Physical Refining

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ABSTRACT

By reviewing current commercial physical refining processes a prospectus is suggested for the future objectives in this field of edible oil processing. The paper reviews widely used physical refining processes for the relatively high free fatty acid (FFA) laurics and palm oil and a commercial operation for physical refining of maize and sunflower oils. In addition, the relatively new departure of physical refining of soybean oil is discussed using data from recent development work. This system is used to demonstrate present trends in the development sector of the industry. Reference to similar work on pretreatment of rapeseed oil is included. The discussion is used to suggest guidelines for design of a flexible physical refining system for application to major oils processed by European refiners. There is still no physical refining process that can handle successfully on a commercial scale all qualities of soybean oil. We must envisage a system of physical refining that is able to deal with the most difficult soybean oil and thus assume it will handle all the less difficult oils.

INTRODUCTION

This paper is primarily concerned with a review of physical refining techniques. However, some brief introductory comment on the traditional chemical refining route (Fig. 1) is worthwhile.

Classical Processing

The crude oil is first degummed—a process by which hydratable and nonhydratable phospholipids are removed from the crude oil. The former are removed by water/steam treatment and gravitational separation from the oil mass. Gums which remain in the oil after such treatment require treatment by acid (usually phosphoric) to enable removal by gravitational techniques.

After degumming, the free fatty acids (FFA) naturally present in the oil are neutralized with caustic soda, to form a soapstock which is removed by mechanical separation from the neutral oil. Some neutral oil is occluded in the soapstock and thus represents a process 'loss'.

The third stage is decolorization or 'bleaching'. In this stage at least a portion of unwanted pigments in the neutral oil is adsorbed onto a diatomaceous earth which is removed from neutral, bleached oil by filtration.

The final stage in this classical refining route is deodorization. This comprises a vacuum steam distillation of unwanted and odoriferous material from the oil bulk to give a product with organoleptic properties suitable for human edible consumption. Some color and free fatty acid reduction also takes place during deodorization.

The soapstock produced during crude oil neutralization and separated by sedimentation or centrifugation cannot normally be disposed of without further treatment. The standard treatment for soapstock is addition of concentrated mineral acid to give an 'acid oil'. Such oil requires water washing and drying before sale. The water washing provides an effluent stream—usually of high sulphate content since the acid most commonly used is sulphuric.

In addition to the treatment stages described above, it is often necessary to remove relatively high melting point waxes from the oil. Should these waxes remain in the finished product they will cause an unattractive cloudy appearance during storage of bottled liquid cooking oils.

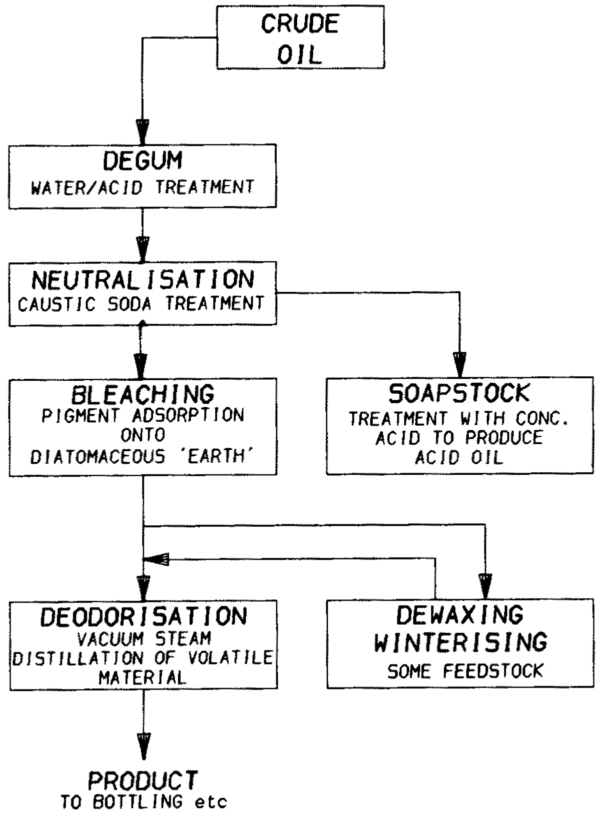

FIG. 1. Classical refining scheme.

The position of the dewaxing stage within the classical scheme varies widely according to convenience, practical considerations and individual oil process requirements.

Waxes can also adversely effect losses at the neutralization stage and yet crystallization becomes more efficient as the substance purity improves.

Physical Refining

Physical refining (Fig. 2) has been known with limited application for many years. The basis of the technique is the use of deodorizers for steam distillation of fatty acids as well as odoriferous volatiles from the oil. In this way, it is possible to eliminate the caustic soda neutralization stage and hence the major source of neutral oil loss in the classical refining scheme. The consequent elimination of soapstock and its treatment brings further advantages; eliminating an effluent stream from the soapstock splitting and providing higher grade distilled fatty acids, instead of the previous 'acid oil'.

