De-Oiling Contaminated Bleaching Clay by High-Pressure Extraction

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The disposal and re-use of spent bleaching clay from the vegetable oil processing industry is a problem of growing importance.

Although today the only practical way of removal of the spent material is disposal, extraction with organic solvents is a well-known method of de-oiling contaminated bleaching clay. In our investigations we compare the extractibility of two different types of bleaching clays with CO_2 as a solvent. All experiments were carried out with a high-pressure extraction plant. The extraction and separation conditions, temperature and pressure, as well as the CO_2 mass flow, were varied during experiments. The aim of our investigations was a complete separation of the oil from the adsorbent. The latter should then be re-used as bleaching clay. The oil and the bleaching clay were analyzed and tested, respectively. The results show that oil of good quality can be recovered and the bleaching clay still has an activity approximately 50% of fresh clay.

KEY WORDS: Adsorbent, bleaching clay, carbon dioxide, de-oiling, high-pressure extraction, oil recovery, spent bleaching clay, vegetable oil.

The refining of seed oils and fats requires several steps to remove from the raw materials those components that are harmful to health or that are deleterious to storage quality, outward appearance or edibility. The classical process steps for this purpose are degumming, neutralizing, bleaching and deodorizing.

The purpose of the bleaching process is to remove undesirable substances such as soap residues, traces of heavy metals, autoxidation products, pesticide traces and residues of phosphorus compounds, as well as colored matter (carotenoids, chlorophyll, blood pigments from animal fats). Bleaching processes may be subdivided into four groups: heat bleaching; hydrogen bleaching; chemical bleaching; and bleaching by adsorption on solids.

Bleaching by heat, hydration or chemical additives essentially represents the decolorization of oils and fats. Adsorptive bleaching not only removes colored matter, but also fulfills the other requirements of the bleaching process. It is therefore more appropriate to describe this type of bleaching as adsorptive purification. The bleaching clays employed for adsorption must be mechanically robust and must possess a high specific area by weight.

Bleaching clay is a general term for clay-like, water-containing aluminosilicates containing various proportions of magnesium, calcium and iron. These are clay minerals, sediments arising from shattering processes (1). According to Kaufmann (2), bleaching earths are subdivided into two groups—the naturally active clays form one group, and the highly active clays form the other. Fuller's earth, for example, is one of the naturally active clays. Minerals such as montmorillonite have either negligible bleaching activity or none at all in the untreated state. According to Zschau (3), montmorillonite is the starting material for all activated bleaching clays. The ratio of silicic acid to clay is 4:1 in this aluminium hydrosilicate. To make it suitable for bleaching purposes, montmorillonite is subjected to acid treatment, which replaces cations by protons, and partially dissolves the original crystal structure. Aluminium, iron and magnesium are removed from the crystal lattice, considerably increasing the internal surface area. Activated bleaching clays are characterized by a high adsorptive capacity, acid and catalytic properties, ion-exchange capacity, and particle-size distribution.

In adsorptive bleaching, two types of adsorption are distinguished—physical adsorption, which is reversible and is based upon weak intermolecular forces; and chemisorption, which is generally irreversible. Catalytic chemical reactions prevent the recovery of chemisorbed components in the original form. The temperature and physical circumstances determine the relative proportion of the two types of adsorption in the overall process.

The bleaching process is carried out in an autoclave, where up to 2.5% (w/w) bleaching clay is mixed under vacuum with the fat or oil to be bleached. After completion of the bleaching process, the bleaching clay is filtered from the oil. However, the clay contains 30–40% (w/w) oil. This contaminated bleaching clay must be treated in some way before disposal. The waste-disposal process, however, results in the loss of this oil, together with the bleaching earth itself (4,5).

The aims of the present investigations are to separate the oil from the adsorbent as well as to recover the bleaching clay in the best possible re-usable condition. Both aims are to be achieved by means of solid-liquid extraction with highly compressed gases as the solvent. The gas initially used is carbon dioxide. The advantage of extraction with highly compressed gases lies in the ready and selective separation of the oil from the spent bleaching clay. A further important advantage of high-pressure extraction is the elimination of flammable solvents, which increases safety.

METHODS AND MATERIALS

Experimental plant. Batch extraction experiments were performed in the high-pressure extraction plant represented in Figure 1. The significant parts of the plant are an extractor, a separator, a reservoir, a pump and several heat-exchangers. The vessels are double-walled, and the outer cavities may be used for temperature-control purposes.

