TABLE IV

Results of Refining Tests

Oil sample		Color		FFA %	PV mg/kg	IV	P mg/kg	Fe mg/kg	Ca mg/kg	S mg/kg	AOM mg/kg
		R	Y								
Water degumming											
Starting oil	(1")	3.5	50	0.70	4.62	120.8	541	2.47	224	3.2	–
Degummed oil	(1")	3.2	40	0.61	5.82	121.2	185	1.24	172	1.9	–
Neutralized oil	(1")	2.7	35	0.03	–	–	0.40	0.55	5.1	–	–
Bleached oil	(1")	0.2	1.5	0.07	–	121.5	0.31	0.25	2.3	–	–
Deodorized oil	(5 ¼")	0.4	4	0.02	0.0	120.8	–	–	–	0.21	20
after 2 weeks	(5 ¼")	0.5	5	0.02	0.41	–	–	–	–	–	–
Citric acid degumming											
Starting oil	(1")	3.5	50	0.70	4.62	120.8	541	2.47	224	3.2	–
Degummed oil	(1")	3.1	40	0.53	6.20	121.8	50.0	0.68	40.4	1.6	–
Neutralized oil	(1")	2.6	35	0.03	–	–	8.2	0.50	17.6	–	–
Bleached oil	(1")	0.2	1.5	0.07	–	121.6	0.38	0.36	1.7	–	–
Deodorized oil	(5 ¼")	0.4	4	0.01	0.0	121.3	–	–	–	0.19	20
After 2 weeks	(5 ¼")	0.5	5	0.01	0.38	–	–	–	–	–	–
Maleic anhydride degumming											
Starting oil	(1")	3.5	50	0.70	4.62	120.8	541	2.47	224	3.2	–
Degummed oil	(1")	3.1	35	0.46	5.64	121.2	33.3	0.96	20.3	1.5	–
Neutralized oil	(1")	2.4	35	0.03	–	–	0.73	0.39	2.9	–	–
Bleached oil	(1")	0.2	1.5	0.06	–	120.8	0.15	0.38	1.5	–	–
Deodorized oil	(5 ¼")	0.3	3	0.01	0.0	120.5	–	–	–	0.25	20
after 2 weeks	(5 ¼")	0.4	4	0.01	0.39	–	–	–	–	–	–

from 300 g to 330 L, a scale-up factor of ca. 1,000, we feel confident that the results may be reproduced easily in a commercial operation. Further product improvement may be expected from more uniform contact in a fully continuous process.

ACKNOWLEDGMENTS

The Canola Council of Canada sponsored this work, and permitted its publication. The technical assistance was provided by D. Mudt and the staff of the P.O.S. Pilot Plant Corporation.

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[Received September 9, 1982]

Current Practices in Continuous Cottonseed Miscella Refining

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ABSTRACT

Miscella refining of crude cottonseed oil has become a generally accepted commercial process for the past 20 years. The simple and efficient continuous process for removal of undesirable impurities is described, having changed little in its basic form since discovery 40 years ago. The individual unit processes, control systems, process flow charts, chemical reactions and oil-to-hexane ratios used in miscella refining are described. The several advantages to miscella refining vs conventional oil refining are noted.

INTRODUCTION

The solvent extraction of crude oil from cottonseed has been a commercial reality for the past 60 years. Before solvent extraction, the crude cottonseed oil was extracted mechanically by hydraulic and expeller-type presses. The mechanically extracted crude oils typically contain fewer nonglyceride impurities than solvent-extracted oils, making them easier to refine, but having the disadvantage of leaving a higher oil content in the meal. After World War II, the prepressing of cottonseed, followed by solvent extraction and direct solvent extraction, has become increasingly predominant in the industry. Solvent-extracted cottonseed has resulted in high oil yields, but also higher oil refining losses. The higher refining losses are due to the greater extraction of gossypol and other nonglyceride components and a decrease in the oil content of the solvent extracted meal to 1% or less (1).

The high-temperature solvent stripping following extraction yields a very dark colored crude oil. The dark color in the crude oil may be difficult to remove by conventional refining methods, if the color has been set by high-temperature degradation products of gossypol and other related pigments (1).