The basis of physical refining is a combined fatty acid distillation and deodorization (often termed steam refining). Steam refining facilities are now incorporated almost as standard in edible oil deodorizers. All the many designs available incorporate means of rapidly varying temperature and sparge steam conditions to suit particular oils and FFA

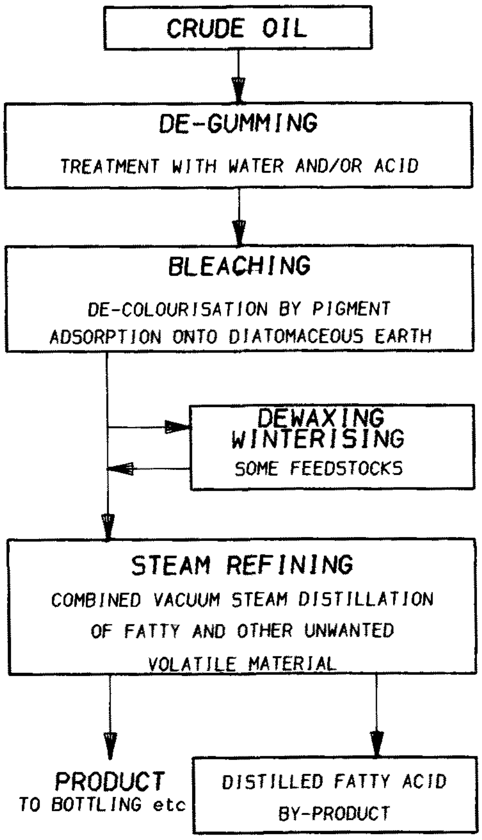

FIG. 2. Typical physical refining scheme.

levels. However, to succeed here the crude feedstock requires a 'pretreatment stage', effectively to remove 'gums', trace metals, pigments and, in some cases, waxes.

Without an effective pretreatment, the steam refining stage cannot hope to produce an oil of color and stability characteristics comparable to the classical refined product.

The extent of the pretreatment stage is dependent on the particular oil and its quality. Some oils such as the common laurics and palm oil require simple systems while others such as soybean oil require rigorous degumming stages.

In terms of deciding the type of pretreatment/refining system necessary for particular oil qualities Alfa Laval have put forward some general guidelines:

- Oils containing less than 0.1% nonhydratable phosphatides and less than 2 ppm iron can be physically refined using the so-called 'dry pretreatment' systems.
- Oils containing less than 0.5% nonhydratable phosphatides and less than 2 ppm iron will require a 'wet pretreatment' or 'superdegumming' if they are to be physically refined.

By inference we therefore need to treat oils containing nonhydratable phosphatides and iron at levels in excess of those given above by traditional caustic refining.

These criteria rely only upon two particular qualities of the feedstocks. There are, however, several other suggested criteria for assessing physical refinability such as the oxidative state of the feedstock in particular.

PHYSICAL REFINING USING 'DRY PRETREATMENT'

By 1976, the physical route had become the preferred method for refining of palm oils—particularly those produced in Malaysia where major efforts in plant breeding, harvesting and improved extraction systems had made significant improvements in quality of the crude oil.

With minor variations the basic scheme described by Sullivan (1) has continued to take over from classical refining of this particular oil.

Many proprietary systems are available for this pretreatment and two typical examples are described below.

The Alfa Laval System

The crude oil is continuously heated and pumped into a stainless steel reaction mixer where it is treated with phosphoric acid (Fig. 3).

The deaerated oil is pumped to a slurry tank where activated bleaching clay is continuously added at a controlled rate. The slurry is then heated—first in a regenerative heat exchanger with outgoing bleached oil, and then with steam in a second heat exchanger—before entering the bleacher. The main reaction, facilitated by proper agitation, takes place in the bleacher. Trace metals and a large proportion of the coloring matter are removed here.

The slurry of hot oil and bleaching clay is then passed through one of two filters for complete removal of the bleaching clay before going to the steam refining stage.

Such pretreatment systems are operating successfully not only on palm oil but also palm kernel oil, coconut oil and tallow which like palm oil are characterized by low phospholipid content. Relatively high FFA in these oils enhance the low refining factor attractions of physical refining—1.2 times the FFA compared to up to twice the FFA in the classical scheme.

The Simon-Rosedowns System

The crude oil is continuously pumped via a deaeration system and heater to a multistage vacuum reactor/bleacher. (The reactor/bleacher is shown in Figure 4 and is normally constructed in stainless steel.) The oil now at reaction temperature is mixed with phosphoric acid. A reaction time is allowed in the upper compartment and during this time the oil is brought to bleaching temperature.

After this reaction/heating stage, the oil passes to the second compartment where it is dosed with the required amount of deaerated bleaching earth. Subsequent compartments allow time for the bleaching to be effected.