The solvent is compressed by means of a single-cylinder piston pump whose cylinder head is cooled to remove the heat arising from compression. The solvent, which has become charged with useful material in the extractor, is expanded in a pneumatically controlled high-pressure butterfly valve. The carbon dioxide withdrawn from a storage tank is cooled in a condenser and collected in the buffer vessel. The piston pump compresses the liquid carbon dioxide to extraction pressure and passes it *via* an

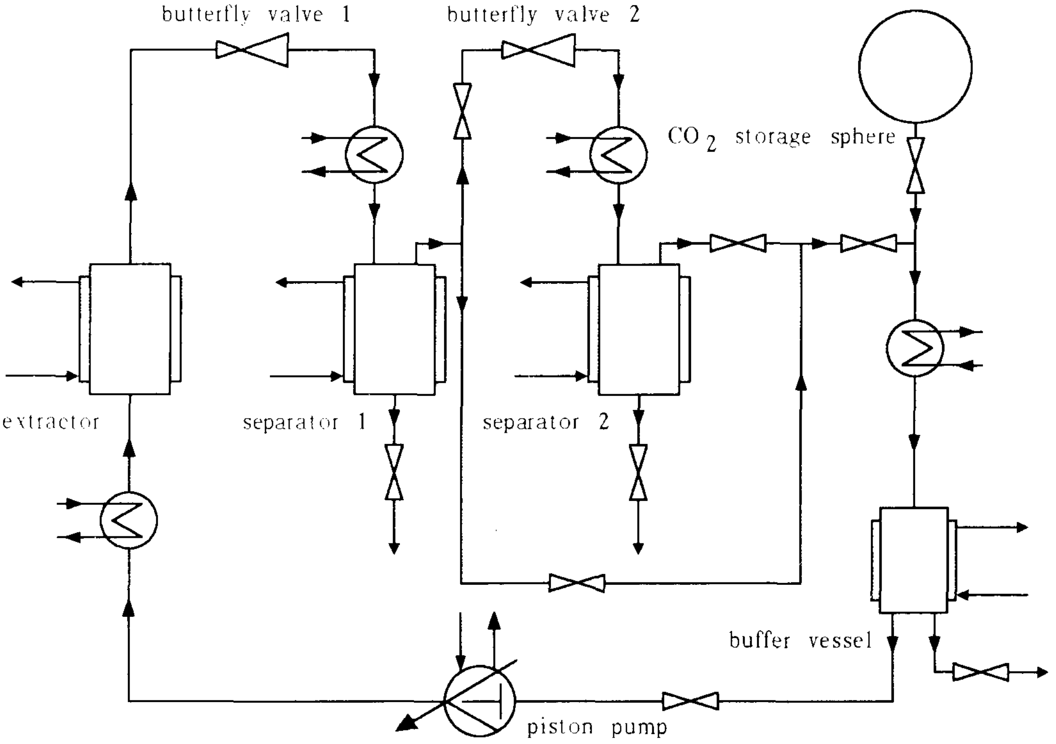

FIG. 1. Schematic representation of the high-pressure extraction plant.

evaporator to the extractor. The charged solvent passes through the first butterfly valve and a further evaporator to the first separator, where part of the extract separates from the solvent. The remainder is led *via* the second butterfly valve and an evaporator to the second separator, where the remaining extract separates out. The gaseous carbon dioxide is finally condensed and returned to the extraction process.

Measurements were made of the quantities of extract in the first and second separators, of the solvent temperature at various points in the plant, and of the mass flow. Pressure regulation equipment ensured that the extraction pressure and the separator pressures were held constant.

Experimental program. The experimental materials employed came from the bleaching stage of industrial refinement, and were removed warm directly after filtration and sealed into an airtight container. The material used in the first experimental series was bleaching clay contaminated with palm oil.

The parameters investigated were: Extraction pressure P_{EX} = 350, 500, and 750 bar; and mass flow, $\dot{m}_{CO_2}$ = 4, 6, and 8 kg/hr. The extraction temperature Θ_{EX} = 80°C and the separation temperature Θ_{Ab} = 70°C were held constant, and one-stage separation at P_{Ab} = 60 bar was employed. The mass of starting material was 380 g in this series of experiments.

The material employed in the second experimental series was bleaching clay contaminated with rapeseed oil, also from industrial refining. The parameters investigated here were: Extraction pressure, P_{Ex} = 350 and 500 bar; extraction temperature, Θ_{Ex} = 50 and 80°C; and mass flow $\dot{m}_{CO_2}$ between 4 and 12 kg/hr. In the one-stage separation, P_{Ab} = 60 bar and Θ_{Ab} = 55°C. In the two-stage separation, P_{Ab_1} = 140 bar, Θ_{Ab_1} = 55°C and P_{ab_2} = 60 bar, Θ_{Ab_2} = 30°C, respectively. The mass of extractor starting material was 350 g in this second experimental series.

RESULTS AND DISCUSSION

Evaluation of the extraction curves. The gravimetrically determined mass gain of the extract in the separator during the experiment is expressed relative to the total mass of extractable matter in the starting material. This quotient represents the ordinate value $m_{extract}/(m_{tot}-m_{solid})$. The abscissa value is the ratio of the employed mass of carbon dioxide to the total mass of extractable matter in the starting material, $m_{CO_2}/(m_{tot}-m_{solid})$.

