♣Modeling the Solvent Extraction of Oilseeds[1]

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A computer model and an experimental procedure for generating data needed in the model have been developed for the oilseed extraction process. The experiments are relatively simple and are performed with a bench-top extractor. Experimental results and modeling calculations are presented for the extraction of cottonseed using hexane, isopropanol and ethanol. The calculations show that in an alcohol extraction using a chill separation, isopropanol's greater oil miscibility allows for a lower solvent-to-feed ratio than does ethanol. Using the latter solvent, however, achieves lower residual lipids in the extracted meal because recycled ethanol contains less oil than recycled isopropanol.

Solvent extraction of oilseeds accounts for over 90% of the vegetable oil produced in the U.S. In recent years there has been considerable interest in both industry and government in a suitable replacement for hexane, the solvent currently used (1-5). At present, ethyl and isopropanol (6) appear to be the most likely candidates. Hron et al. are developing a process that uses ethanol in the solvent extraction of cottonseed (7,8). Scaling up the process from the laboratory to a pilot plant facility, formerly used for hexane extraction, required changes in the existing physical facilities and in operating conditions. To assure proper sizing of new equipment and as a guide in the selection of operating conditions, a computer model of the extraction process was developed. This paper describes that model. The results of laboratory experiments performed to generate the input data needed for the model also are presented. In its present form, this model is a useful tool for providing the kind of information mentioned above. It can also be used to make economic comparisons among alternate processing conditions and strategies. Such a study is currently underway. However, more experimental data are needed if the model is to be used in the design of new commercial extraction facilities, as an expert computer system for the day-to-day management of an existing oil mill, or for incorporation in an automatic computer control system.

STRUCTURE OF MODEL

The model, written in FORTRAN, uses a Gaussian elimination to solve a set of material balance and equilibrium equations. The flow rates and concentrations of solids, solvent and oil in all streams entering and leaving each unit are calculated. Within the extraction unit there is a stage-to-stage calculation where one of two values is computed, depending on what is to be accomplished with the model. If an existing extractor is to be modeled, then the number

of stages is known. The number is put into the model and the residual lipids in the flakes extracted by that number of stages are calculated. If, on the other hand, an extractor is to be designed to achieve a particular residual lipid value, then this residual lipid value is put into the model and the number of stages required to achieve this value is calculated. While the analyses of both deep bed and shallow bed extractors are similar, this study focuses on the mathematically simpler shallow bed extractor (9). In summary, as input to the model the following quantities are needed:

- The mass flow rate of feed flakes.
- The lipid and moisture content of feed flakes.
- Miscella/solids equilibrium data.
- The number of extractor stages or desired residual lipids in extracted flakes.

For an alcoholic extraction the following input also is needed:

- Oil/ethanol solubility data at the extractor and separator temperatures.
- The percent solids in the marc leaving the press.

The output from the model contains the following:

- The mass flow rate of solids, solvent and oil in all streams.
- The residual lipids in the extracted flakes or the number of extractor stages.

MATERIAL BALANCES AND EQUILIBRIUM EQUATIONS

There are typically two types of equations needed in the modeling of a process: material balance equations and equilibrium equations. To model its function, every unit or piece of equipment in the process will need one or more material balances and, depending on the nature of the unit, one or more equilibrium equations. Consider, for example, the surge tank shown on Figure 1. For an alcohol extraction there are three streams entering the tank and one stream leaving. The function of this tank is to collect the incoming material and provide a single output stream to the extractor. Two material balances are needed to fully describe this operation:

> Sum of mass flow rates of
> oil in incoming streams –
> Mass flow rate of
> oil in outgoing stream = 0

> Sum of mass flow rates of
> solvent in incoming streams –
> Mass flow rate of
> solvent in outgoing stream = 0

Now consider the chill separation used in the alcohol extraction process. Once the miscella leaves the extractor it is cooled to about 5 C. Two phases are formed, a heavy phase consisting of mostly oil and gums with about 15% ethanol and a light phase consisting of ethanol with about 3% oil. These two phases are then separated by centrifugation. Four equations are needed to describe this operation. In addition to material balances, similar to the previous two equations, two equilibrium equations are also needed:

