Empirical Modeling of Soybean Oil Hydrogenation[1]

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ABSTRACT

Empirical hydrogenation models were generated from statistically designed laboratory experiments. These models, consisting of a set of polynomial equations, relate the operating variables of soybean oil hydrogenation to properties of the reaction and of the fat produced. These properties include reaction rate, *trans*-isomer content and melting point. Operating variables included in the models were temperature, hydrogen pressure, catalyst concentration, agitation rate and iodine value.

The effects of catalyst concentration and agitation rate were found to be significant in determining *trans*-isomer content, which in turn influences the melting characteristics of the hydrogenated oil. Pressures above 30 psig were found to have little effect on *trans*-isomer content, although pressure was very important in determining reaction rate. Reaction temperature was observed as the most important factor in determining the *trans*-isomer content for a given iodine value. Generally, 50 to 60% *trans* isomer content is predicted by the model for the iodine value range and operating conditions used in this study. Thus, these predictive models can assist in scaling up hydrogenation processes and in determining the optimum operating parameters for running commercial hydrogenation.

INTRODUCTION

Several different methods have been reported for modeling the complex series of reactions that occur during vegetable oil hydrogenation. Such modeling can have several possible uses, for example, in scale-up, in process control and in process optimization. Most models reported in the literature have been kinetic models based on simplified reaction schemes (1-4). These models are reasonably successful for specific reactors but generally are unable to account for the mass transfer differences between reactors.

Some researchers (5) have created models that partially overcome this limitation by including terms that relate the hydrogen transfer to the liquid. Other researchers, such as Bern et al. (6), have approached the task of predicting reaction parameters by using empirical equations that account for mass-transfer rates. Chen et al. (7) proposed a power-series model to predict reaction selectivity. Such a model can be used for scale-up purposes when certain terms relating to power input and mass-transfer characteristics are calculated.

Another class of models includes empirical equations based on direct experimental data. Dutton et al. (8) produced plots relating reaction rate, selectivity and *trans*-isomer content to reaction variables. Allen and Covey (9) likewise developed a *trans*-content model predicting the effects of temperature, pressure and catalyst concentration. These models are limited for scale-up or optimization, principally because they predict values only for oils of a fixed iodine value. A means to relate the models to other reactors and to cover a wider iodine-value range would greatly improve this type of model.

The present work introduces empirical models for hydrogenation that incorporate the major operating variables along with a term relating to the mass-transfer characteristics of the reactor. The responses modeled were chosen to provide improved indicators for reaction control and hence control of fat-product characteristics. Reaction rate, selectivity, *trans*-isomer content and melting point serve to define both the reaction and the product formed when iodine value (i.e., degree of hydrogen addition) is considered as an independent variable. The result is a model that systematically describes the process of oil hydrogenation by prediction of reaction behavior and of fat quality.

EXPERIMENTAL

To develop the models for soybean oil hydrogenation, a Box-Behnken response-surface design was chosen with five independent variables: reaction temperature, hydrogen pressure, catalyst concentration (as a weight percent), agitation (as measured by stirrer rpm), and the extent of unsaturation (as measured by iodine value). The reaction variables were varied systematically over the course of a randomized set of 46 hydrogenations. The equations were developed to predict reaction responses for variables that fall within the ranges defined by the parameter values.

All reactions were conducted in a two-liter Parr pressure reactor. After introduction of 1300 g of refined and bleached soybean oil (Table I) plus the catalyst (20% nickel in saturated soybean oil flakes), the reactor was sealed. The vessel was evacuated during the heat-up cycle and then the stirrer turned off during the introduction of hydrogen to the headspace. Reaction was initiated when the stirrer was restarted. Hydrogenation progress was monitored by measurement of the hydrogen pressure drop in a supply tank. At the completion of each reaction the hydrogen was withdrawn and the oil cooled to 80 C. After filtration, the hydrogenated oil was analyzed by AOCS standard methods; the analytical results are given in Table II.

The responses to be predicted—the dependent variables—are reaction time, overall reaction rate, selectivity of reaction, *trans*-isomer content and Wiley melting point. Least-squares regression techniques were used to generate a series of polynomial equations that predict the responses based on the values of the five variables (10). The variables were transformed to a common statistical scale of −1 to +1 so that the coefficients for each term in the model equations give the relative magnitude of the effect of that term. Using coded values, as (actual value-median value)/(1/2 range), in the statistical calculations also greatly simplifies model development and evaluation.