Figure 2 shows a typical extraction curve. There is an initial linear rise, corresponding to a constant rate of increase in the amount of extract in the separator, followed by a "knee" and the transition to an asymptotic curve. The initial part of the curve yields the initial concentration corresponding to the experimental parameters. The extract passing into the solvent comes from the surface and near surface zones of the bleaching clay. In this region, the resistance to mass transfer is provided by the solvent. In the asymptotic region, the extract must diffuse to the surface from the deeper-lying zones of the bleaching clay. The bleaching clay possesses a lattice structure whose pore diameter lies between 20 and 60 Å. The useful material to be extracted lies within this capillary system

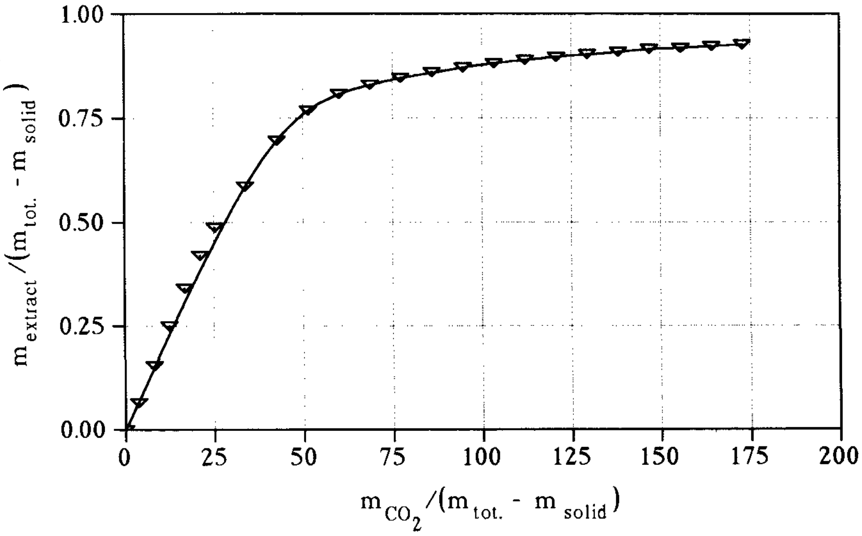

FIG. 2. Typical course of the extraction of bleaching clay.

and is held back by capillary forces. Mass transport from the capillaries to the surface of the system must, therefore, take place before mass transfer to the solvent is possible. Therefore, in this region of the curve resistance is provided by the bleaching clay, and extraction thus takes place more slowly. The degree of extraction, being the quantity of extracted material relative to the total quantity of extractable material, lies between 93 and 97% for all experiments performed.

Influence of various parameters on the extraction curve. The solvent properties of supercritical gases are, above all, influenced by temperature and pressure. The influence of the extraction pressure at constant temperature and constant mass flow will now be described in terms of extraction experiments performed on bleaching clay contaminated with palm oil. Figure 3 shows extraction curves at 350, 500 and 750 bar. An increase in the concentration within the linear region is clearly seen, as is a later transition to the asymptotic region at higher pressures. The increase of solubility in carbon dioxide with increasing pressure, which corresponds to the increased concentrations within the linear regions of Figure 3, is in agreement with the work of Quirin (6), who observed an initial increase of pressure along the solubility isotherm until a maximum is reached, after which the solubility decreases (Fig. 4). The pressure region investigated here, 350 to 750 bar, lies in the rising region of the isotherm. The increase in solubility from 500 to 750 bar is more than that from 350 to 500 bar, indicating that the solubility maximum is not being approached.

Apart from this, the extraction curves of Figure 3 exhibit three regions, in contrast to the single curve already described. The explanation for this effect is that the bleaching clay extracted here has been supplemented with small quantities of active charcoal, as is usual when bleaching palm oil. The two adsorbents differ in their adsorptive properties. According to Patterson (7), bleaching clay adsorbs up to 70% of its own weight in oil, whereas active charcoal is able to adsorb up to 150% of its own weight. In general, the bleaching clay is supplemented with about 5% active charcoal. Within the first linear region, useful material is extracted from the surface of both adsorbents, but within the second region, extraction is now mainly from the surface of the active charcoal alone. The extraction of useful material from the bleaching clay is now limited by resistance within this adsorbent, *i.e.*, the asymptotic region has already been reached for the bleaching clay component. Since the proportion of active charcoal is low, however, its influence on the mass transfer remains small.

Figure 5 shows the influence of mass flow on the extraction at constant pressure of bleaching clay contaminated with palm oil. For a mass flow of 6 kg/hr, the maximum concentration is seen at the start of extraction, the concentration is less at 4 and at 8 kg/hr. Bleaching clay consists of fine particles, 40% of which are smaller than 25 μm (information provided by Süd-Chemie, AG, Germany). A mass flow of 4 kg/hr is still insufficient to achieve complete flow around the individual particles, and channel formation apparently occurs. At 8 kg/hr, the residence time in the extractor is insufficient to achieve saturation of the solvent.