On discharge from the bottom compartment, the mixture passes to the filtration system. Two vertical leaf pressure filters are used—one working while the other is cleaning. After a final polishing filter the oil is passed to the steam refining deodorizer.

Physical Refining With 'Wet' Pretreatment

For oil other than those mentioned above, wet pretreatment systems are necessary.

The Sentraal Westileke Ko-operative of Viljoenskroon, South Africa, produces maize or corn oil from corn germ. Until 1978, this factory operated a classical small capacity refinery. The plant processed high FFA maize oil from the dry milling system together with sunflower and groundnut oils. Refining losses associated with this operation were those commonly occurring in such traditional plants and since the FFA of the maize oil averaged ca. 8%, these losses were highly significant.

In conjunction with Simon-Rosedowns Limited of the UK, a process and plant was developed for physical refining of this high FFA feedstock, together with sunflower oil.

The development is worthy of further note since it demonstrates how equipment used in a conventional

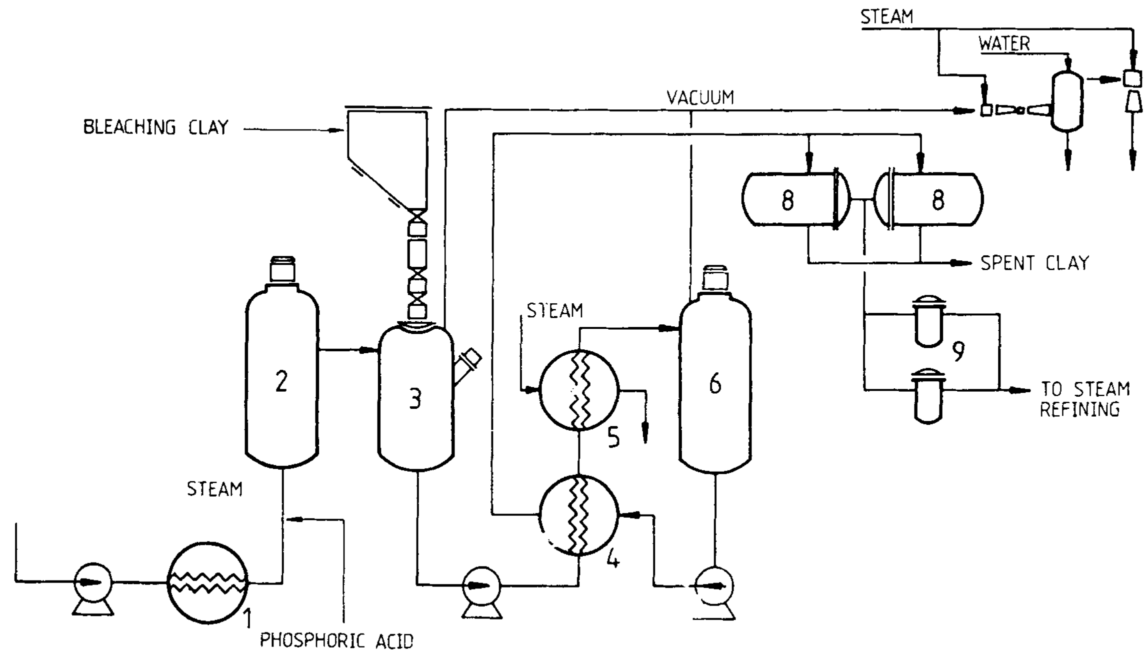

FIG. 3. Alfa Laval system.

Pretreatment				Bleaching	
1	Crude oil preheater	4	Regenerative heat exchanger	7	Ejector system for slurry tank and bleacher
2	Pretreatment mixer	5	Oil heater	8	Bleaching filters
3	Slurry tank	6	Bleacher	9	Polishing filters