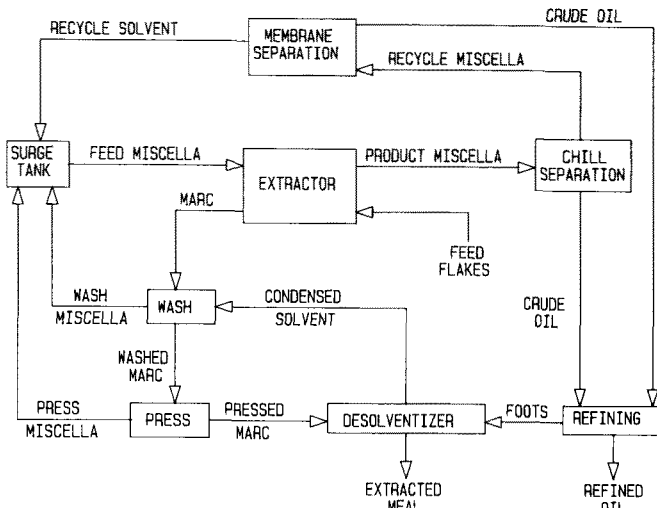*To whom correspondence should be addressed.

FIG. 1. Detailed schematic of ethanol extraction process.

The mass flow rate of oil in the light phase/
the total mass flow rate of the light phase = F(T)

The mass flow rate of oil in the heavy phase/
the total mass flow rate of the heavy phase = G(T)

Where F(T) and G(T) represent functions of temperature which, for ethanol at 5 C, are equal to 0.03 and 0.85, respectively. There are two more types of equilibrium equations associated with the streams containing flakes. To understand these equations it is helpful to consider what occurs when the solvent comes in contact with the flakes. If oilseed flakes are completely wetted with a solvent and allowed to drain, a plot of the weight of solvent and oil on the flakes per weight of insoluble solids (M/I) versus drain time could be obtained as shown in Figure 2. Initially, the
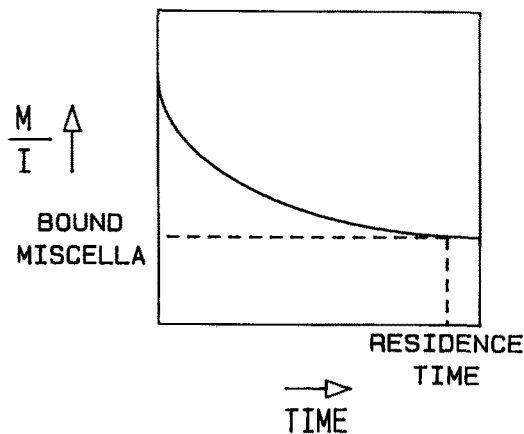

FIG. 2. Ratio of weight of miscella on flakes (M) to weight of inert solids (I) versus drain time.

miscella drains rapidly. As time increases, the draining slows and eventually M/I reaches a constant value. The remaining oil and solvent are either bound within the cells of the flakes are bound to the surface of the flakes. The time to reach a constant value can be considered a residence time for an extraction in a given stage because it is the time it takes free miscella at the top of the bed to drain through to the bottom of the bed. For the shallow bed extractor, residence time should therefore correspond to the time it takes the bed to travel from one spray to the next.

It is possible that different oil concentrations in the miscella cause changes in the binding forces such that the constant or final value of M/I discussed above changes. To calculate the number of stages necessary to achieve a desired residual lipids content or to calculate the residual lipids for a given number of stages it is necessary to know the final value of M/I as a function of the total concentration of oil bound to the flakes (xF). Further, it is necessary to know xF as a function of the concentration of oil in the miscella drained from the flakes (xS). There are at least two reasons why the values for xF and xS are not the same. If the flakes exert a preferential adsorption for either the oil or solvent, then xF will differ from xS. Second, if the oil is only partially miscible in the solvent then the oil and solvent bound to the flakes consist of two phases, a homogeneous oil-solvent phase and an undissolved oil phase. Since xF refers to the total concentration of oil in both of these phases taken together it differs from xS, which refers only to a homogeneous phase. This last point is expanded upon when the experimental results are discussed, later in this study. The details of how these equilibrium relationships are used in the stage calculation will not be discussed here because this topic is discussed elsewhere (10). The two phenomena just discussed, that is, the amount of miscella bound to the flakes after extraction versus the concentration of oil in that miscella and the concentration of oil in the drained miscella versus the concentraton of oil in the miscella bound to the flakes, give the two equilibrium equations needed for the streams containing flakes.