In contrast to palm oil, the extraction curves for rapeseed oil, shown in Figure 6, exhibit no clear maximum, even though the mass flow was increased to 12 kg/hr. An increase in mass flow improves the extraction, although the concentration in the linear region scarcely changes. As the flow velocity is increased, a later "knee" to the asymptotic region is observed. Apart from the flow around the bleaching clay particles, extraction behavior depends not only on the residence time but also upon the type of useful material to be extracted.

To give an example, we consider the extraction at $\Theta = 80°C$ and $p = 500$ bar (parameters otherwise identical), where the initial concentrations are about 36 g extract/kg CO_2 for rapeseed oil, and 18 g extract/kg CO_2 for palm oil. Thus, the effect of viscosity on mass transfer is different for palm oil and rapeseed oil in the extraction process of bleaching clay. Also, the adsorption of oil is probably important for the feasability of the extraction pro-

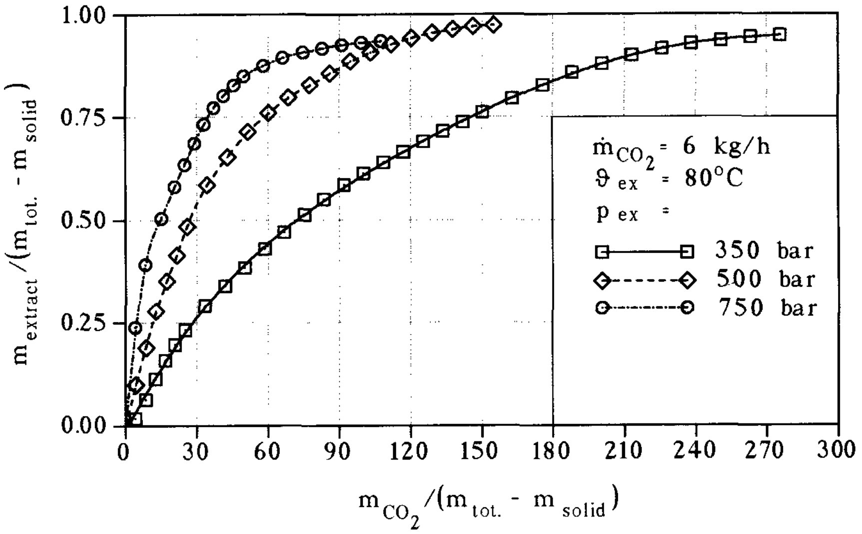

FIG. 3. Effect of extraction pressure on the extraction of bleaching clay contaminated with palm oil, with one-stage separation (p_{Ab} = 60 bar, Θ_{Ab} = 70°C).

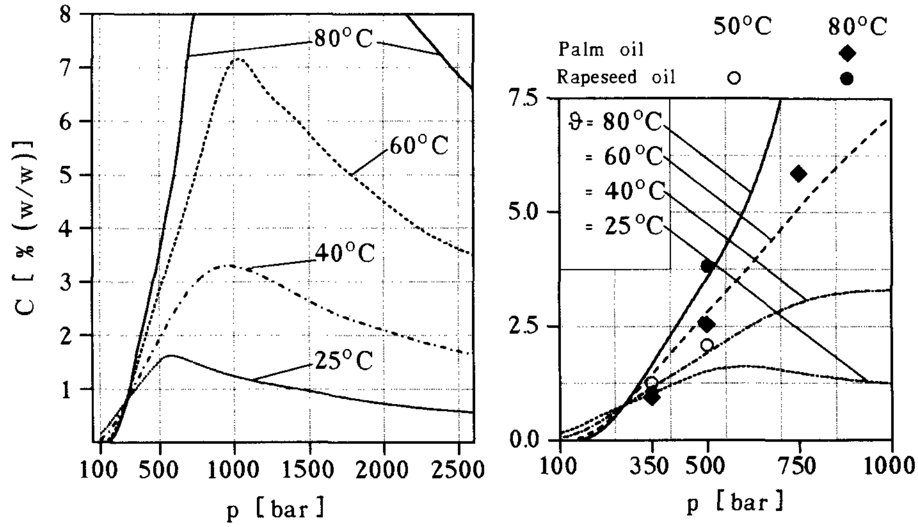

FIG. 4. a, Graphic representation of solubilities determined by Quirin (6). b, Comparision of Quirin's solubilities (6) with the values for palm oil and rapeseed oil determined in the present study.

cess. Comparing the extraction curves for rapeseed oil in Figure 6 with palm oil at 350 bar in Figure 3, the difference becomes obvious. It seems as if the bleaching clay adsorption of palm oil is more distinctive than it is for rapeseed oil.