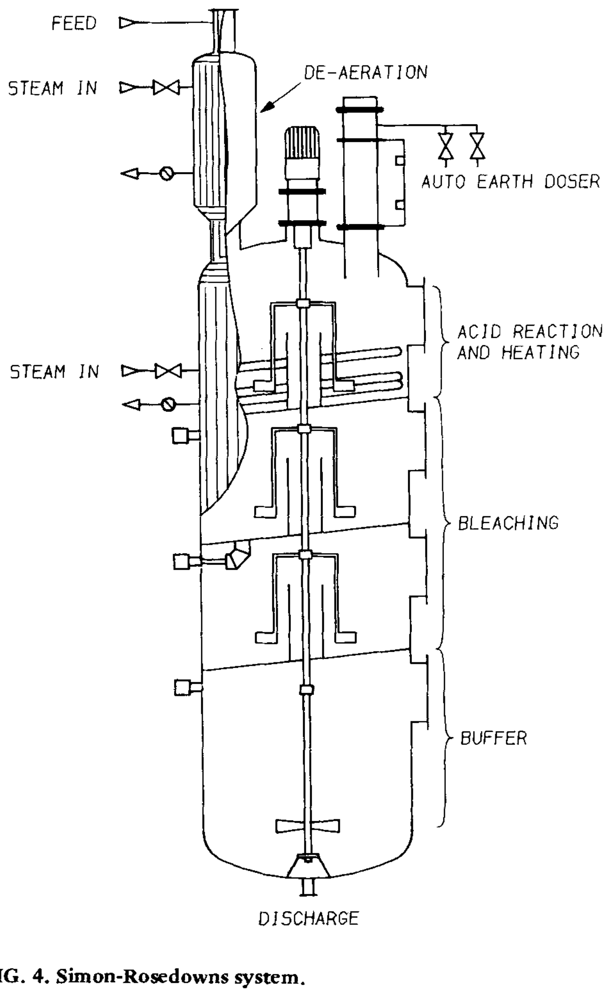

FIG. 4. Simon-Rosedowns system.

refinery can be extensively utilized in a physical refining alternative.

Pretreatment. Figure 5 shows the degumming system. Two centrifuges were originally used in series for continuous neutralizing and washing. They are now connected in parallel and each capable of degumming oil using water and/or phosphoric acid.

Figure 6 shows the batch bleaching system, used in the original refinery for batch neutralizing as well as bleaching. The system was modified to bleaching only with improved heating and more modern filtration systems.

The degummed and bleached oils then require dewaxing. This is done by conventional means and subsequently sent to the steam refining/deodorization section.

Steam refining stage. The Rosedowns Econoflow deodorizer (Fig. 7) is typical of modern deodorizer designs used in this distillation stage. Utilizing the patented Votator deodorizing tray principle (2), the unit allows for continuous deaeration and feed oil/product oil interchange to give 80% heat recuperation. The deodorization stages are, however, semicontinuous to give well defined residence at 3/5 torr. The final heating of the oil to deodorizing temperature of 220 C for sunflower oil and 260 C for maize oil, and the later cooling stages are done under sparge steam conditions. Thus, the risks of polymerization and degradation affecting organoleptic qualities are much reduced in these stages of the process.

Maize/Sunflower Oils

Successful results (Table I) from this commercial scheme were reported at the AOCS/ISF 1980 Conference (3). The scheme allows treatment of the oil with 0.15% phosphoric acid at 60-80 C for some 20 min. The mixture is then passed to a high speed centrifuge where, with some assistance from a small water addition, the precipitated gums are

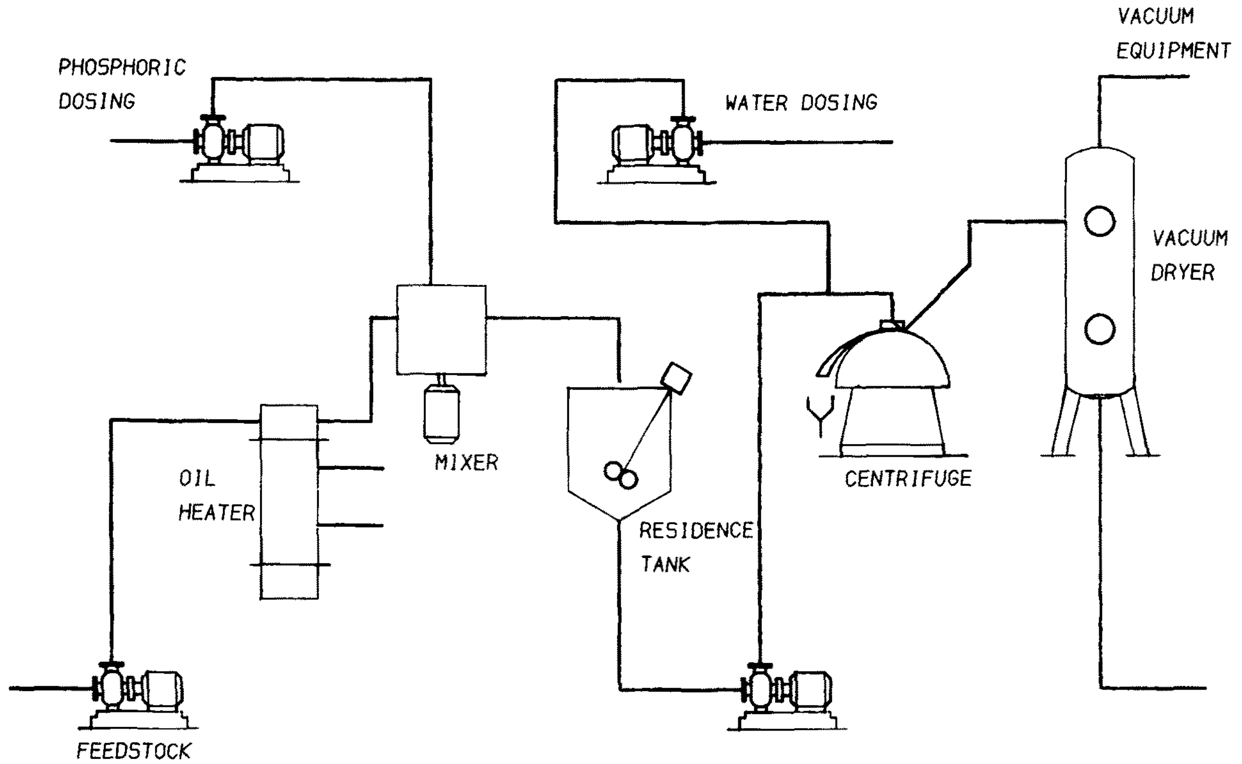

FIG. 5. Degumming unit.