RESULTS AND DISCUSSION

The results from the statistical modeling were a series of equations that empirically predict responses. The model for reaction rate (IV/min), given below, fits the experimental

TABLE I

Soybean Oil Analysis Data

Iodine value	131.7
Peroxide value	1.9 meq/kg
Free fatty acid	0.04%
Moisture	0.03%
Soap	2.4 ppm
Unsaponifiables	0.53%
Trans isomers	3.5%
Fatty acid composition:	
C18:3	8.7%
C18:2	54.2%
C18:1	20.7%
C18:0	3.3%

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TABLE II

Hydrogenation Experimental Data

Expt'l. order	Temp. C	Pressure (psig)	Catalyst conc. (wt %)	Agitation (rpm)	Wijs IV	Overall		% *Trans* isomers	Wiley melting point	Diene selectivity (SD)
						Rate (IV/min)	Time (min)			
1	171	27.5	0.55	600	67.2	0.79	80.4	54.7	106	31.5
2	171	27.5	0.1	600	78.6	0.61	88.7	43	88.7	126.7
3	171	27.5	0.55	600	67.6	0.8	79.7	55.2	106.5	18.1
4	171	27.5	0.55	600	68.4	0.8	79.7	48.9	105.4	33.6
5	171	27.5	0.55	400	77.8	0.23	238.5	46.1	89.6	415
6	171	27.5	0.1	600	57.4	0.46	159.5	45.9	117.9	26.3
7	138	50	0.55	600	67.3	0.59	108	43.7	106.2	16.1
8	171	5	0.55	600	77.4	0.32	167.8	45.6	89.6	195.2
9	204	5	0.55	600	66.7	0.44	145.5	59.6	109.9	17
10	171	27.5	1	600	78.3	0.97	55.2	43.3	98.8	37
11	171	27.5	0.1	800	67.8	1.23	51.8	47.5	106.3	79.4
12	171	50	1	600	67.7	1.43	44.7	55	107.2	23
13	171	27.5	0.55	800	78.6	2.08	26	40.8	90.3	118
14	171	27.5	1	400	67.3	0.22	285	58.2	109.4	26
15	204	27.5	0.55	800	68.2	3.13	20.4	59	106.2	20.5
16	171	27.5	0.55	600	68.3	0.72	88	52.8	104.4	29.1
17	171	27.5	0.1	400	66.8	0.12	523	51.3	105.4	82.3
18	171	27.5	1	800	67.9	2.11	30.3	53.1	106.7	31
19	171	50	0.55	400	67.2	0.25	258	58.3	107.6	29
20	204	27.5	1	600	67.7	0.91	70	57.9	106.2	25
21	171	5	1	600	67	0.34	185	58.8	107.2	31
22	138	27.5	0.55	600	56.2	0.3	243.2	46.5	119.5	8.7
23	138	27.5	1	600	67.5	0.36	179.3	44.6	105.4	16.4
24	204	27.5	0.55	400	57.4	0.31	236.1	53.7	120.9	11.7
25	171	5	0.55	800	68.6	0.7	91	56.9	104.4	36
26	171	50	0.55	600	59.6	1.06	69.4	50.8	116.6	14.5
27	204	27.5	0.55	600	77.4	1.45	37	47.5	91.8	57
28	171	50	0.55	800	68	3.11	20.5	51.9	104.5	31.4
29	204	27.5	0.1	600	66.9	0.88	72.7	54.5	105.5	66.9
30	138	27.5	0.55	800	67.6	1.09	58.4	40.3	108.7	15
31	171	50	0.1	600	67.8	0.89	71.5	48.6	104.5	72
32	171	50	0.55	600	78.4	1.2	44.7	41.7	89.6	45
33	171	27.5	0.55	800	57.5	1.76	41.9	51.3	121.1	12
34	171	27.5	0.55	400	56.8	0.17	423	49.6	120.6	13
35	171	27.5	0.55	600	67.7	0.75	85.2	53.6	107.2	77.9
36	204	50	0.55	600	67.9	2.39	26.7	57.9	106.2	21.7
37	171	5	0.55	600	57.2	0.28	265	51.2	120.7	13
38	204	27.5	0.55	600	57	1.21	60.7	51.8	121.3	11.4
39	138	27.5	0.55	400	67.8	0.09	733	52.6	104	19.9
40	138	5	0.55	600	67.7	0.13	504	49.3	106.2	23
41	171	27.5	0.55	600	67.8	0.73	86.8	54.6	105.1	88.1
42	171	5	0.1	600	67.6	0.17	369.9	50.5	104.4	55.8
43	171	5	0.55	400	68.8	0.07	971	60.8	105.4	23.6
44	138	27.5	0.1	600	67.7	0.2	323	42.5	104	16.4
45	138	27.5	0.55	600	78.5	0.39	138	37.8	92.1	41
46	171	27.5	1	600	57.8	0.77	95.1	52.2	121.1	13.1

data well and is typical of the kind of results obtained in this study.