The solubilities depicted in Figure 4b confirm this explanation. The solubility of rapeseed oil is a little higher than that of palm oil at 350 bar.

In the course of the experiments with bleaching clay contaminated with rapeseed oil, the influence of the separation process was investigated (Fig. 7). There is a trend to similar curves in all experiments, but the curves for single-stage separation always lie somewhat below the two-stage curves. The solvent capacity of carbon dioxide at 60 bar and 55°C (one-stage separation) or at 60 bar and 30°C (second separator of two-stage separation) is practically zero in both cases; so, there should be no detectable difference between the curves for one- and two-stage separation. This phenomenon might be explained if small quantities of extract are being carried over from the one-stage extractor into the circulation. The carbon dioxide returning to the extractor thus has a small initial loading and can no longer take up the same quantity of extract as can the extract-free solvent initially entering the extractor. Two-stage separation appears to result in complete separation so that no extract passes into circulation.

Clear differences are seen in the fractions from one- and two-stage separation. Whereas one-stage separation yields an extract that is not completely clear, two-stage separa-

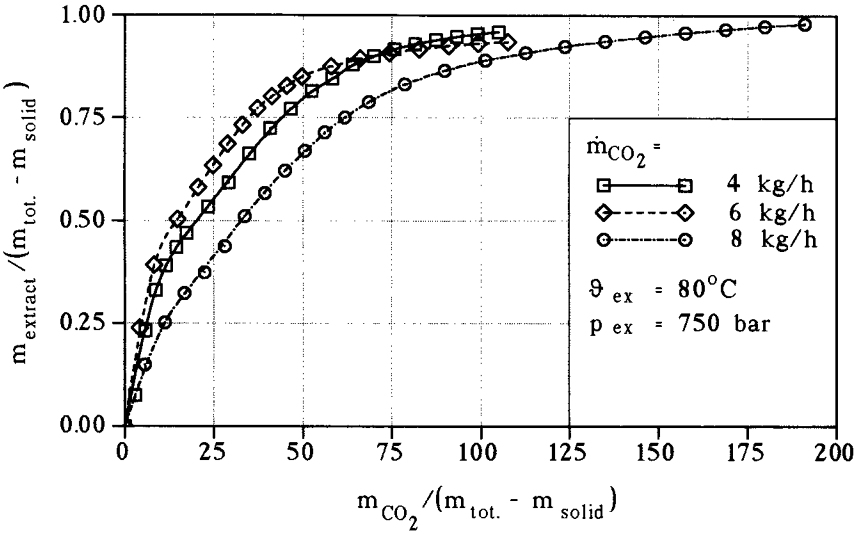

FIG. 5. Effect of mass flow on the extraction of bleaching clay contaminated with palm oil, with one-stage separation.

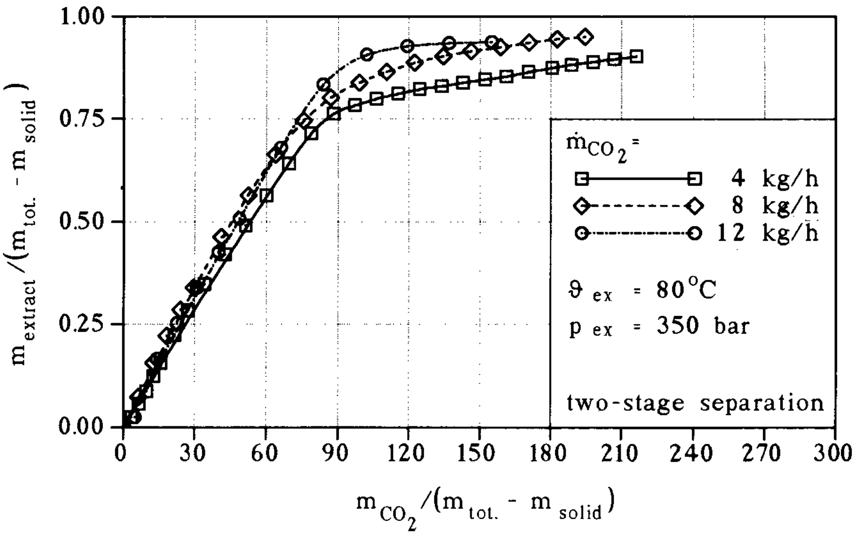

FIG. 6. Effect of mass flow on the extraction of bleaching clay contaminated with rapeseed oil, with two-stage separation.

tion yields a clear first fraction and a second fraction that consists mainly of a transparent liquid phase overlaid by a separate, intensely colored second phase.