To summarize, several kinds of equilibrium information are needed to model the solvent extraction process:
• The weight of miscella bound to the flakes per unit weight of solid as a function of the concentration of oil in the bound miscella.
• The concentration of oil in the drained miscella versus the concentration of oil in the bound miscella.

Further, if the oil is only partially miscible in the solvent, as is the case with ethanol and isopropanol, then the following solubility data must be known:
• The maximum solubility of oil in solvent at the extraction temperature.
• The maximum solubility of oil in solvent at the cooling temperature.
• The maximum solubility of solvent in oil at the cooling temperature.

There is, at present, no reliable theoretical method for obtaining the above information. It must be determined experimentally (11).

EXPERIMENTAL

Although the major thrust of this study was to model an ethanol extraction process, equilibrium data was obtained for hexane and isopropanol as well as ethanol. The solvents used in the experiments were commercial grade. Mississippi cottonseed was used. It was dehulled, flaked to about 0.03 cm (0.01 inch), and dried to about 2% moisture in an oilseed extraction pilot plant facility. Drying the flakes is necessary in an alcohol extraction so that the solvent does not pick up moisture and reduce its miscibility with oil (12).

Oil-ethanol solubility. A given vegetable oil can have various fatty acid arrangements in the triglyceride. It can also have different amounts of free fatty acids and other nontriglyceride components, depending on the method of extraction. This variability affects its solubility in various solvents. To determine the oil/ethanol solubility for cottonseed oil in an ethanol extraction process the following experiments were performed at different temperatures: A benchtop extractor (Fig. 3) was charged with 350 g of full fat cottonseed flakes, dried to about 3% moisture, and 500 g of 95% aqueous ethanol. The extractor, 30 cm long and 10 cm in diameter, was made of stainless steel and was jacketed. Water from a circulating constant temperature bath was used as the heating medium. The top of the extractor was covered with a metal plate and gasket to keep the system vapor tight. The solvent was circulated through the extractor for 30 min while the system was kept at the desired temperature. A peristaltic pump was used for solvent circulation. At the end of the extraction time, the miscella was drained and the extracted flakes were removed. The extractor was then recharged with another 350 g of full fat flakes, and the previously drained miscella was added and circulated for another 30 min. This procedure was then repeated a third time to assure that the miscella contained the most oil
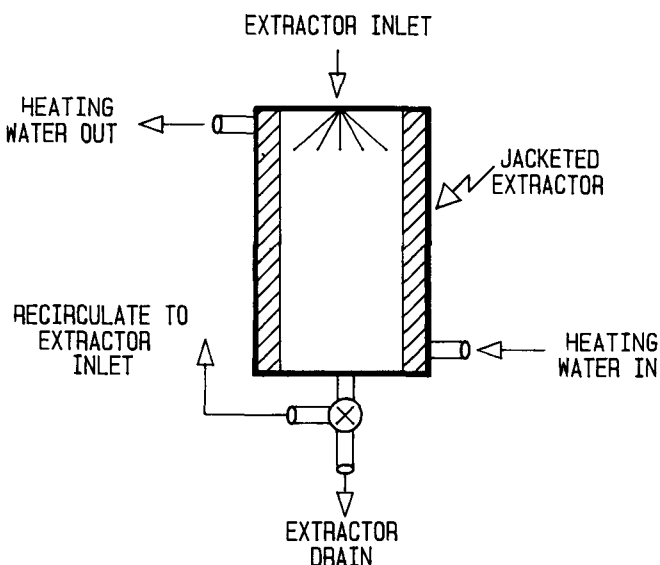

EXTRACTOR INLET

HEATING WATER OUT

JACKETED EXTRACTOR

RECIRCULATE TO EXTRACTOR INLET

HEATING WATER IN

EXTRACTOR DRAIN

FIG. 3. Benchtop extractor used to determine equilibrium relationships.

possible at the given temperature. Further extractions did not increase the oil concentration in the miscella. After the third extraction, the drained miscella was weighed, desolventized in a rotary vacuum evaporator and the weight of the remaining oil found. In order to determine the amount of petroleum ether solubles contained in the oil it was necessary to redissolve the desolventized oil in petroleum ether and filter out and weigh any insoluble material. The percent petroleum ether solubles can then be calculated, and it is this quantity that is used for oil solubility. To determine solubilities at the chilling temperatures, the oil was extracted at 75 C and cooled to the desired temperature, thus forming two phases. The solubilities in both phases are then determined as previously described.