Of the many hydrocarbon solvents investigated for use in oilseed extraction, commercial hexane has become the most widely used solvent. With hexane as the dominant solvent, most miscella refining is carried out in a hexane/oil miscella. A notable exception is the Vaccarino process in which the solvent extraction and miscella refining are accomplished with acetone as the solvent (2).

The advantages of miscella refining were first described in a patent granted to Thurman in 1941; subsequent basic patents were granted to Mattikow in 1951 and Cavanagh in 1957 (3). Of the three patents, only the Cavanagh patent, which is known as the Ranchers' Process, has been developed commercially with a small number of plants using the Ranchers' Process, in operation since the mid-1950s (6,8).

Although the main advantages of miscella refining were known since the 1950s, it was not until the early 1960s that the process gained commercial acceptance. The development of large-size mills with year-round mill operation, changing economic conditions decreasing the profit margin between the cottonseed and the crude oil and the development of equipment and technology to allow a totally enclosed system helped increase the acceptance of miscella refining. Since the 1960s, approximately 30 new miscella refineries have been installed worldwide using the DeLaval Miscella Refining Process. The basic DeLaval process, developed by Crauer and Pennington in the early 1960s, is a simple, easily controlled, continuous miscella caustic refining system with an acid pretreatment (4). The basic DeLaval processing steps have remained the same since its development, but the process has been streamlined to improve the operation and reduce energy and maintenance costs.

PROCESS DESCRIPTION

The system and data presented in this paper will be from the DeLaval Miscella Refining Process. A brief process description follows.

The crude miscella feedstock from the extractor is first adjusted to the desired miscella concentration either by controlled evaporation in the first stage evaporator or blending in a feed tank.

The crude miscella is pumped through a heat exchanger to bring the miscella up to desired processing temperature.

The crude miscella proceeds through a flow measuring device, with a ratio controller for the caustic soda reagent addition system, and enters the acid pretreatment addition and mixing section.

The pretreated crude miscella then enters the caustic soda addition and mixing section where the caustic is intimately mixed and dispersed. The crude miscella/caustic mixture is then contacted for a period of time to allow for proper refining to occur. The reacted mixture then passes through a trim heat exchanger to ensure the proper temperature for centrifugation in the Alfa-Laval hermetic miscella centrifuge. The light-colored, refined miscella is easily separated from the dark brown gelatinous soapstock in the specially designed centrifuge.

The refined miscella then reenters the extraction plant stripping system for removal of remaining hexane.

PROCESS PARAMETERS AND CHEMISTRY

A detailed review of the process operating parameters and chemistry will reveal the many advantages miscella refining offers.

The process will operate on a feedstock from a variety of sources—direct solvent-extracted crude miscella, a blend of prepressed oil with solvent-extracted crude miscella from the prepress cake or a reconstituted blend of crude oil from any source with hexane. With the DeLaval Miscella Refining Process, the direct solvent-extracted crude miscellas and blended prepress solvent-extracted crude miscellas refine most efficiently at the 60-65% oil:35-40% hexane ratio. Reconstituted expeller-press oil refines better at a 50:50 ratio (5). As the oil content is raised above 65%, the amount of neutral oil entrained in the soapstock during separation increases, lowering the refining yields (4). An incidental benefit of refining in the miscella state is the reduced viscosity and specific gravity as compared to 100% cottonseed oil in conventional refining. Cottonseed at 32 C has a viscosity of 45 cS and a specific gravity of 0.91 compared to a 65:35 miscella viscosity of 4.5 cS and a specific gravity of 0.815. Pumping, heating, mixing and separation are all made easier due to the miscella's properties, thereby reducing energy requirement.

The major advantage of miscella refining over conventional refining is in the immediate refining of the crude miscella directly after the oil has been extracted and before the solvent stripping has set the color. In the direct solvent-extracted miscella, the desired oil:hexane ratio can be held by using a temperature controller on the first stage evaporator. It is important that the first stage evaporator be of the proper size and design to obtain the desired miscella concentration at an exit temperature of 49-54 C with 74 C maximum. Evaporator temperatures above 74 C will cause the oil's color to become set and prove difficult to refine.