A parameter that has not yet been discussed is the influence of extraction temperature, represented in Figures 8 and 9. Figure 8 shows that an increase in temperature at an extraction pressure of 350 bar results in poorer extraction behavior. Figure 9 shows that extraction is better at 80°C than at 50°C at an extraction pressure of 500 bar. The temperature dependence of solubility in carbon dioxide has already been mentioned. Quirin (6) found in his investigations that the solubility isotherms become steeper as the temperature rises, *i.e.*, the initial concentration rises. However, there is a pressure range over which the solubility falls with rising temperature. Above that pressure range the inverse behavior is observed, and the solubility rises with temperature. Quirin, who performed his investigations with soya oil, found this region to lie between 250 and 300 bar. For the rapeseed oil investigated here, this region lies above 350 bar.

This result shows clearly that no general behavior pattern can be defined for the solubility of vegetable oils in liquid and in supercritical carbon dioxide. The concentrations determined in the present experiments are compared with Quirin's results in Figure 4b.

Evaluation of recovered products. The bleaching clays de-oiled by extraction were investigated, as were the recovered oil fractions. The oil samples were analyzed

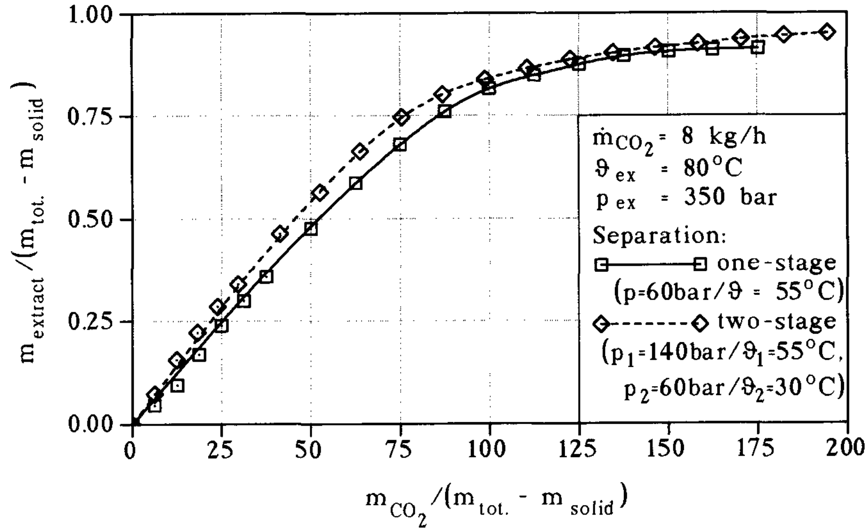

FIG. 7. Comparison of two extraction curves for one- and two-stage separation of bleaching clay contaminated with rapeseed oil.

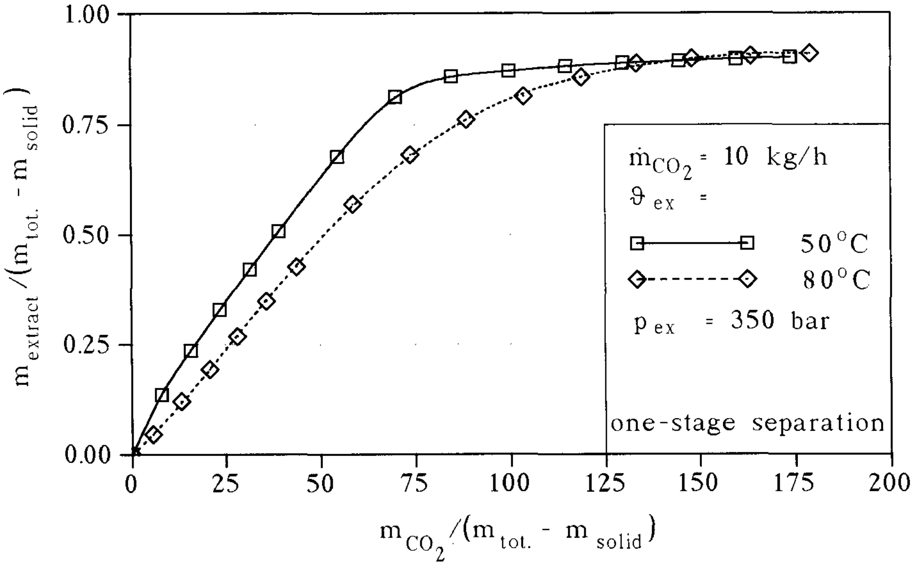

FIG. 8. Effect of temperature on the course of extraction at the extraction pressure p_{Ex} = 350 bar.

for free fatty acids (FFA), peroxide number, anisidine number and water content. The Lovibond color index (5 1/4″ for the palm oil investigations, 2″ for rapeseed oil investigations) was determined (8). For some samples a fatty acid spectrum was recorded. The remaining activity and important data of the de-oiled bleaching clay were investigated.

