Orleans, 1962.
4. Eisenhauer, R. A., R. E. Beal, and E. L. Griffin, Abstr. Papers, AOCS meeting, Chicago, 1961.
5. Friedrich, J. P., E. W. Bell, and R. E. Beal. JAOCS, *39*, 420 (1962).

[Received March 26, 1963—Accepted July 15, 1963]

Effect of Seed Preparation on Efficiency and Oil Quality in Filtration Extraction of Rapeseed[1]

J. R. REYNOLDS,[2] and C. G. YOUNGS, National Research Council of Canada, Prairie Regional Laboratory, Saskatoon, Canada

Abstract

The application of filtration extraction to rapeseed is discussed with particular emphasis on the effect of seed preparation on the hydrogenation characteristics of the oil. It was found that cooking the crushed seed without the addition of water, and at temperatures not exceeding 220F, produced a satisfactory oil. Under these conditions extraction efficiency was good and the resulting meal showed no harmful effects in feeding trials with mice.

Introduction

THERE HAVE been a number of reports and papers (1–7) on filtration extraction of a variety of oil seeds. However, we believe that we have overcome some unique problems associated with the extraction of rapeseed, and this paper discusses how various changes in the handling and cooking of rapeseed have a marked effect on plant performance and oil quality.

Rapeseed has a high oil content, 38–46%, and tends to disintegrate into fines when placed in hexane. Therefore, it is generally considered necessary to prepress prior to solvent extraction. The ability of the filtration extraction unit to handle both high oil content and fines was the basis of a decision to convert from expeller processing to straight solvent extraction.

Experimental

Figure 1 is a schematic diagram of the filtration extraction unit as used in rapeseed processing. The cleaned seed is rolled and then cooked in a five-high stack cooker. The cooked flakes are rapidly cooled in an evaporative step called "crisping." The material is re-rolled and conveyed to the solvent extraction section of the plant. The re-rolled seed is fed continuously into the extractor and conveyed down its length as a slurry with miscella and slowly agitated to accomplish maximum extraction of the oil with minimum disintegration of the flakes. The slurry is laid down on the rotating horizontal screen filter. The concentrated miscella drains through the filter, leaving the marc on the pan ca. 2 in. thick. As the filter rotates, the cake is washed: first with concentrated miscella to remove fines prior to stripping; then with two washes of decreasing strength miscella; and finally with pure solvent. The miscella from the second wash is fed to the extractor to make up the slurry. The marc is continuously removed and discharged into a conveyor to the desolventizer.

In the initial plant start-up we were concerned with two main points: 1) attaining low residual lipids in the meal at the rated capacity of the plant, and 2) obtaining oil suitable for the edible trade and meal acceptable for animal feeds. The latter was of prime concern because of problems attributed to sulfur-containing compounds, viz., isothiocyanates and thiooxazolidones, present in rapeseed but not present in most other oil seeds. Specifically, these problems are extraction of a portion of the sulfur compounds with the oil, resulting in catalyst poisoning during

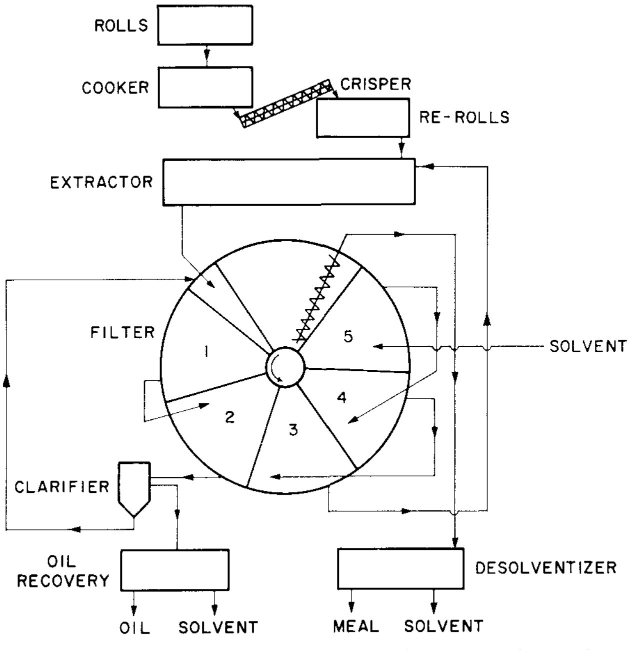

FIG. 1. Schematic diagram of filtration extraction unit as applied to rapeseed.

---

[1] Presented at AOCS meeting in Toronto, 1962. N.R.C. 7667.

[2] Saskatchewan Wheat Pool, Vegetable Oil Division, Saskatoon, Sask.