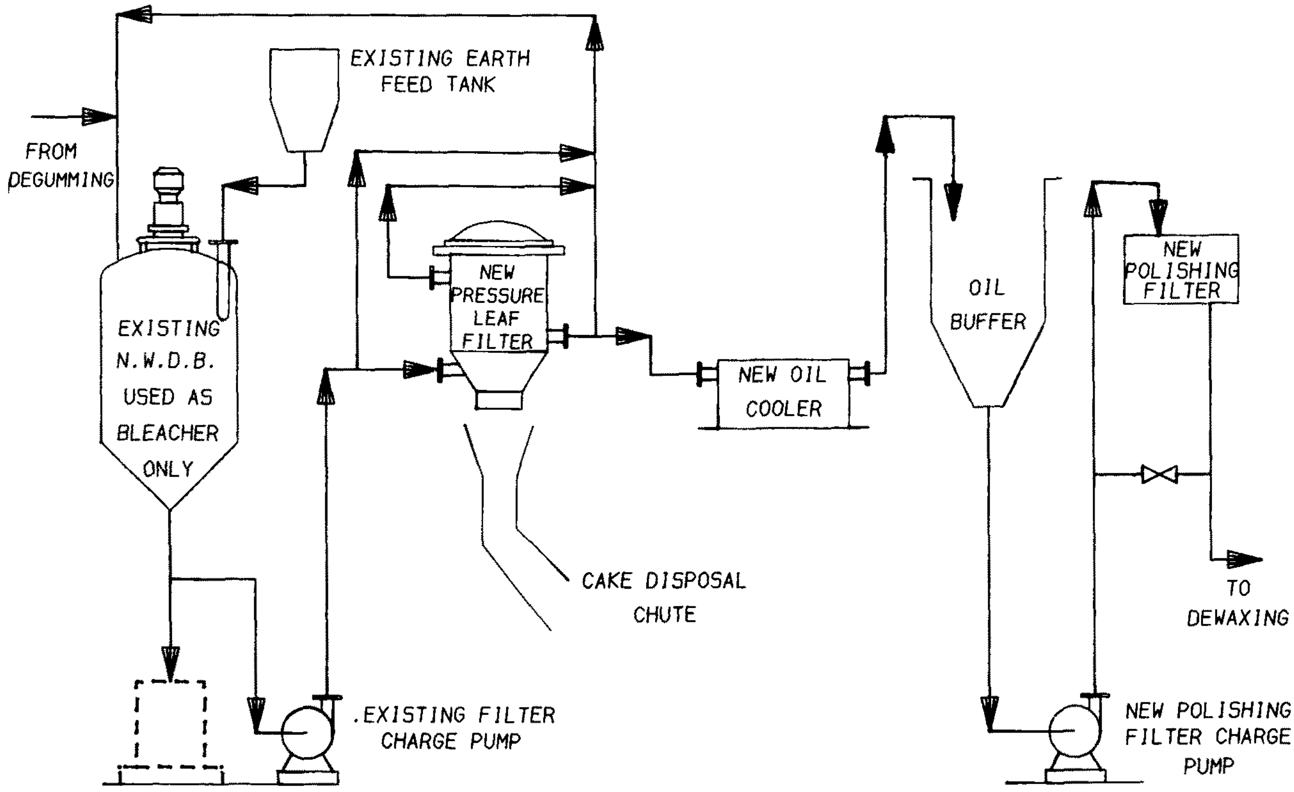

FIG. 6. Modified batch bleaching unit.