$$\text{RATE} = .803 + .477(\text{T}) + .528(\text{P}) + .159(\text{C}) + .854(\text{A})$$

$$+ .062\ (\text{IV}) + .370(\text{T})\ (\text{P}) + .438(\text{T})\ (\text{A})$$

$$+ .556(\text{P})\ (\text{A}) + .196(\text{C})\ (\text{A}) - .141(\text{C})^2$$

$$\text{R}^2 = 0.96 \qquad [1]$$

Cross-product and quadratic terms were added to provide for best fit possible. As expected, the temperature (T) and pressure (P) coefficients are large, indicating the importance of these variables to the rate of reaction. The agitation term (A) is large, which is an indication of the importance of both thermal and gas-liquid mass-transfer factors. From the cross-product terms, which reflect interactions between independent variables, we can see that the agitation rate also has a significant effect on the ultimate impact of temperature and pressure on the response. Since the stirrer speed can be related to the power input (6) and Reynolds number (7), it is possible to relate this equation to reactors of different size. Generally, when the mass-transfer rates are matched for different reactors, the kinetics and reaction products will be similar. This is the basis for the catalyst comparison method that allows different reactors to be used for AOCS Standard Method Tz 1b-78.

The equation for *trans*-isomer content follows a similar form.

$$\begin{aligned} \mathit{TRANS}\ (\%) &= 53.08 + 5.32(\mathrm{T}) - 1.59(\mathrm{P}) + 2.36(\mathrm{C}) \\ &\quad - 1.97(\mathrm{A}) - 3.55(\mathrm{IV}) + 3.73(\mathrm{T})\,(\mathrm{A}) \\ &\quad - 1.53(\mathrm{C})\,(\mathrm{IV}) - 1.69(\mathrm{T})^2 + 1.30(\mathrm{P})^2 \\ &\quad - 1.35(\mathrm{C})^2 + 1.06(\mathrm{A})^2 - 5.85(\mathrm{IV})^2 \\ \mathrm{R}^2 &= 0.89 \end{aligned} \qquad [2]$$

The relative importance of terms differs from that for reaction rate. However, temperature and iodine value (IV) now have the largest coefficients. Increasing reaction temperature increases the *trans* content, but continuing the hydrogenation past 80 IV serves mainly to decrease the *trans* content.

In the absence of hydrogen, the *trans*-isomerization reaction would be expected to proceed to some equilibrium value. It has been shown in this laboratory that isomerization takes place when catalyst is in contact with hot oil, either under a vacuum or under a nitrogen atmosphere. During hydrogenation reaction, the *trans* isomers also are being removed by hydrogen addition to the double bonds; the two reactions are in competition. Different reaction conditions thus can change the *trans*-isomer peak height or the iodine value at which the peak occurs in a plot of fatty acid composition versus iodine value. Predictive curves can be generated from the *trans*-isomer model to illustrate this effect.

The complexity of the model equations makes it impractical to use routine calculations to predict results and to visualize trends. Therefore, an interactive program was written for a microcomputer to calculate predictions for specific sets of conditions. Also, a computer-generated series of response-surface plots for each of the models was developed to visualize the effects on response of two variables, or dimensions, at a time. Since this study had five independent variables, three variables must be fixed for each plot. Therefore, a series of plots must be used to assist in interpretation and prediction.

In the plot shown in Figure 1 for rate of hydrogenation, for instance, temperature and pressure are varied along the two axes while iodine value, agitation and catalyst concentration are held constant. The rates appear as the contour curves within the plots. At 200 C and 48 psig hydrogen, the expected rate is 1.8 IV/min; for a typical IV drop of 64 IV units, a reaction time of 36 min is predicted. Increasing the pressure increases the rate rapidly; the effect is even more pronounced at higher temperatures. Reaction rates determined from these plots can be used for cost minimization. For instance, the minimum catalyst needed, consistent with daily production requirements, can be calculated.