Evaporator exit temperatures of 49-54 C also conserve energy since the crude miscella feed to the refinery should be in this range and hotter oil would have to be cooled before refining.

To maintain the benefits of immediate refining, it is preferable to refine fresh crude oil miscella within the first two hours, and minimize storage time (4). However, crude miscella of up to 24 hours old has been successfully refined with the DeLaval Process.

It is important to have at least two crude miscella feed tanks for the refinery to maintain a homogeneous mixture of the desired oil:hexane ratio and to allow for flow rate surges. As with any continuous process, if the feedstock is not a homogeneous one, the process will suffer impaired performance, such as higher refining losses and lower refined oil quality.

Another desirable quality of the crude miscella is a solids content of 0.05% or less. A higher content will invariably lead to more frequent cleaning of the centrifugal separator and lower productivity. Proper operation of the oil mill will usually be sufficient to produce this low solids content. If meal fines are a problem, a liquid cyclone or filter may be used to remove them prior to the first stage evaporator. In dealing with prepress oil, it is desirable to filter the oil before it is blended into miscella.

The acid pretreatment system allows the processing of a wide range of crude oil quality. The acid pretreatment usually varies between 100 ppm and 500 ppm by weight of oil depending on the quality of the crude. It has been reported that some off-grade crudes have required pretreatment as high as 1800 ppm (4,5). An acid such as phosphoric or glacial acetic has been found to be effective in improving oil quality and reducing refining losses. Phosphoric acid is used more commonly due to its less corrosive properties and better commercial availability. Off-grade crude and early-season production have required, historically, a higher dosage of acid to obtain a lower bleach color and reduced refining losses. As the season progresses, the acid dosage may be reduced without a reduction in oil quality. The amount of acid pretreatment also depends on where the cottonseed was grown and the local seasonal conditions. The acid is mixed with the miscella in a static mixer providing an intimately dispersed acid phase which immediately reacts with the crude miscella.

The pretreated crude miscella is then alkali-refined using dilute caustic soda in a 16-24 degree Baume concentration at a 0.2-0.5% excess treat over the theoretical required for neutralizing the free fatty acids. The caustic treat is based on the free fatty acid content on an oil basis. The chemical reaction of the dilute caustic with the free fatty acids proceeds rapidly at a temperature of 54-57 C, with no adverse affects on the finished oil quality or increase in refining loss.

The alkali reaction section of the miscella refinery is composed of two different types of mixing equipment necessary to complete the refining. The first mixing section is a series of four static mixers of which any one or all may be used in series. The static mixers produce a high-intensity mixing providing intimate dispersal of the dilute caustic phase in the miscella. By varying the number of mixers in series using bypass valves, the degree of mixing can be controlled.

As the reaction mixture leaves the intimate dispersal mixing section, the reaction between the free fatty acid and caustic has been completed and a soap micelle has been formed. The second mixing section allows for the continued reaction between the soap/reagent phase and the partially refined oil/hexane phase. A series of specially designed Sullivan Systems low-speed retention mixers provides the additional reaction time with the proper contacting to complete the miscella refining. As with the static mixers, it is possible to use all or none of the retention mixers. The determining factor on how many retention mixers to use is based on the crude miscella quality and the refining results obtained.

Here the small soap micelles start to agglomerate forming larger clusters with little oil entrainment. The phosphatides, gossypol and other color bodies are then adsorbed onto the soap clusters. The adsorption of the impurities is a slow process which is influenced by temperature with the optimum being between 54 and 59 C. A lower miscella temperature will increase the required contacting time to obtain a light-colored oil (4,5).

The retention mixers are designed to provide enough mixing to keep the soap micelles in suspension without creating an emulsion that would be difficult to separate centrifugally. Refining in the miscella state offers the advantages that the soap tends not to entrain oil and the miscella-caustic mixture does not emulsify readily, helping to keep refining losses to a minimum.

