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Flash Desolventizing Defatted Soybean Meals Washed with Aqueous Alcohols to Yield a High-Protein Product

G. C. MUSTAKAS, L. D. KIRK, and E. L. GRIFFIN, JR., Northern Regional Research Laboratory,¹ Peoria, Illinois

Abstract

A vapor-type desolventizer was developed previously at this laboratory to recover hexane and concentrated alcohols from soybean meals. The work reported in this paper extends the application of this unit to the recovery of dilute alcohols. Soybean protein meals washed with aqueous alcohols are debittered to yield a better flavored product with a significant increase in protein content. The protein of defatted meal was increased from about 50 to 70 or 75% by washing with methanol, ethanol, or isopropyl alcohol in a concentration range of 50-70%. System modifications and critical variables were investigated so as to minimize residual alcohol and to yield a free-flowing homogeneous product. Residual alcohol in the desolventized flakes was 0.25-1.0%. Facility of removal followed the order—methanol, isopropyl alcohol, and ethanol. Two-stage flash desolventization as well as the use of the more dilute alcohols resulted in lower residual alcohol content of the desolventized product. After a minimum value for residual alcohol in the flakes is reached, further removal is difficult. However, water continues to be removed so that the alcohol/water ratio becomes higher with an increased vaporization force as with increased temperature. It is postulated that the alcohol is held by adsorption or hydrogen bonding. The desolventized products analyzed: protein 72-77%; Nitrogen Solubility Index 4-16; water absorption values 328-410%. The products were light-colored, granular, and free flowing. The soybean flakes extracted with methanol exhibited the best flavor.

A GROWING INTEREST in vegetable protein concentrates for foods has also increased interest in new methods for producing these concentrates. One method of increasing the protein concentration of soybean meal is to extract with dilute alcohols. This reduces the concentration of sugars and other alcohol-soluble compounds of the meal, thereby raising the protein content. The alcohols also remove a substantial amount of the beany flavor (1). Alcohol-water mixtures cannot be satisfactorily removed with

conventional-type desolventizing equipment without adversely affecting the product. Such equipment degrades the protein through contact with hot metal surfaces during long retention periods. This produces such undesirable effects as moisture balling, scorching, denaturation, loss of bulkiness and poor moisture absorption properties which are undesirable in high-quality food products. A flash desolventizing unit, developed previously at this laboratory (2-4), permits extremely short retention time of meals in contact with high-temperature vapors.

This paper reports pilot-plant investigations on the recovery of aqueous alcohols from extracted soybean flakes by flash desolventizing. System modifications and critical variables affecting the degree of desolventization were evaluated, as well as changes in protein content, protein solubility, water absorption, and taste acceptance of the desolventized products.

Materials and Methods

Wet, defatted, soybean flakes extracted with methanol, ethanol, or isopropyl alcohol containing 30-50% water were furnished by a cooperating firm; but about half the runs were made on dry flakes rewetted with alcohol at the Northern Laboratory.

Moisture in the spent flakes was determined by the Karl Fischer method. Alcohol content was taken as the difference between the % total volatile and the % moisture. Total volatile was determined by oven drying in a Brabender moisture tester for 2 hr at 120C. Also, alcohol values in the desolventized flakes above 2% were determined by this procedure.

Small quantities of residual alcohol in the desolventized flakes were analyzed by a modified esterification procedure (5) for primary alcohols. Residual alcohol was extracted from the flake sample by refluxing with acetone in a Butt extraction apparatus. The boiling flask contained acetone and also phthalic anhydride to esterify the extracted alcohol in a reaction medium of pyridine.

Nitrogen Solubility Index (NSI) for the measurement of water-soluble protein was determined by a modified method of Smith and Circle (6) in which the water-solids mixture was agitated for 2 hr at 25C with flat-blade paddles at 125 rpm. NSI equals water soluble protein ÷ total protein × 100.