The variation in *trans*-isomer content is plotted for temperature and pressure changes in Figure 2. Increasing temperature always gives higher *trans*-isomer concentrations. Pressure seems to have an effect only up to about 30 psig; after that, increasing pressure has relatively little effect on *trans* content. Why doesn't higher pressure increase the *trans*-isomer content in the example? One explanation is that mass transfer of the hydrogen through the bulk liquid ceases to be the limiting factor; instead, diffusion of hydrogen near the catalyst surface becomes limiting.

The amount of hydrogen available on the catalyst surface is sufficient to make the hydrogen addition to the double bonds exceed the bond rearrangement reactions. The *trans*-isomer model is consistent with observations (11) that factors that deplete the hydrogen concentration on the catalyst surface led to greater isomerization (i.e., increasing temperature or catalyst concentration). Greater amounts of hydrogen adsorbed on the catalyst surface, likewise, reduce isomerization (i.e., increased pressure or agitation). As can be seen in Figure 3, the model predicts that increasing hydrogen pressure or agitation rate results in lower *trans*-isomer content. The model puts numerical values on the previously qualitative observations regarding the effect of hydrogen availability.

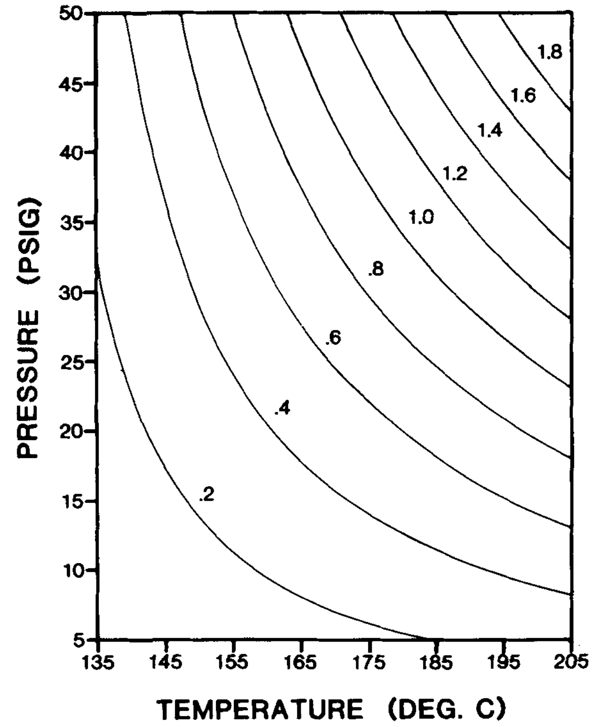

FIG. 1. Effect of pressure and temperature on reaction rate, IV/min (IV = 70, agitation = 600 rpm, catalyst concentration = 0.3%).

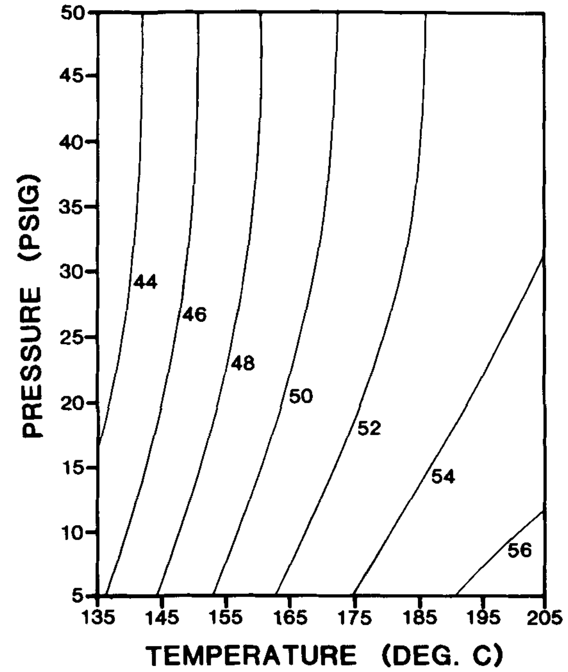

FIG. 2. Effect of pressure and temperature on percent *trans* isomer content. (IV = 70, agitation = 600 rpm, catalyst concentration = 0.3%).

The effect of hydrogen availability on *trans*-isomer content is further illustrated by changing the catalyst concentration (Fig. 4). If the catalyst concentration is increased, the effect is to lower the hydrogen availability and hence the *trans*-isomer content, as illustrated by the response-surface plot. More catalyst increases the hydrogen usage and leads to higher *trans*-isomer content. As we saw before, however, greater agitation can reduce the *trans*-isomer content. The effects are non-linear and more pronounced for changes in catalyst concentration.