Following the retention mixers, the miscella mixture then proceeds through a trim heater where the temperature is adjusted to 57 C to obtain the best separation in the Alfa-Laval hermetic centrifuge. This is the upper temperature limit for separation purposes, for, at a temperature of 59 C (4), the hexane will begin to vaporize on discharge with the soapstock causing a nonflowing foamy soapstock that is unpumpable.

Separation of soapstock and refined miscella is accomplished readily due to the large difference in specific gravity. Miscella at 47 C and a 65:35 ratio has a specific gravity of 0.795 and the soapstock has one of close to 1.0. Due to this large specific gravity difference, the outlet seal of the separator has been designed specially to provide an opening larger than that of a standard centrifuge, from which the soapstock discharges to prevent an uncontrolled back pressure buildup.

The hermetic centrifuge allows the pressurization of the total system, including the separator, and eliminates the possibility of solvent loss. The hermetic seal is achieved using double concentric mechanical seals lubricated and cooled with water at the inlet and outlet of the separator, which allows feed pressures of up to 125 psig.

A manual back pressure control on the refined miscella outlet maintains the proper separation interface location in the separator bowl and disc stack. The proper interface location will give a light clear yellow refined miscella. The soap content of the miscella will be less than 50 ppm and usually in the range of 10-50 ppm. The soapstock produced is a dark brown gelatinous material with 1-3% hexane content, normally (4). Soapstock hexane levels of up to 6% have been reported (7). The low soap content of the refined miscella eliminates the need of the conventional water washing stage.

Historical data accumulated over the years since the process' development has shown refining losses typically 30-40% under the AOCS cup loss and finished oil bleached color usually 50% lower than that of the official cup results. The improvement seen in the refined oil varies according to the growing region and seed quality, but always equals or exceeds the official AOCS cup results. The refined miscella proceeds on to the second stage evaporator and final strippers for hexane removal. The refined oil is then pumped through a cooler to refined oil storage or polish-filtered for removal of traces of soap prior to storage.

The removal of the gums, color bodies and other impurities in miscella refining helps prevent loss of efficiency in the evaporators and final strippers. The refined miscella prevents the buildup of a gummy deposit being cooked on to the heat transfer surfaces, resulting in an energy savings to the oil mill and reduced maintenance cleanings of the equipment.

The soapstock, with its low hexane content, is usually pumped directly to the desolventizer-toaster for recovery of the hexane. The addition of soapstock to the meal in the desolventizer-toaster helps prevent excessively dusty meal, gives it a more natural appearance and makes it easier to handle and pelletize. The soapstock generally increases weight and fat content of the meal by approximately 0.9%, and adds to its nutrient and commercial value as an animal feed. The soapstock also tends to decrease the free gossypol content remaining in the solvent extracted meal (9,10).

It is recommended that plants also have a soapstock storage tank to allow operation to continue in the refinery if a temporary meal supply problem develops in the desolventizer-toaster.

The addition of the soapstock to the meal in the desolventizer-toaster not only increases its value, but solves a typical oil refinery pollution problem. For plants that do not wish to add the soapstock back to the meal, a soapstock desolventizing system can be added to recover the hexane content. The desolventized soapstock can then be acidulated to recover the fatty acid fraction as an acid oil. The acidulation process also produces a new pollution problem for oil mills in the disposal of the acid water fraction. Soapstock desolventizing and acidulation is usually not attractive for those oil mills not currently connected with an existing oil refinery's waste treatment system.

Looking at current economic conditions in the market place, the price differential between crude cottonseed oil and PBSY refined cottonseed oil has varied between 1.5 and 4 cents per pound in the recent past with highs of up to 7 cents per pound. The favorable price differential for the oil mill operator yields a fast payback of the cost of the miscella refinery and a greater profit margin in his oil sales. Even when the price of crude and PBSY are equal, the oil mills producing PBSY will have a more desirable product, enabling production volumes to remain up. The crude producer may be required to pay a penalty under these conditions and have more difficulty selling his total production. Current trends in the USA are for salad oil producers to prefer not to purchase crude cottonseed oil due to the processing difficulties and buy only a PBSY miscella refined oil.