¹A Laboratory of the Northern Utilization Research and Development Division, U.S.D.A.

Water absorption of the desolventized flakes was measured by the amount of water absorbed at 190F by 100 g of flakes. Free liquor was separated by centrifuging.

Composition of the vapors was determined by sampling the vapor at the blower discharge, separating the condensable components, and analyzing the non-condensables by Orsat gas analysis.

Equipment and Procedure

Rewetting of dry soybean flakes was carried out in a Kennedy continuous countercurrent horizontal extractor, or batchwise in stainless-steel drums. The extraction unit measured 10 in by 20 ft, with 20 extraction cells or stages.

Figure 1 portrays the flash desolventizer. The main

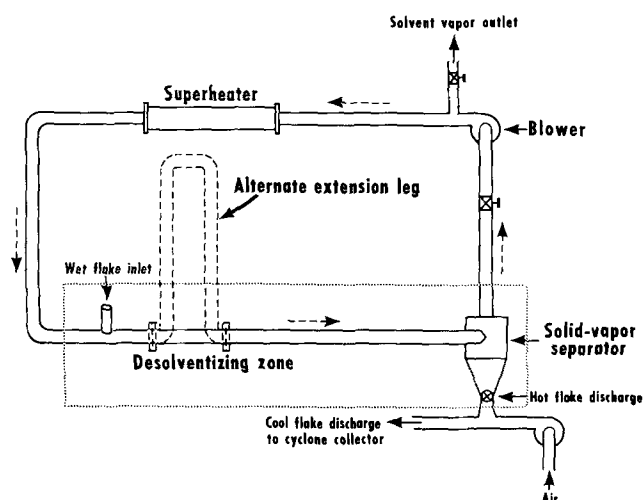


FIG. 1. Flow diagram of flash desolventizer.

element of the system consists of 3-in ID galvanized steel tubing which forms a closed circuit with a superheater, turboblower, and a cyclone collector. Duct work, blower, and cyclone separator are wrapped with steam tracer copper tubing and covered with magnesia insulation. The desolventizing zone is encircled by the dotted lines in Figure 1. This ductwork consists of a 45° riser for a distance of 3½ ft, followed by a horizontal run of straight 3-in ID insulated duct, approximately 18½ ft long. For some runs, a 4-ft horizontal section midway in the desolventizing zone was replaced with an extension leg consisting of a vertical inverted U section, 10 ft high with upflow and downflow legs on 27-in centers. The upflow leg was constructed from 4-in ID duct; whereas the downflow leg was reduced to 3-in ID duct. The extension leg added 4 elbows and doubled the overall length of the desolventizing zone to 37 ft. Vapors withdrawn from the system passed through a dust filter and a shell and tube heat exchanger for condensation. A pneumatic system consisting of a blower, 38 ft of conveying duct, and a cyclone collector was designed to receive the hot flakes discharged at the cyclone base by a rotary valve.

In the first 6 runs, a single-pass shell and tube superheater with 1-in OD stainless-steel tubes and heat transfer area of 21 ft² was used with steam at 115–120 psig. For the remaining runs, this unit was replaced by a single-pass shell and tube superheater with ¾-in OD stainless-steel tubes and heat transfer area of 50 ft². Starting with the 14th run, steam pressure to the larger superheater was increased to

250 psig and continued throughout the remaining runs. Concurrently with this change, the vertical extension leg was also added to the system.

In a typical run, where soybean flakes were rewetted at the laboratory, the flakes were conveyed in the extractor countercurrent to the flow of solvent. Flakes leaving the last stage were drained on an inclined drag-link conveyor and were moved by a transverse screw conveyor with choke feed to the desolventizer. For several runs, the soybean flakes were wetted batchwise in stainless-steel drums, or were furnished already wet by the cooperator. For these runs, the extractor was used merely as a feeder to the desolventizer.