These response-surface plots can assist in the scale-up to larger reactors, which is often difficult to predict. Each rpm value here represents a mass-transport rate that is partially determined by reactor geometry and agitator type. The model provides a means to match reactors by solving the equations for the agitation level that gives equivalent *trans*-isomer content when temperature, pressure and iodine value are matched.

No suitable model could be obtained for reaction selectivity for fatty acid dienes over monoenes (SD). The best-fit model had a correlation coefficient (R^2) of less than 0.75 and was judged inadequate. Table II contains the selectivity values calculated for each reaction (12). The range in values was quite large, from 8.7 to 415. Examination of the data reveals that very high selectivity values occur only for iodine values of 77 to 79, while low values occur in batches with IV equal to 56 to 58. The final iodine value seems to play a greater role in determining selectivity than any of the other variables. It appears from this data that selectivity comparisons are meaningful only when comparing fats of nearly the same IV.

Another response variable for which a model was developed is the Wiley melting point. This analytical measurement is sometimes used as an end point or quality-control check in hydrogenations to produce margarines or shortenings.

$$\text{Melting Point} = 105.48 + 1.69(C) - 13.76(IV) - 1.12(T)(IV) + 1.46(C)(IV)$$

$$R^2 = 0.97 \qquad [3]$$

This equation relates melting point to the IV of the fat when the catalyst concentration is known. The IV coefficient is the dominant term, but both reaction temperature and catalyst concentration also influence the melting point. The model shows that a nearly linear relationship exists over a range of 60 to 80 IV (Fig. 5). However, reaction conditions, which in turn affect selectivity and *trans*-isomer content, create a family of melting-point versus iodine-value lines. For the 30-degree range in melting point observed here, a variation of 3 to 8% is possible for a given IV. The model might be used to estimate reaction endpoint by choosing a line corresponding to reaction conditions and then stopping reaction at the IV appropriate for the desired melting point.

A series of empirical models is especially helpful for creating new products or effecting product changes when a large data base is not available. The optimum reaction conditions can be predicted by an iterative calculation using the computer. The predictive models presented here for catalyzed hydrogenation of soybean oil have the advantage of including more terms and being based on a larger data set than that of other models reported previously in the literature. The models provide a wider range and flexibility than literature models that predict only *trans*-isomer content at a fixed iodine value. The ability to predict

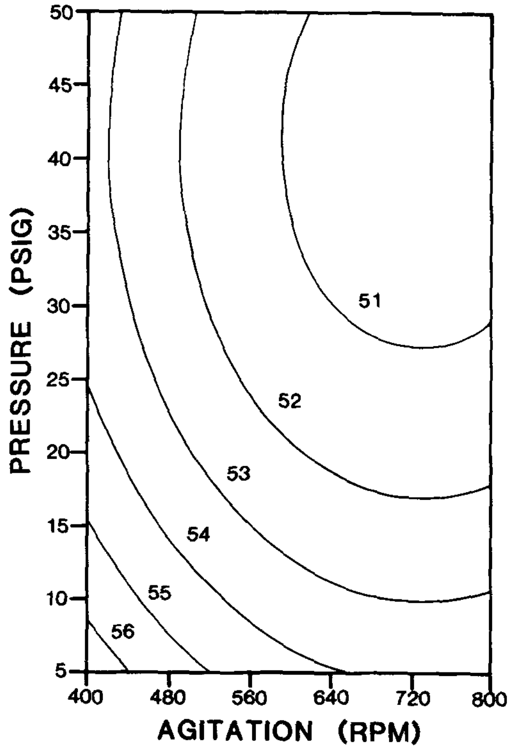

FIG. 3. Effect of pressure and agitation on percent *trans* isomer content. (IV = 70, temperature = 177 C, catalyst concentration = 0.3%).