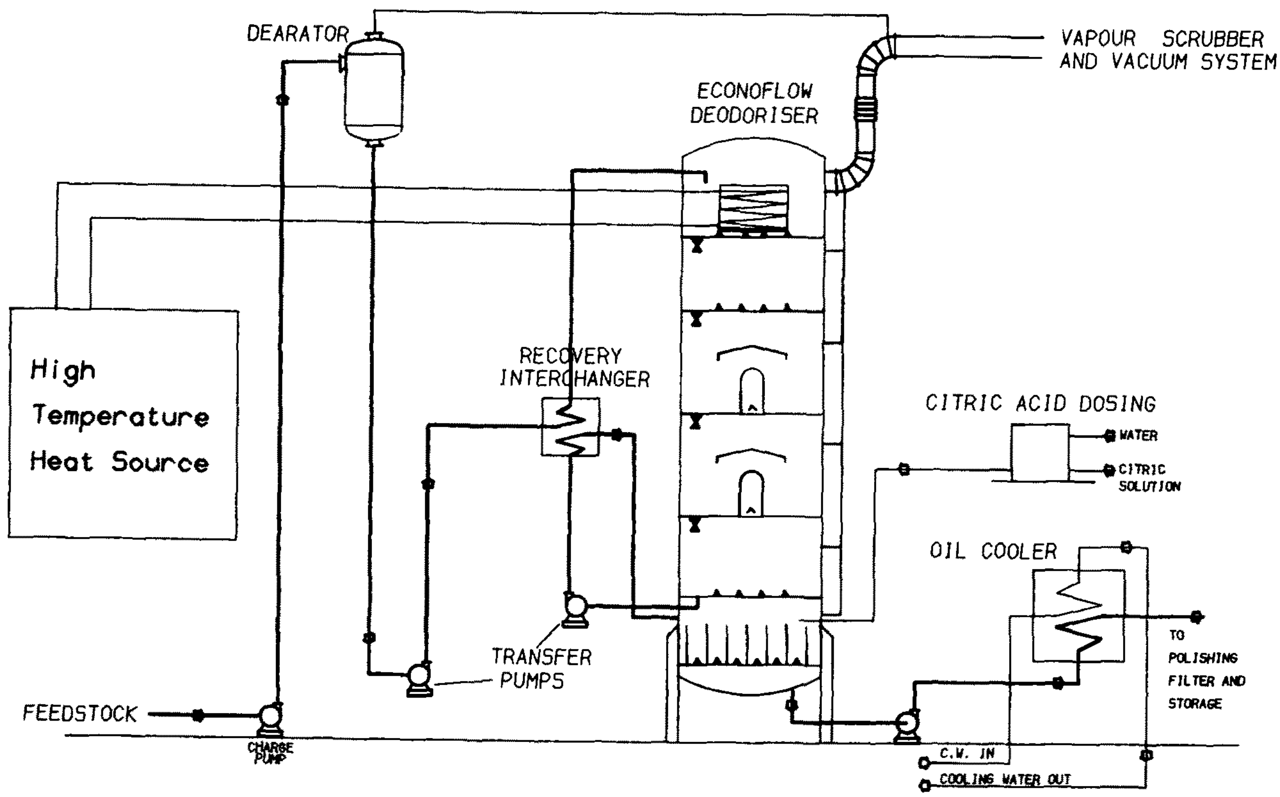

FIG. 7. Econoflow steam refining deodorizer.

TABLE I

Typical Analysis Log Maize Oil

	%FFA	%P	Color Y/R
Feedstock	5.24	0.033	40/4.4 (1")
Degummed		0.005	
Bleached	5.30	0.0012	36/4.2 (5¼")
Dewaxed		0.0011	35/4.0 (5¼")
Steam refined	0.03		34/2.5 (5¼")

Product PV = zero
Distilled fatty acids = 93.5% FFA

separated from the oil. The centrifuged oil is dried, subsequently bleached and passed on to the steam refining deodorization stage.

Soybean Oil Physical Refining

In order that a soybean oil may be successfully physically refined it is most important that it should be received as fresh as possible from the extraction plant. Storage of the oil in contact with atmospheric oxygen will cause oxidative damage and will ultimately reflect in the quality of the physically refined oil.

Soybean oil is available to most prospective refiners as crude degummed oil. That is, oil that has been partially degummed at the extraction plant. The NSPA give quality specifications (Table II) for commercial grade crude degummed soybean oil.

The NSPA quality specifications, however, give no indication of the oxidative state of the oil and are not totally adequate when considering an oil for physical refining.

Development work suggests a more detailed specification is necessary and incorporates an analytical description of the oxidative state of the oil (Table III) using extinction coefficient measurements.

Another important consideration often not controllable by the refiner is the quality of the soybean used in the extraction plant. Bean quality was discussed elsewhere in this conference and by J.T.L. Ong (4).

TABLE II

NSPA Standard for Crude Soybean Oil

FFA	0.750% maximum
Volatiles	0.200% maximum
Insolubles	0.100% maximum
Phosphorus	0.020% maximum
Sediment (Gardner)	0.100% maximum
Lovibond color	5R 5OY (1" cell)

TABLE III

Suggested Specification for Soybean Oil for Physical Refining

FFA	0.75%
Color	5R 5OY maximum
Anisidine value	1.5
Peroxide value	2.0
E232	2.5
E270	0.3
Iron content	2 ppm maximum
Phosphorus	200 ppm maximum

Pretreatment process. A flexible physical refining system for soybean oil comprises several stages:

- Addition of degumming agent to convert the nonhydratable phosphatides to a hydratable state.
- Phosphatide hydration and precipitation.
- Removal of hydrated phosphatides.
- Drying and addition of bleaching earth.
- Removal of bleaching earth.
- Steam refining/deodorization.