Oil-flake equilibrium. The other required data for the model, as was discussed earlier, are information relating both the amount of miscella bound to the flakes after draining and concentrations of oil in drained miscella versus concentrations of oil in bound miscella. These data were obtained using the bench extractor discussed above. After heating the extractor to the desired operating temperature for a given solvent, it was charged with 350 g of flakes. Heated solvent (600 g) was then added and circulated through the flakes for 30 min. A sparger was used at the inlet to provide an even distribution of solvent over the flake bed. At the end of the extraction period the miscella was drained from the extractor. After draining, the flakes were removed from the extractor and immediately weighed. This was done quickly and with little exposure of the wet flakes to the atmosphere so that solvent vaporization was minimized. The flakes were air desolventized for about 12 hr and then in a forced draft oven for 2 hr at 101 C. After desolventization the flakes were reweighed to determine their solvent content immediately after draining. A modified AOCS residual lipid analysis was performed on these flakes and, using this value along with the weight of solvent, two desired quantities were then calculated: the weight of miscella bound to the flakes per unit weight of solids and the concentration of oil in the bound miscella. The concentration of oil in the drained miscella was determined as described previously for the solubility experiments. To obtain the quantities just calculated for a different oil concentration of the bound miscella the experiment described above was changed slightly. After the miscella was drained from the flakes it was discarded and a second batch of fresh solvent was added to the flakes. This new solvent was also circulated through the flake bed for 30 min. The rest of the experiment and the analysis were the same as described for the single charge of solvent. The oil concentrations for both drained and bound miscella were lower when two charges of fresh solvent were used than when a single charge was used. Three or more charges were used to obtain equilibrium data at still lower oil concentrations. Hexane, 91% isopropanol and 95% ethanol were used as solvents. The extraction temperatures were 60 C for hexane, 78 C for isopropyl and 75 C for ethanol.

Drain times. A final set of experiments was performed to determine the length of time needed to

drain a flake bed saturated with miscella which, as discussed earlier, corresponds to the residence time in an extraction stage. The extractor was charged with flakes to a height of 10 cm, and ethanol was circulated through it for 30 min. It was then allowed to drain for 1 min. The flakes were removed and the weight of miscella remaining on the flakes per unit weight of solids was determined. The reactor was then recharged and the above experiment was repeated except that the drain time was increased to 2 min. This experiment was performed repeatedly for drain times up to 7 min. In order to determine the drain time as a function of bed height, two more sets of experiments were then performed in a manner similar to the above except that the extractor was charged with 18- and 25-cm-high flake beds.

RESULTS AND DISCUSSION

Solubilities. At its boiling point, 78 C, 95% ethanol has a 12% oil solubility. At 75 C, a realistic operating temperature, the solubility is 10%. The 12% solubility of cottonseed oil in 95% aqueous ethanol, measured in this work, is greater than previously reported values (13,14). These other studies, however, have used expeller-produced crude oil or commercially refined oil in their determinations whereas in this study ethanol-extracted crude oil was used. Apparently, some of the nontriglyceride components extracted by

the ethanol are also soluble in petroleum ether. At 5 C the solubility of oil in the lighter phase in 3%. The heavier phase contains 85% oil. Decreasing the temperature below 5 C does not appreciably affect the solubility.