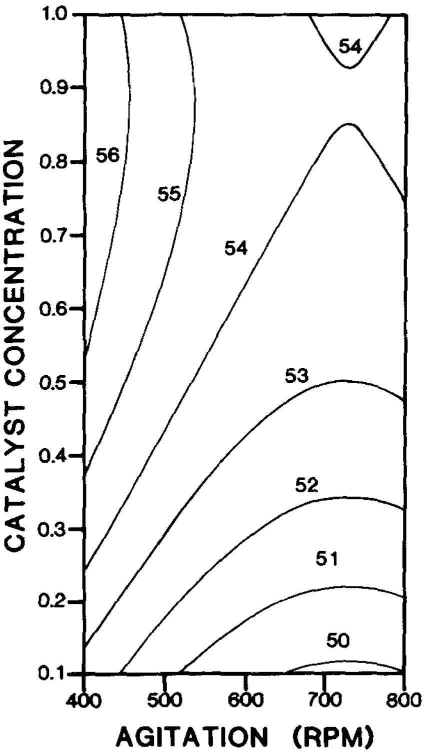

FIG. 4. Effect of catalyst concentration and agitation level on percent *trans* isomer content. (IV = 70, temperature = 177 C, pressure = 20 psig).

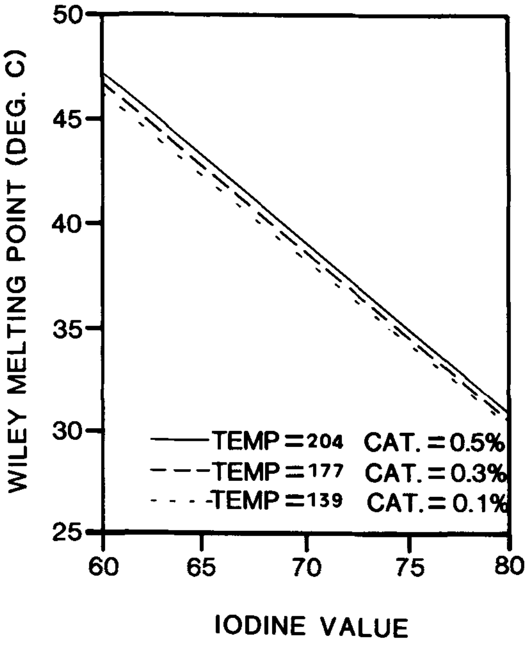

FIG. 5. Wiley melting point (°C) as a function of iodine value, based on model predictions.

quantitatively the reaction rate, *trans*-isomer content and melting point is valuable for improving process and product development. Models for other oils or products could be developed easily, using the techniques presented here.

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High Pressure Extraction of Oil Seed[1]

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ABSTRACT

For calculation of phase equilibria of the system seed oil/CO_2, an equation of state published in the literature has been fitted to experimental data of that system. The results thus obtained are of only limited use in designing a supercritical extraction process. The experimental investigation of the mass transfer kinetics is much more significant. Mechanical processing of the oil seed's cell wall structure has been shown to be of great importance. The best specific yields were achieved with material that had been mechanically pre-deoiled and thereby broken open. Yields are increased considerably by use of the gas mixture CO_2/propane or other special gas mixtures or by the addition of refrigerants. However, the extraction times achieved in batch operation, together with the mass product nature of oil seed, make a continuous supercritical extraction essential if operation is to become economic relative to the conventional hexane extraction. To this end, the energetics of the process have been calculated, and practical possibilities for continuous operation are discussed.

INTRODUCTION

During the past two decades, the development of high pressure extraction has resulted in intensive research in the processing of natural products (1). The solvent CO_2 has become important for reasons of safety and economics. The extraction of solids is especially of interest for materials which are present in small amounts and which yield high quality products after extraction. The reason lies in the relatively high investment and energy costs of a high pressure plant, where at present only batch processing is possible, with the associated loading and emptying times. Because of the problems that have been encountered in extraction of the mass-product oil seed with conventional solvents the question has been raised whether high pressure extraction, using solvents which do not pose safety and health hazards, might replace the conventional, potentially explosive, hexane extraction.

COMPARISON OF HEXANE EXTRACTION AND HIGH PRESSURE EXTRACTION

In conventional oilseed processing, a distinction is made between oil-rich seeds (for example rape, corn germ, sunflower) and less oil-rich seeds (for example soybean, cottonseed) (Fig. 1). The latter generally are extracted directly, after mechanical and thermal treatment to break open the cells. The most significant oil crop is without doubt the soybean, for which the worldwide seed oil production was 15 million tons in 1982 (2). Seeds with a higher oil content, on the other hand, are mechanically pre-deoiled in a cage screw press prior to extraction. In the case of rapeseed, which is increasingly important in the European market, the resulting press cake has a residual oil content of 18 to 20%. This material is extracted afterwards; the oil thus obtained must be separated from solvent by distillation,

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