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The Adsorption of Fatty Acids from Vegetable Oils with Zeolites and Bleaching Clay/Zeolite Blends

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ABSTRACT

The adsorption of model fatty acids (heptanoic, oleic), using spiked vegetable oils, was studied using different kinds of zeolites (A-zeolite, X, Y-zeolites, mordenite), Y-zeolite exchanged with different cations (alkali, alkaline earth, transition metal ions), and with bleaching clay/zeolite blends. The adsorption process was shown to be governed by the molecular sieving properties of the zeolites involved as well as the electrostatic field strengths of the exchange cations. Facile interparticle diffusion of cations between clay and zeolite particles in the blends was verified by electron microprobe analysis and shown to cause unexpected results with respect to bleaching and fatty acid removal.

INTRODUCTION

Fatty acids are a natural component of vegetable oils and animal fats and are also generated during contact of these oils with high activity bleaching clays (1). Normally, other than the loss in oil they represent, they are not a problem because they can be removed during deodorization. However, in those cases where bleaching is to be conducted without subsequent deodorization, or where there are other constraints on removing the fatty acids by distillation, there will then be a problem of removing the entrained acids from the product oil. As one part of a program to develop a specialty bleaching clay formulation for such applications, we examined the use of zeolites to accomplish this objective. This work is reported here.

The generation of free fatty acids during bleaching with acid-activated clays is a fairly complex process that can involve any number of contributing factors including moisture content of the oil, soap content, atmosphere present, temperature and time of contact (1). Acid-activated bleaching clays possess some very strong Brönsted acid sites on their surfaces (2,3,4) and the acid-catalyzed hydrolysis (5) of the glyceride ester linkage by these surface acid sites is presumably a major source of free fatty acids generated during the bleaching operation. Soap decomposition to yield free fatty acid as a consequence of sodium ion adsorption by the clay has been suggested (6) as another mechanism for fatty acid generation during bleaching. Whatever the detailed mechanism(s) responsible for free fatty acid rise during bleaching operations, the role of high-activity clays in generating these acids is clearly implicated since neutral or only slightly acid clays often reduce fatty acids somewhat through preferential adsorption (1).

Besides the surface Brönsted or "intrinsic" surface acidity mentioned above, the acid-activated montmorillonites used as bleaching clays will also contain a certain amount of unwashed acid salts which impart an additional acidity component termed "residual" acidity. This type of acidity is related directly to free fatty acid rise in the bleaching of oils (7). Both residual and intrinsic acidity can be reduced, the former by improved washing, the latter by ion-exchange with alkali or alkaline earth cations. However, the result, in both cases, is usually reduced bleaching efficiency. It has been shown (8), for instance, that acid-activated bleaching clay subsequently exchanged with sodium cations exhibits only 1/5 the adsorptive capacity for β-carotene as it does in its fully activated form.

An alternative approach, given the seemingly irrevocable nature of the correlation between clay acidity and bleaching efficiency (and its consequences with respect to the tradeoffs between free fatty acid generation and color reduction), was needed. We chose to concentrate on trying to adsorb fatty acids selectively from the oil, simultaneously as they were formed. In particular, we were interested in studying zeolites for this role since claims (9) had already been made that X-zeolite could be used for the closely related process of removing fatty acids from used cooking oils (color reduction was not studied).

That such a selectivity for fatty acids over the parent triglyceride molecule should exist might be expected from a consideration of the known molecular sieving properties of zeolites and the large size differences between fatty acid vs triglyceride molecules. In addition, a study by workers in Spain (10) had already shown a very low adsorption of triglyceride molecules on X-zeolite as compared to the fatty acids.

Keeping in mind that zeolites are crystalline aluminosilicates exhibiting a broad range of chemical and physical properties depending on their uniquely specific array of structural atoms and exchangeable (mobile) cations (11), we wanted to know how such differences might affect the selectivity and capacity for adsorbing fatty acid molecules from vegetable oils. Specifically, we wanted to know how internal structure (type of zeolite), type of exchangeable cation present, and silica/alumina ratio would affect fatty acid adsorption. These factors are known (12,13) to influence adsorption of hydrocarbons by zeolites.

During the course of our work employing clay/zeolite blends, we discovered evidence of a surprisingly facile cross-