Equilibrium curves. The results of the equilibrium experiments are shown in Figures 4 and 5. Data points clustered together are results of the repetition of one-charge, two-charge and three-charge experiments. In the ethanol extractions four- and five-charge experiments also were performed. For each solvent at least five repetitive experiments were performed for each number of charges. Some of the data points overlap on the plots because several of the repetitions produced very close results. In Figure 4, as the oil concentrations increase, the slope of the line on the drained miscella versus bound miscella curve for ethanol is greater than that for the isopropanol curve which in turn is greater than that for the hexane curve which has a constant slope of 1. This behavior can be explained by considering that on a molecular level there is a driving force, or potential, which causes the oil to dissolve in the solvent. If the oil is only partially miscible in the solvent, then this force decreases as the concentration of oil in the solvent increases and goes to zero at the saturation concentration. Since isopropanol has a greater saturation
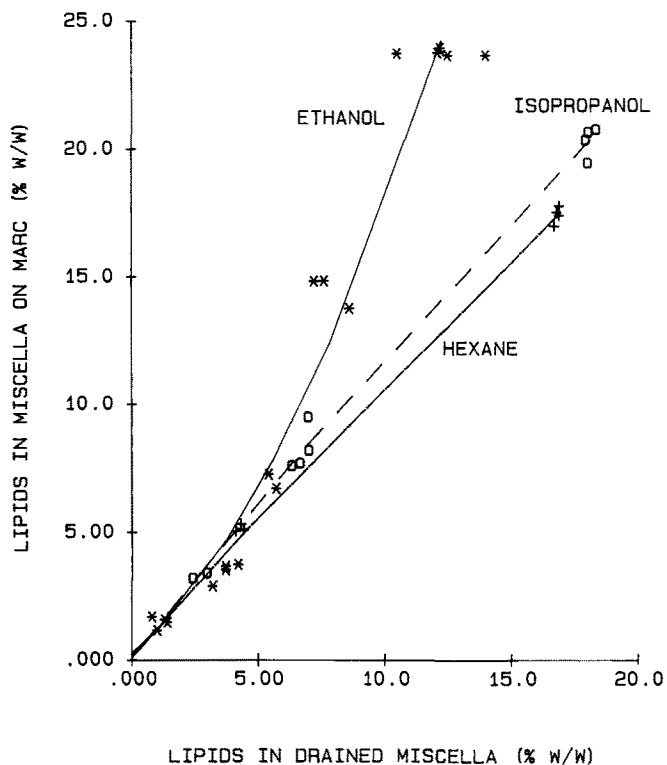
FIG. 4. Experimentally determined values for the lipid concentration of the miscella remaining on the marc after draining versus the lipid concentration of the drained miscella.
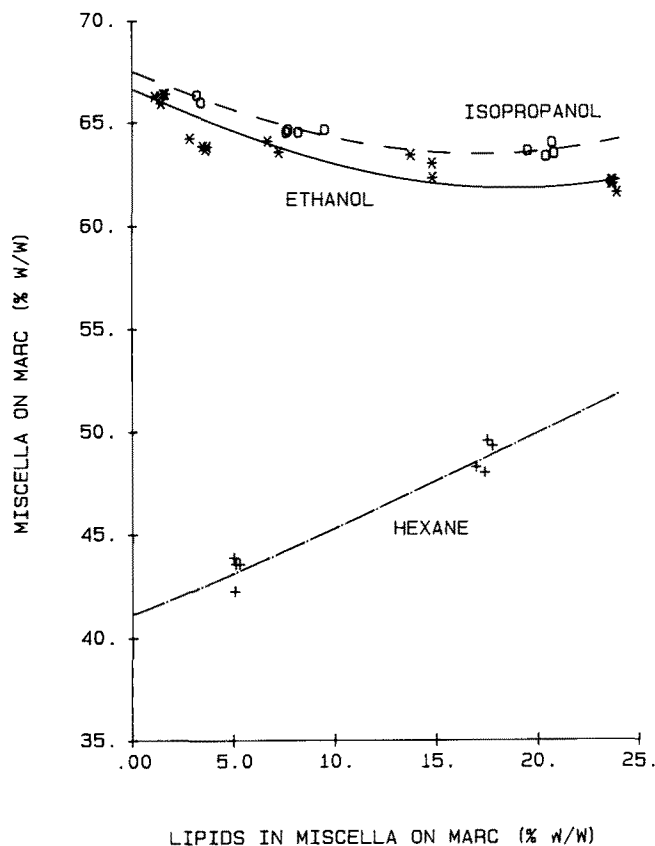
FIG. 5. Experimentally determined values for the weight percent of miscella on the marc after draining versus the lipid concentration of that miscella.