The alcohol-wet solids entered the desolventizer by gravity and were rendered essentially free of solvent by being suspended in a vapor steam which was superheated by indirect steam to temperatures above the condensation point. The solid material was maintained in suspension for only a few seconds during which the desolventizing took place, and the fluidized solids were simultaneously conveyed to the cyclone for separation of the solvent vapor. The vapors were bled out of the system at the blower discharge and passed through a cloth dust filter before condensation and collection. Hot flakes were discharged at the cyclone base by a rotary valve into the pneumatic air-cooling system. Air drawn into this duct cooled the flakes to room temperature. Carbon dioxide was used at the feed inlet to minimize condensation of hot recirculating vapors on the feed flakes and also at the cyclone discharge valve to reduce air leakage into the system.

Temperature and static pressures were measured at selected points of the desolventizer by thermocouples and water manometers, respectively. Temperature of the hot desolventized flakes was measured directly below the rotary discharge valve by collection in an enclosed cup containing a thermocouple.

Vapor velocity measurements in the desolventizer were made by Pitot tube, located between the superheater and solids inlet.

Temperature, feed rate, choice of alcohol, alcohol concentration, and superheater steam pressure were the variables studied in a series of 22 runs and correlated with residual alcohol content in the desolventized product.

The effect of particle size of the feed solids on desolventizing was studied in one run. The feed was ground so that 83% of the meal was of 60–100 mesh. Feed stock used in the remaining runs was ground so that 88.5% of the material was retained on a 40-mesh screen.

Feed rate to the desolventizer was controlled so that products of reasonably low residual alcohol content could be obtained in a single pass. Feed rates of 4–40 lb per hr (alcohol wet basis) were investigated.

In addition, 2-stage operation, moisture tempering, and steam injection were investigated. Two-stage desolventization experiments were carried out by re-passing the desolventized flakes through the desolventizer. Moisture tempering consisted of adding water to the single-stage desolventized flakes to a range of 15–20%, tempering for 2 hr, and then recycling the tempered material through a second desolventizing pass. Composition of the recycle vapor was modified by the injection of live steam into the vapor stream to study this effect on residual alcohol. As a result, the noncondensable vapors were largely displaced with superheated water vapor.

In the desolventizer operations without steam in-

TABLE I
Desolventization Process Data on Defatted Soybean Meals Washed with Aqueous Alcohols

Unit	50% Methanol			70% Methanol			50% Ethanol			70% Ethanol			50% Isopropyl alcohol			70% Isopropyl alcohol		
	Run 3	Run 7	Run 8	Run 16	Run 17	Run 1	Run 2	Run 19	Run 14	Run 18	Run 21	Run 20						
Desolventization stage.....	1	2	1	1	1	1	1	1	1	1	1	1						
Wet-flake feed rate.....	30	20	10	10	4	40	30	20	10	20	20	20						
Superheater steam pressure.....	117	119	116	255	264	118	118	118	10	230	230	230						
Superheater area.....	21	→	50	50	37	21	21	50	50	30	30	30						
Length of desolventizing zone.....	18.5	→	18.5	57	57	18.5	18.5	→	→	37	→	→						
Steam injection at superheater inlet (120 psig).....	None	None	6	None	None	None	None	→	→	None	→	→						
Vapor velocity.....	53	52	70.0	61.4	65.6	65.6	65.6	65.2	72.4	69.1	67.7	67.1						
Inlet vapor temperature.....	315	317	328	373	370	313	314	314	376	371	380	378						
Spent vapor temperature.....	274	284	272	312	320	323	274	287	312	322	313	322						
Desolventized flakes.....	145	192	150	200	215	145	160	200	205	225	205	240						
Feed flakes.....	55.81	23.78	55.85	50.01	46.74	53.03	39.90	16.12	49.53	5.62	46.70	5.62						
Total volatiles.....	23.95	6.31	26.05	18.18	12.74	33.19	19.97	6.26	16.93	1.92	27.51	1.92						
Ethanol.....																		
Isopropyl alcohol.....																		
Desolventized flakes: ^a																		
Total volatiles ^b	28.72	8.53	21.42	2.20	1.23	23.75	17.01	7.04	2.98	0.78	4.05	1.90						
Ethanol ^b	6.87	1.17	4.94	0.73	0.46	9.11	7.50	1.25	1.26	0.38	1.71	1.15						
Isopropyl alcohol ^b																		
Protein content ^c	8.8	7.8	12.7	74.2	73.5	16.3	14.4	15.6	77.0	74.6	73.9	73.2						
Nitrogen Solubility Index ^c	370	395	410	368	368	360	400	400	368	350	343	343						
Water absorption ^c																		