Table 1 lists the results for the oil samples. Table 2 shows the mean fatty acid compositions of the extracted oil samples together with the expected values as percentages. The fluctuations seen in Table 1 do not, as might be supposed, result from the various extraction parameters. Rather, the increase of the FFA content results from the longer refrigerator storage time of some samples after extraction. In none of the experiments described did the extraction parameters have any influence upon the quality of the oil or of the extracted bleaching clay. All loaded bleaching clays were de-oiled to approximately the same degree of extraction, so that the oil compositions did not differ. In the temperature range between 50 and 80°C there is no detectable change in the characteristic values investigated, so that this influence can be excluded here, also.

The oils extracted from palm oil bleaching clays are of good overall quality. This is confirmed by the color, which is only slightly more intense than that of refined palm oil. The comparison values used here, however, make a final evaluation difficult, because they are guide values from

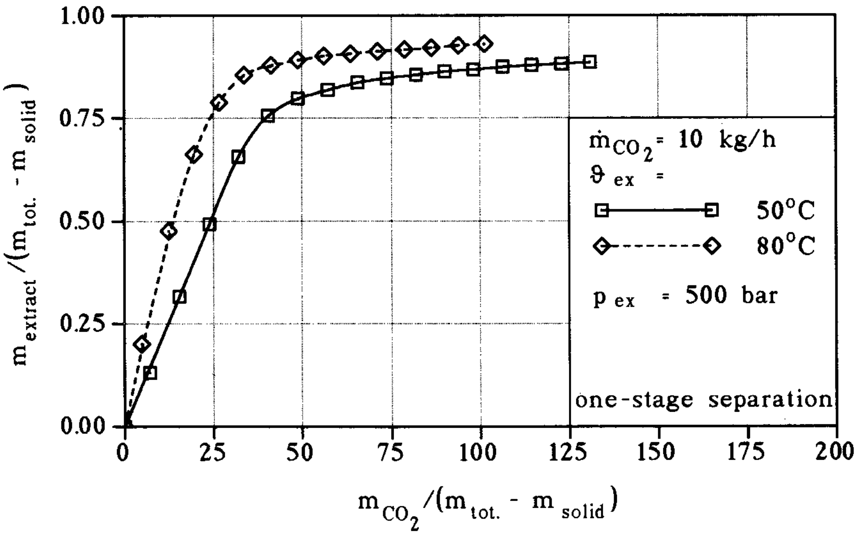

FIG. 9. Effect of temperature on the course of extraction at the extraction pressure p_{Ex} = 500 bar.

TABLE 1

Properties of Oils Extracted from Spent Bleaching Clays

	Extract from palm oil bleaching clay (%)	Extract from rapeseed oil bleaching clay (%)	Comparison values[a] Edible oils and fats	
			Refined	Non-refined
FFA content	0.6-1.38		<1.92%[b]	<19.18%[b]
		2.05-3.38	<1.93%[c]	<22.38%[c]
Peroxide number	0.4-1.6	0.1-2.74	<10	
Anisidine number	12.2-16.3	10.5-11.3	—	
Water content	<0.1	<0.13	—	
Color number				
Red	2.0-3.1	1.0-1.4	—	
Yellow	32-40	8-11	—	

[a] Ref. 7.

[b] Calculated from the acid number for palm oil.

[c] Calculated from the acid number for rapeseed oil.

TABLE 2

Fatty Acid Composition for Extracted Oils from Spent Bleaching Clays

Fatty acid	Extracted palm oil	Expected values for palm oil	Extracted rapeseed oil	Expected values for rapeseed oil
C12	0.39	<1.2	—	—
C14	1.31	1	—	—
C16	45.28	45	4.07	5
C16:1	—	—	0.29	0.3
C18	4.6	5	1.36	1.5
C18:1	37.14	38	57.84	57
C18:2	10.58	10	22.13	22
C18:3	0.35	0.5	10.08	10
C20	0.33	0.5	—	—
C20:1	—	—	1.48	1.5
Other	—	—	1.75	2.7

TABLE 3

Remaining Bleaching Activity of Extracted Bleaching Clays

Bleaching clay	Bleaching of de-acidified rapeseed oil				Bleaching of raw palm oil			
		Lovibond				Lovibond		
	% (w/w)	Red	Yellow	Chlorophyll (ppm)	% (w/w)	Red	Yellow	Carotene (ppm)
Control bleaching clay	1.0	0.9	10	0.17	2.5	4.1	70+	11.2
Non-activated bleaching clay	1.0	9.0	70+	3.47	—	—	—	—
"Palm oil bleaching clay"	1.0	2.5	56	0.33	2.5	14	70+	59.6
	2.0	1.7	19	0.11				
"Rapeseed oil bleaching clay"	1.0	2.7	38.8	0.57	2.5	14	70+	52.7
Unbleached		10	70+	4.40		—[a]	—[a]	267

[a] Measurement not possible.

the Bundesanzeiger, Leitsätze für Speisefette und Speiseöle (Guidelines for Edible Fats and Oils) (9). A better evaluation would be possible if the quality of the starting material and fully-refined oil were known. Since they are not known, however, we have used the guide values here. But even then, the palm oil is almost of raffinate quality and could be improved to within the permissible limits by re-bleaching, for example, with a small percentage of bleaching earth. The extraction yields a product with a fatty acid composition that corresponds fully with the expected values for a pure palm oil (Table 2). The selective solvent behavior of carbon dioxide thus permits the palm oil present in the bleaching clay to be recovered with a degree of extraction up to 97%, as already described.