concentration than ethanol, its driving force decreases more slowly than ethanol over the same concentration range. Because hexane is completely miscible with oil, its driving force is not a function of concentration. In an alcohol extraction, due to a reduction in the driving force, the miscella bound to the flakes after draining consists of two parts, the alcohol with dissolved oil and the unextracted oil. It is not necessary to consider the unextracted oil and actual bound miscella as two distinct species, but rather to treat them as a bound miscella having an oil concentration greater than saturation (7). For example, at a concentration of 12% in the drained ethanol miscella, the saturation point at the temperature of the experiment, the bound miscella contains 24% oil. Further, when the concentration of oil in the drained ethanol miscella is 8%, the bound miscella concentration is 14%. This shows that even though the drained miscella is not saturated there is still unextracted oil in the flakes because the concentration of 14% is greater than the saturation concentration of 12%. It is not until the drained miscella contains less than about 5% oil that the bound and drained concentrations are approximately equal. Figure 5 shows the amount of miscella left on the flakes as a function of the amount of oil in that miscella. The percentages are calculated on a weight basis. It is interesting to note that as the percentage of oil in the miscella on the marc increases, the amount of miscella bound to the marc increases when hexane is the solvent but decreases when alcohol is the solvent. This pattern remains when the percentages are calculated on a volume basis. A possible explanation for this is that the more oil there is in a hexane miscella the more viscous the liquid becomes and the less it drains. The alcohols, on the other hand, are more polar than hexane and have a greater affinity for the flakes. The addition of oil to the alcohol reduces the polarity of the liquid and facilitates draining.

Drain curve. The results of the ethanol draining experiments are shown in Figure 6. The points shown represent the time it took flakes to drain free miscella at each bed height. Draining for longer periods than shown did not decrease the ratio of bound miscella to solids. As discussed earlier, these times represent the optimum residence time in each stage. For example, if the bed depth is 25 cm then it takes about 6.5 min to drain the bed. Consequently, if the solvent spraying heads are, say, 130 cm apart, then the bed speed through the extractor should be 20 cm/min. It is important to note that the bed should not be allowed to become dry and should be operated at near flooding conditions.

Examples of modeling calculations. Using the above laboratory data as input to the computer model, various parameters of a pilot or commercial scale extraction operation can be computed. Figure 7 shows the calculated minimum solvent-to-feed ratio for the three solvents considered in this study. It ranges from a value of 1 in hexane to almost 4 in ethanol, the least miscible of the three. These results are for a chill separation of the alcohol solvents and an evaporative separation of hexane. For the alcohol solvents, this factor is a function of both the concentration of oil in the fresh miscella and the solubility of oil in the alcohol at the extraction temperature. That is, at this
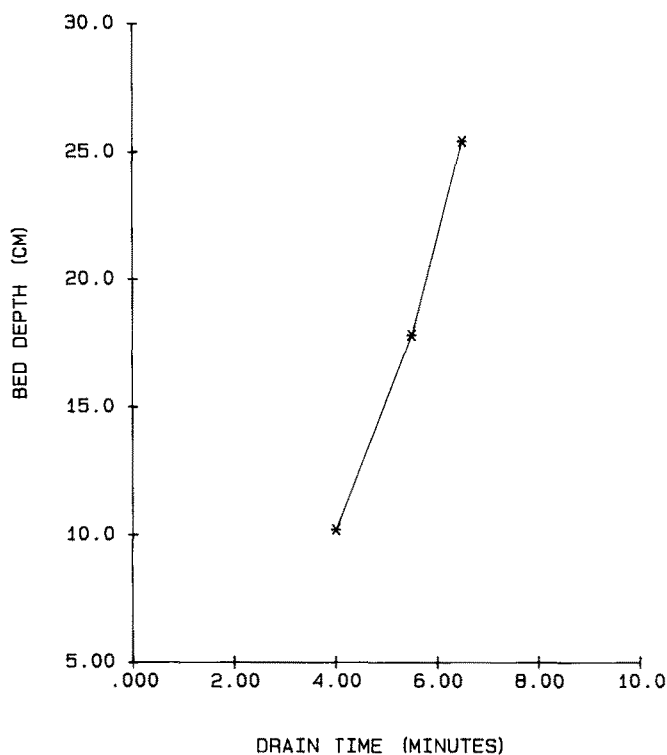
FIG. 6. Experimentally determined time needed to drain the free miscella from a bed of flakes for three different bed heights.
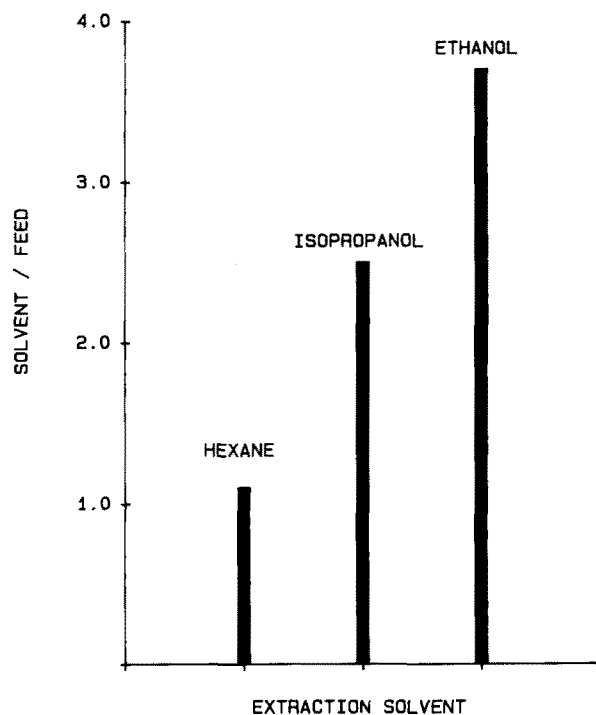
FIG. 7. Model calculation of the solvent to feed ratios for the three solvents considered in this study.