^a Feed to second stage moisture-tempered.
^b Analyses based on hot desolventized flakes.
^c Analyses based on cool desolventized flakes.

jection, substantial quantities of air entry into the vapor stream was unavoidable since vapor seals at the solids inlet and outlet of the desolventizer were ineffective. Carbon dioxide was bled into the system at these locations to eliminate explosion hazards. Improved vapor seals at the solids inlet and discharge points would be recommended to eliminate noncondensables in the vapor system.

Results and Discussion

Table I shows detail process data for the alcohol systems methanol, ethanol, and isopropyl alcohol, respectively, at 50 and 70% concentrations. Operating conditions, total volatiles, residual alcohol, and other product characteristics are also shown.

Increasing heat-transfer area and steam pressure, as well as using the extension leg, gave higher vapor and solids temperatures and lower volatile contents in the desolventized flakes. Recycle vapor temperatures leaving the superheater were increased from approximately 315 to 375F. Inserting the extension leg increased retention time in the desolventizing duct both by enlarging the cross-sectional duct area, and almost doubling the overall length. Figure 2 shows the variation of residual product volatiles with the feed rate for the 50% methanol system using the modified desolventizer system.

Fine grinding of the feed stock lowered the residual volatiles in the desolventized flakes, but not the residual alcohol, as shown in Table II where 40-100 mesh and 20-40 mesh alcohol-washed meals were desolventized. The finer mesh feed retained significantly more volatiles in the spent flakes stream.

TABLE II
Effect of Feed Particle Size on Residual Volatiles in the Desolventized Flakes

Feed particle size range ^a U.S. sieve series	Total volatiles		Residual alcohol
	Spent flakes	Hot desolventized flakes	Hot desolventized flakes
	%	%	%
40-100	63.6	2.0	1.1
20-40	51.9	4.4	0.9

^a Mesh size of approximately 90% of the material.

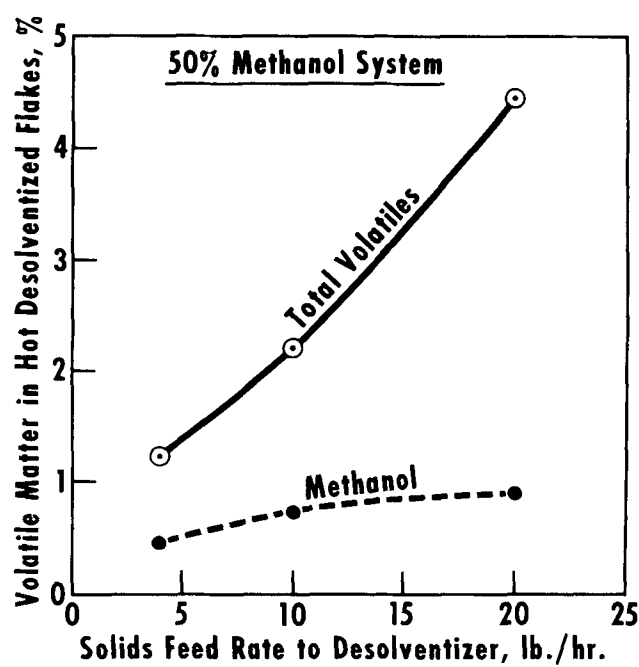


FIG. 2. Effect of solids feed rate (alcohol wet basis) on total volatiles and residual methanol in hot desolventized flakes.