The results for rapeseed oil, particularly regarding the free fatty acids, are less satisfactory than for palm oil. The values for FFA content are up to 1.8 times higher than the legally recommended limits. But in this case, the quality of the starting material, as well as that of the refined oil, is unknown, making a final verdict on the extracted product impossible. However, the values for peroxide number, anisidine number and color number are good. Overall, the extraction of bleaching clay contaminated with rapeseed oil yields an extract that is considerably better than an unrefined oil and which, like palm oil, can be improved in quality by slight re-treatment. Concerning the fatty acid composition, there is no difference from the results of the palm oil investigations. As may be seen in Table 2, the proportions of individual fatty acids in the extract lie in the region of the expected values for rapeseed oil.

Apart from oil recovery, a further aim was the regeneration of oil-contaminated bleaching clay. In order to evaluate the extent to which this aim can be achieved by the method described here, the extracted bleaching clay was subjected to bleaching tests. Changes in the physical data were also investigated. Bleaching clay as initially used for bleaching served as the control sample. The specific surface area of all extracted bleaching clays is 40% less than that of fresh clay. Regarding pore volume, a distinction must be made between "palm oil bleaching clay" and "rapeseed oil bleaching clay". The pore volume of "palm oil bleaching clay" decreased in comparison to fresh clay by about 50% in the range up to 800 Å, about 40% in the range up to 250 Å, and about 45% in the range up to 140 Å. The decrease for "rapeseed oil bleaching clay" is less pronounced, and is about 35% in the range up to 800 Å, about 30% in the range up to 250 Å, and about 35% up to 140 Å.

Palm oil contains a high proportion of carotenoids, extended chain-like molecules, which apparently bind tightly within the pores of the bleaching clay and cannot be removed by extraction. This leads to a large decrease in the remaining pore volume. Rapeseed oil, on the other hand, instead contains a high proportion of chlorophylls, highly complex large-volume molecules. Unlike carotenoids, they are not able to occupy the pores, but are more likely to be chemisorbed at the acid centers of the bleaching clay.

The remaining bleaching activity of the extracted bleaching clay has been investigated in experiments with de-acidified rapeseed oil and with untreated palm oil. The results are listed in Table 3. In comparison to fresh bleaching clay (control bleaching clay), the same dosage of extracted bleaching clay exhibits decreased activity.

Palm oil bleaching clay, when employed for the bleaching of de-acidified rapeseed oil, retains about half the activity for the removal of chlorophyll. The decolorization of rapeseed oil succeeds to only 1/3 as measured by the color number red, and to only 1/6 as measured by the color number yellow. Doubling the dosage of the extracted bleaching clay results in an improvement. The result for the removal of chlorophyll is then even better than that for fresh bleaching clay, whilst 50% of the original decolorization capacity still remains.

Rapeseed oil bleaching clay exhibited a decrease of about 70% for all three criteria investigated here. The dosage was not increased, though this would undoubtedly have resulted in an improvement, as was the case for palm oil bleaching clay.

The extracted bleaching clays did not differ in their ability to bleach untreated palm oil. There remained 20% residual activity for the removal of carotene, and 30% for decolorization.

The results from these investigations show clearly that extracted bleaching clays still possess residual activity. An increase in dosage achieves even better removal of chlorophyll than does bleaching with fresh bleaching clay. The effect upon bleaching activity of a mixture of recovered and fresh bleaching clays, however, remains to be evaluated.

Finally, a few comments should be added concerning the comparison of extraction processes with CO_2 and organic solvents.

As mentioned earlier, our experiments covered the extraction with supercritical CO_2 as a solvent. However, extraction by means of organic solvents has been used long before to de-oil bleaching clay. Ong (10) researched the use of bleaching clay with soybean oil using hexane as a solvent. The oil content of this spent earth was 30% before and 5% after extraction. In terms of extraction yields the results are identical for hexane and CO_2.

According to Weber (11) the advantages of extraction with hexane are the high efficiency and good quality of the extracted oil. Our experiments with CO_2 as a solvent resulted in oil yields of up to 97% and excellent oil qualities (Tables 1 and 2). Thus, the advantages mentioned by Weber are also applicable to the extraction with CO_2.

The extraction with hexane has the advantage that it can be a continuous process. However, Eggers (12) reported that high-pressure extraction of oil seeds with entry and exit by the "screw-principal" is possible. A similar technique should be possible for the extraction of bleaching clay with supercritical CO_2 and will be investigated in the near future.

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