ratio the miscella in the flakes leaving the extractor has the same oil concentration as the fresh miscella entering the extractor. Consequently, an increase in this ratio has no effect on the residual lipids which are greater than 1% for both alcohol solvents under these conditions. Since hexane is completely miscible with oil, its solvent-to-feed ratio is governed by the desired residual lipids, which is 1% for this case. Figure 8 shows the percent residual lipids remaining in the extracted flakes after desolventization as a function of the number of stages in the extractor. These results are with pressing the marc in the alcohol extractions. Hexane requires seven stages to reach the minimum residual lipids. Ethyl and isopropanol require eight stages to reach minimums. Notice that because isopropyl has a greater oil solubility, 6% at 5 C, than ethanol, 3% at 5 C, the recyle stream in the isopropyl process will have a higher concentration of oil and hence leave more oil in the extracted flakes. Figure 9 shows the pounds of solvent in the flakes stream entering the desolventizer. The load on the desolventizer is significantly increased with the alcohol solvents. Even when the marc is pressed, there is about 25% more alcohol going to the desolventizer than there would be in a hexane extraction. Further, because the alcohols are less volatile than hexane, this increased load represents a large energy increase. Karnofsky (15) has pointed out the many difficulties in the desolventization of water miscible solvents. This operation has received little attention in studies on alcohol extractions. However, it is
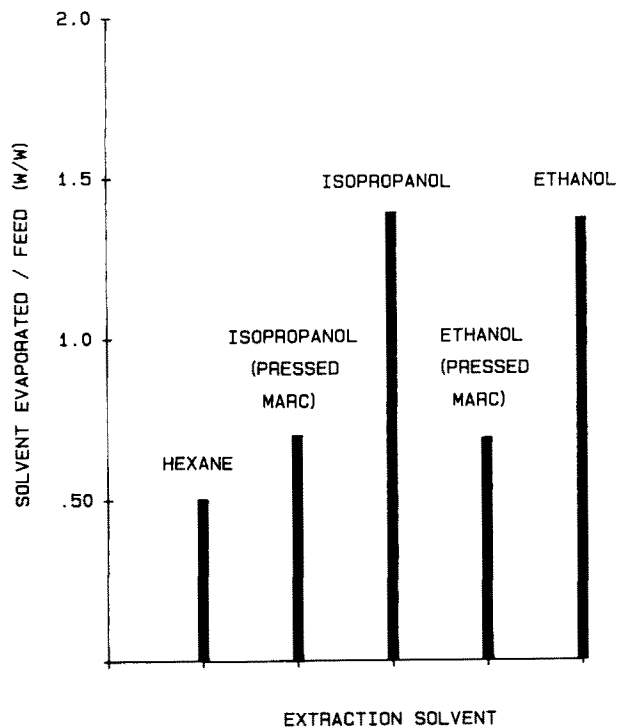