Ease of alcohol removal in the desolventizer followed the order: methanol, isopropyl alcohol, and ethanol. Theoretically, the rate of removal would depend upon the relative (a) latent heats (b) boiling points, (c) azeotrope compositions, and (d) other factors such as adsorption. If each property alone were controlling, the ease of removal for the alcohols would be expected, as follows:

Latent heat: Isopropyl alcohol, ethanol, methanol

Boiling point: Methanol, ethanol, isopropyl alcohol

Azeotrope composition: Ethanol, isopropyl alcohol

Methanol has the lowest boiling point, and since it forms no azeotrope, a simple distillation is followed. Our finding that isopropyl alcohol is removed more readily than ethanol can be explained if it is assumed that the lower latent heat of isopropyl alcohol is more controlling than its boiling point. Figure 3 compares the relative degree of removal of the three alcohols at concentrations of 50 and 70%; also the effect of temperature, alcohol concentration, and a second desolventization step on residual alcohol content. A similar pattern of solvent removal was observed at both alcohol concentrations.

Two-Stage Operation. Two-stage desolventization was found to be the most effective technique for reducing the volatiles to low amounts. In general, the feed rate to the second pass was reduced over that of the first pass so that the dry solids throughput remained essentially the same in both cycles. Recycling made possible a reduction of 30–70% in the residual alcohol content of the desolventized flakes as shown in Figures 3 and 4. Residual alcohol in the flakes was reduced to 0.25–1.0% after the second pass. All data are based on residual alcohol in hot desolventized flakes since essentially no further change in residual alcohol took place while air-cooling the flakes. Approximately 1–2% increase in solids moisture content occurred during the cooling cycle because the hot flakes pick up some moisture from the air.

Introduction of Moisture Into the System. The amount of moisture in the system depends upon whether water is introduced by steam injection, tempering, or different alcohol concentrations.

Live steam was injected into the superheater inlet vapor stream at rates of 6–25 lb per hr during the second pass. Figure 4 shows the residual alcohol content of the flakes obtained from a first pass and a recycle of the first-pass flakes for each wash system with and without live steam injection. In all cases where steam injection was used, slightly lower residual alcohols were obtained although total volatiles

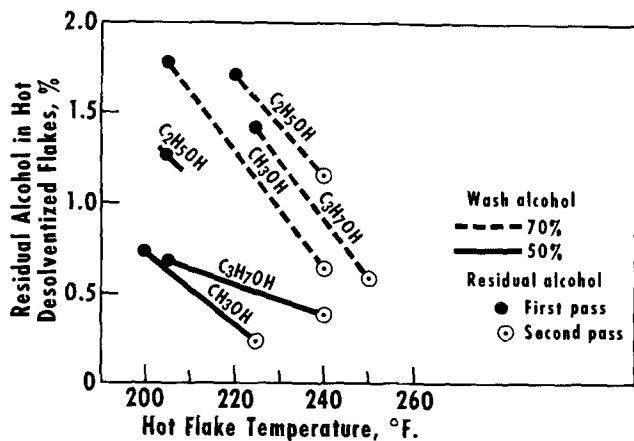


FIG. 3. Effect of temperature, wash alcohol concentration, and number of desolventization passes on residual alcohol content of hot desolventized flakes.