The two most commonly used degumming agents in stage 1 are phosphoric acid (as an 85% solution) and citric acid (as a 20% or 50% aqueous solution).

Phosphoric acid is readily soluble in soybean oil and it may efficiently be dispersed within the oil by the use of simple paddle mixers or in-line static mixers.

Citric acid, however, is much less soluble and its aqueous solution most be thoroughly mixed with the oil using high shear type mixers. The mixture should then be vacuum dried for optimum contact. It is necessary to allow a reaction time for the phosphatide conversion.

Phosphatide hydration in stage 2 is effected by the addition of water to the process stream after the reaction with phosphoric or citric acid.

There must be sufficient water to hydrate the phosphatides and also effectively to wash the oil of excess acid in the separation stage. The hydration and precipitation of the hydrated phosphatides is instantaneous and may be carried out in line to the centrifugal separator. Separation may be, however, improved by allowing time for the precipitated particles to agglomerate.

Further improvement to the separation may be achieved by the addition of floculating agents. The nature of these agents must be scrutinized with a view of toxicity, effective removal from the oil and in particular the effect on the process cost.

A study by Segers of Unilever (5) shows that if the temperature of the mixture of oil and hydrated phosphatides is reduced to below 40 C, the precipitated phosphatides assume a semicrystalline form. This form may be more effectively removed in the centrifugal separator.

It is also important that a continuous disc and bowl type centrifugal separator is used in stage 3. This gives the maximum removal of the phosphatides and minimizes the loss of degummed oil.

The temperature at the separator should be above 60 C, otherwise high oil losses may result. The oil drying, addition of bleaching earth and removal of spent earth is carried out in conventional bleaching, filtration equipment. The bleacher should have the facility to add citric acid to the oil before earth dosing as this assists in removal of trace phosphatides not removed in the previous stages. Steam refining/deodorization is typically done at 250-260 C, 3-5 torr with 1-3% sparge steam.

De Smet Engineering Process

Typical of the pretreatment systems being suggested to cover these essential stages is that proposed by De Smet Engineering of Belgium (Fig. 8).

The feedstock is first reacted with concentrated degumming agent under controlled temperature conditions. After reaction time allowance, the mixture is further treated with diluted degumming agent. Separation of precipitated material is done by centrifugation.

The centrifuged oil is then subjected to a dry pretreatment process using dilute acid and a bleaching earth treatment. The oil now reduced in phosphorous content to 2-4 ppm is sent to the steam refining stage.

Predegummed soybean oil containing 0.3-0.4% phosphatides and 0.8% FFA is said to produce a finished prod-

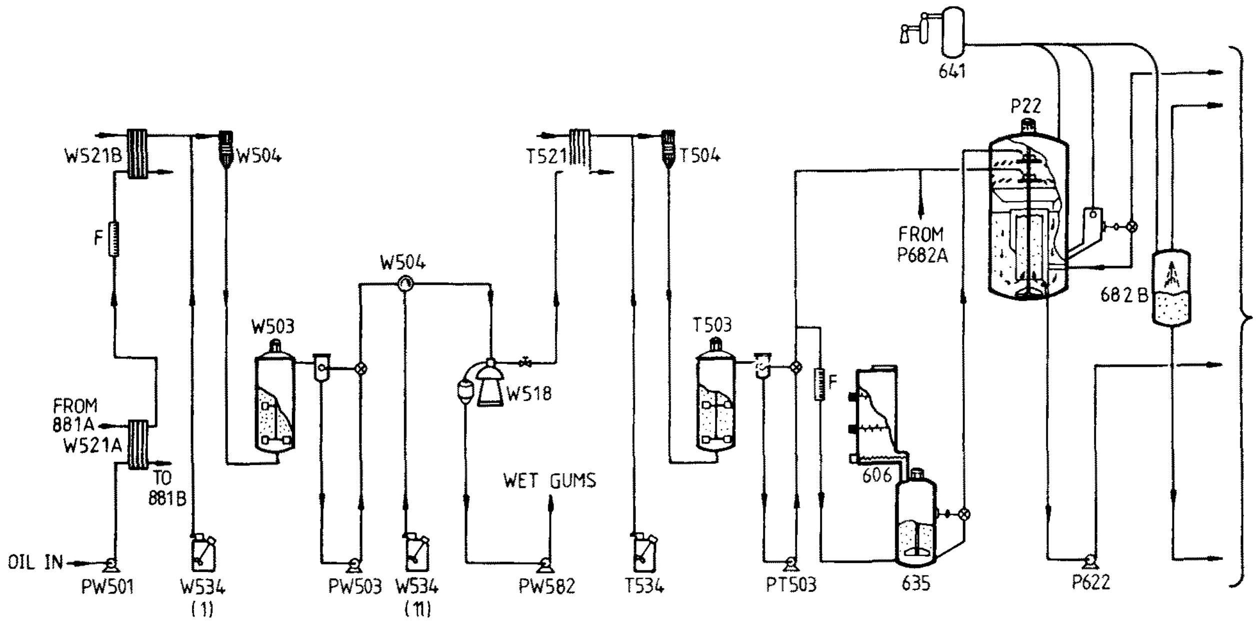

FIG. 8. De Smet process.