FIG. 9. Model calculation of the solvent load on the desolventizer.
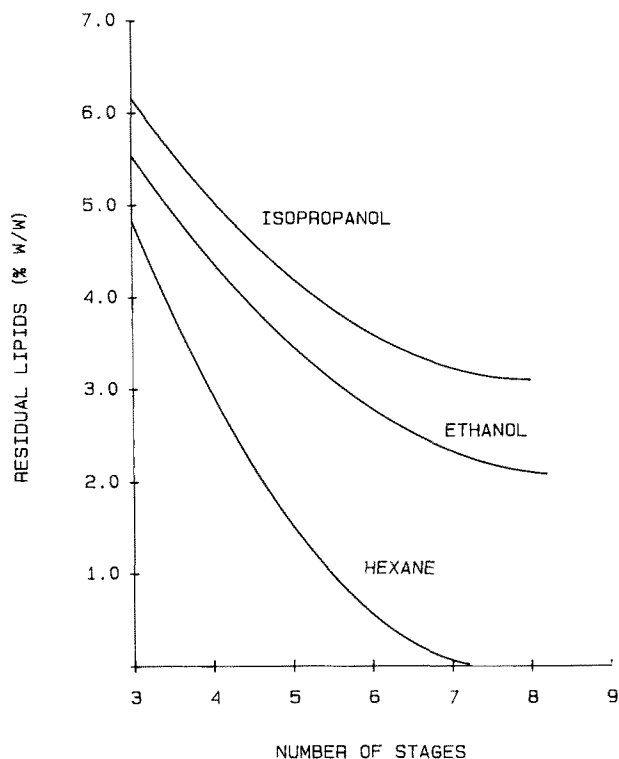

FIG. 8. Model calculation of the percent residual lipids in the extracted flakes versus the number of extraction stages.
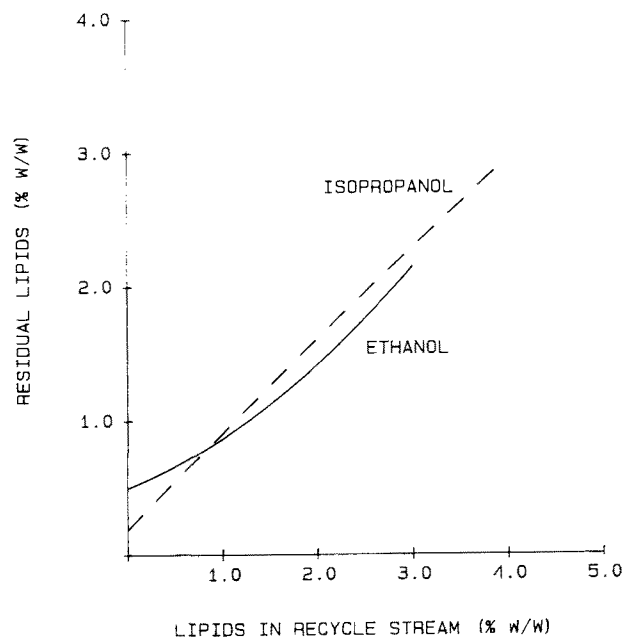

FIG. 10. Model calculation showing the effect of supplemental oil removal on the percent residual lipids.

potentially the most troublesome in achieving commercialization with one of these alternate solvents. It is interesting to consider the effects on residual lipids if the amount of oil in the recycle alcohol streams is reduced to a lower value than is possible with chilling. This can be done with distillation or with a membrane process (Fig. 1). The results of the calculations are shown in Figure 10. It is apparent that for both ethanol and ispropanol the results show that, even with pressing, there must be less than 1% oil in the recycle stream if there is to be less than 1% residual lipids in the extracted flakes.

Mathematical model uses. A mathematical model of a physical process has a variety of uses. Researchers at the SRRC have used the extraction model discussed here in modifying a hexane extraction pilot plant for use as an ethanol extraction plant. It is also an aid in understanding the process and in pointing out areas of difficulty that need more research, such as in desolventization. Cost studies and economic comparisons of alternate process schemes are greatly facilitated by this kind of model. It can also be incorporated in an expert system for use in the day to day operations of an oil mill. Such an expert system would assure uniform operation of the plant and would be an important aid to inexperienced operators. In a more advanced form a process model can be used in automatic computer control. The potential down-stream effects of an upstream disturbance can be predicted and corrected, a definite improvement over standard feedback control.

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