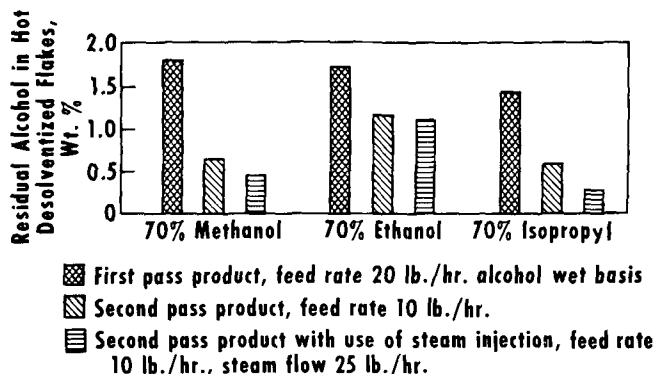


FIG. 4. Effect of second pass desolventization with and without steam injection on residual alcohol content of hot desolventized flakes. (Hot flake temperature was not constant for the data given so that relative volatility between the alcohols is not shown.)

content of the product was increased 30–40%. Moisture content of the desolventizing vapor stream was increased with steam injection to nearly 60% by weight, thereby significantly decreasing the concentration of noncondensables.

Moisture tempering before second-stage desolventizing did not improve results significantly over those from simple recycling or recycling with steam injection. The additional steps of moisture addition and blending do not appear justified.

Lower residual alcohols were obtained by desolventizing flakes washed with 50% rather than 70% alcohols for the 3 alcohols used (Figure 3). Water content and total volatiles of spent flakes washed with 50% alcohol averaged approximately 33 and 54%, respectively. With 70% alcohol, the spent flakes analyzed 20% water and 49% total volatiles.

Evidence of H Bonding. When the data for alcohol removal are correlated with hot flake temperature, the curves show that as temperature is increased, water is removed more rapidly than alcohol. This also occurred in previous work with 95 volume per cent ethanol. These data show that a small amount of alcohol is quite strongly bound within the soybean solid matrix. This evidence supports previous knowledge about the associated state of alcohol molecules leading to hydrogen bonding of alcohol to the protein molecule. Our data also indicate that some alcohol is bonded in preference to water. This bonding is demonstrated by a plot of the ratio of alcohol to water in the volatiles remaining in the product against temperature of the desolventized product, or versus total volatiles in the product, as shown in Figure 5 for the 50% methanol wash system. A sharp rise is noted at the 1% level in the curve for total volatiles. This point corresponds to a hot flake temperature of approximately 218F at which it is extremely difficult to remove the remaining alcohol. Figure 6 shows variation of the residual alcohol and total volatiles content of the product versus hot flake temperature, again illustrating the difficulty of removing the last traces of alcohol.

Product Characteristics. The products contained 72 to 77% (m.f.b.) protein, and were highly denatured. Denaturation would be expected from washing in dilute alcohol. The differences in protein content of the final products obtained with the various alcohols are not necessarily significant as the washing step was not a part of our study. NSI values of the washed flakes were in the range of 13–24 and in

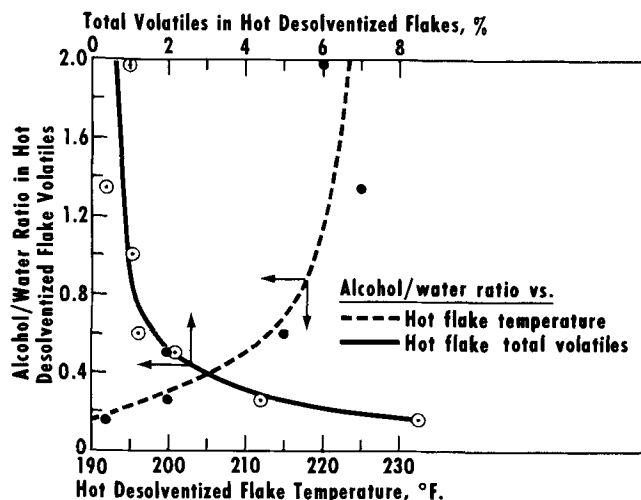


FIG. 5. Alcohol/water ratio in hot desolventized flake volatiles; 50% methanol system.

desolventizing, the protein was further denatured to an NSI range of 7-16.