Acid degumming

W503	First degumming reactor
W504	Degumming contractors
W518	Degumming centrifuge
W521 B	Oil heater
W521 A	Oil-oil heat exchanger
W534	Dosing pumps for degumming agent

Dry pretreatment

T503	Second degumming reactor
T504	Degumming contractor
T521	Oil heater
T534	Dosing pump for degumming agent
P	Pumps
F	Flowmeter
V	Heating medium
S	Live steam

Bleaching filtration

603	Bleaching clay holding tank
606	Bleaching clay dosing device
622	Vacuum bleacher
635	Oil-clay mixer
641	Vacuum device
682 B	Filtered oil tank

uct of 14-15 hr AOM with acceptable color and FFA levels.

Recent Work

Recent work by Simon-Rosedowns has concentrated on using only one acid and one water addition. By varying operating conditions in respect of temperatures, pressures and addition rates the system will deal with varying qualities of feedstock.

The table of results in Table IV shows three trial runs using predegummed soybean oil commercially available in the UK. Steam refining/deodorization conditions were common to all trials, variations being limited to the pretreatment stage. Successes such as that in trial 1 have been consistently reproduced.

Two further results are included to show that pretreated oil with phosphorus content above 10 ppm could not, however, be steam refined to give acceptable quality products. Even though the AOM stability appears statisfactory the oils were below standard from considerations of flavor.

Bleaching earth usage at 1.5% is high and process economics would benefit from a reduction by improvements at the centrifuge separation stage. These improvements are possible based on concepts already mentioned.

Rapeseed/Canola

Another oil of increasing availability and importance is Canola. Some mention of the work on this oil is therefore of importance.

Older types of Canola contained 180-250 ppm of phosphorus and 98.5% of neutral oil. United Oilseeds Products Ltd. of Canada is now producing a 'special quality degummed Canola oil' (Table V).

Comparatively low phosphorus content oil is thus commercially available to the refiner. Lower pheophytin contents also assist the physical refiner in avoiding product color problems with this oil.

The new oil has been physically refined on a commercial scale dry pretreatment system using 0.07% phosphoric acid, 1.5-2.0% bleaching earth at 110 C, and steam refined at 260-270 C.

TABLE V

Canola Data[a]

Special quality degummed soy oil	
FFA	1.0% maximum
M + I	0.3%
Phosphorus	30 ppm maximum
Neutral oil	99%
Sulphur	5 ppm maximum
Pheophytin	10/20 ppm
Pretreatment/steam refining conditions	
Phosphoric acid	0.07%
Earth addition	1.5/2.0% at 110 C
Deodorizing conditions	260/270 C at 5 torr

[a]Courtesy of United Oilseeds Products Ltd., Canada.

The products were 97.4% refined, bleached and deodorized (RBD) with 1.3% distillate on an initial FFA of 0.72%. The product had an FFA of 0.028% and acceptable color and flavor characteristics.

The trial was relatively short and further work will optimize acid usage and reduce bleaching earth concentrations to give a viable process with acceptable product quality.

ACKNOWLEDGMENTS

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REFERENCES

1. Sullivan, F.E., JAOCS 53:358 (1976).
2. Lineberry, R.D., and F.A. Dudrow, U.K. Patent 1321299.
3. Forster, A., and H.J. Nel, Presentation at the AOCS/ISF Conference, New York, May 1980.
4. Ong, J.T.L., Fette Seifen, 4:169 (1980).
5. Segers, J., and H.J. Ringers, U.K. Patent 1541017.

TABLE IV

Recent Work—Soybean Oil Physical Refining

Crude analysis	FFA 0.3 PV 0.6	P 103 ppm Color 4R 30Y	AV 0.9	E 232 2.3 E 270 0.3

Pretreatment	Phosphorus content ppm	Physical refined oil: Deodorizer conditions	FFA	PV	AV	Color 5.1/4 Lovibond cell		AOM stability hr to PV 70	Acceptable flavor period (days)
0.1% H_3PO_4 4.5% H_2O 1.5% Tonsil Optimum bleach	2.0		0.05	0	1.1	3Y	0.6R	13	63
0.1% H_3PO_4 4.5% H_2O 1% Tonsil Optimum bleach	13	Temp 260 C Time 30 min % Steam 3% Pressure 3/5mmHg	0.03	0	1.4	6.5Y	1.2R	13	17
0.4% H_3PO_4 2% Tonsil Optimum bleach	26		0.05	0	0.7	4.0Y	0.6R	13	13