The products obtained with the methanol-wash had a better flavor than those washed with either ethanol or isopropyl alcohol. The lower level of taste acceptance for these two alcohols was due partly to some residual taste of solvent. Organoleptic evaluation detected the alcohol even though the chemical analysis for it was relatively low.

Water absorption values of 328 to 410 were obtained for the desolventized products. Absorption values were significantly highest with the 50% methanol-wash. A wide variation in data was obtained for the remaining wash systems. Table III shows the av-

TABLE III
Water Absorption of Desolventized Flakes for Alcoholic Wash Systems

Alcohol	Alcohol conc., %	Water absorption	
		Average value ^a	95% Confidence limit
Methanol.....	50	379	10.3
Ethanol.....	50	352	15.7
Isopropyl alcohol.....	50	341	10.3
Methanol.....	70	358	35.3
Ethanol.....	70	341	6.7
Isopropyl alcohol.....	70	342	10.2

^a Basis—grams water absorbed per 100 g solids.

erage absorption value obtained for each system with the 95% confidence limits calculated for all the samples analyzed.

Conclusions

The flash vapor-type desolventizer can handle soybean flakes washed with aqueous alcohols of rather high water content. Two-stage operation, as well as a less concentrated alcohol, is effective in minimizing residual alcohol in the end product. Steam injection during the second stage gives further reduction in re-

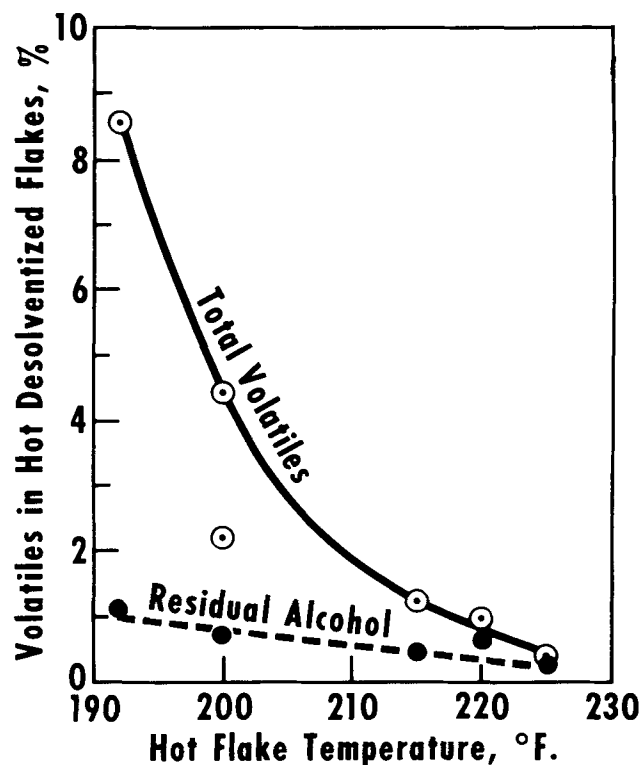


FIG. 6. Variation of hot desolventized flake total volatiles and alcohol content with temperature; 50% methanol system.

sidual alcohol. A small amount of alcohol is strongly bound to the solids and is difficult to remove even under conditions of high-temperature desolventizing.

Important advantages of the flash desolventizer are: 1) Low product holdup, 2) high temperature with short retention time, 3) a system capable of rapid changes, and 4) a granular, free flowing product with minimum color degradation and maximum water absorption.

Acknowledgment

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A Comparison of Several Analytical Techniques for Prediction of Relative Stability of Fats and Oils to Oxidation

W. D. POHLE, R. L. GREGORY, and J. R. TAYLOR, Research Laboratories, Swift & Company, Chicago, Illinois

Abstract

Three analytical methods proposed by various workers for predicting the relative stability of

fats and oils to oxidation have been compared on a series of samples. The Eckey Oxygen Absorption, the modification of the A.S.T.M. Oxy-