INVESTIGATION ON THE USE OF ETHYL ACETATE AS SOLVENT FOR SEEDOIL EXTRACTION

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ABSTRACT

An investigation on the use of ethyl acetate as a solvent for the seedoil industry was carried out. As hexane is the most used solvent in extraction of oil from seeds, the study focuses on the comparison of the two solvents. The parameters studied were: contact time between solvent and seed cake, temperature of the solvent, quantity of solvent used for extraction and type of solvent. The results are presented on a relative basis where hexane is given a factor of 100. From the results obtained it can be seen that ethyl acetate is in general a better solvent than hexane for the two types of seed cakes used, namely cottonseed and sunflower. The relative efficiency of ethyl acetate varies from about 100 to 160 for cottonseed cake from 140 to 250 for sunflower cake.

1.0 INTRODUCTION

Solvent extraction is an important unit operation in the modern vegetable oil production from seeds. The mechanical extraction of oil leaves the cake with about 2-3% (w/w) oil for practically all types of seeds (Swern, 1964), and this indicates that a certain amount of valuable oil is left in the cake. Besides, a cake with such amounts of oil is inferior as a nutritional source for human or animal consumption. This is the reason why solvent extraction is important; since the oil content of the cake is reduced to about 0.5% (w/w) in an efficient process.

The most used solvents in the vegetable oil industry have been benzene, mainly in Europe and hexane, mainly in the United States. Today the position of benzene as a suitable solvent for the extraction of edible oils is jeopardized by its carcinogenic properties. For developing countries with scarce foreign exchange reserves, like Tanzania, which want to embark on seedoil extraction using solvents, the use of the traditional ones would mean their importation, with the consequent drain in foreign reserves. Therefore, such countries have to look for alternative solvents derived from indigeneous materials and not those from petroleum.

The properties that have made hexane so successful in the oil extraction industry are high solvency, low boiling point, low toxicity, and low cost.

In Table 1 some of the common and important properties of both solvents are presented and from there, it can be seen that both are similar, regarding their physical properties. The aim of the present study is to evaluate the use of ethyl acetate as a solvent for seedoil extraction.

The selection of ethyl acetate as the solvent to be studied lies in the fact that it can be produced from molasses from the sugarcane industry and sulfuric acid as catalyst; both of which are locally available. Besides, its price is also competitive, at least in Tanzania, when compared with hexane.

As hexane is the most used solvent for oil extraction the aim of the present study is to determine the comparative value of ethyl acetate for the same purpose; therefore, the results will be given in a relative form where hexane is the basis for comparison.

Usually, the extent of extraction is affected by the following factors:

- The kind of solvent.
- The temperature of the solvent.
- The ratio of solvent to meal.
- The number of extraction stages.
- The contact time.

2.0 EXPERIMENTAL PROCEDURE

Samples of cottonseed and sunflower cake were obtained from the Multipurpose Oilseed Processing Company (MOPROCO) in Morogoro. The oil content in the cakes was determined by extraction with hexane in a Soxhlet apparatus (Fig. 1) for a period of eight hours. This time was chosen after trial tests gave constant weight of the cake sample. The average oil content determined in the cake was 10.0% (w/w) for cottonseed and 3.7% (w/w) for sunflower.

The parameters that were evaluated to determine the extraction efficiency of ethyl acetate were:

- Time of extraction.
- Extraction temperature.
- Effect of quantity of solvent (solvent/meal ratio).

All experiments were repeated using hexane as solvent for comparison.

2.1 CONTACT TIME

In an Erlenmeyer flask, enough oven-dried cake sample and solvent at ambient temperature were placed in order to have a sample-solvent ratio (w/v) of 1:9.3. This ratio was considered convenient after some preliminary tests. The flask was stoppered to eliminate solvent evaporation. The whole system was placed on a magnetic stirrer and agitated gently. Five minutes before the specified contact time, the stirrer was stopped to allow the cake particles to settle. Part of the solution was filtered in order to eliminate suspended matter and an aliquot of 25 ml was placed on a weighted dish. The solution was evaporated gently to avoid spillage, and the weight of the remaining oil was obtained. The concentration obtained for the aliquot was applied to the total volume in the flask and in this way the extracted amount of oil was determined. The procedure was repeated for different contact times.

2.2 EXTRACTION TEMPERATURE

Enough oven dried cake sample was placed in an Erlenmeyer flask in order to have a sample solvent ratio (w/v) of 1:9.3 and put into a water bath at a constant preset temperature. In another flask immersed in the water bath, sufficient solvent was added. When the solvent and the cake had attained the same temperature as the water bath, the required amount of solvent was transferred to the flask with the cake sample, and this was stoppered to avoid evaporation losses. The time of contact was set at 60 minutes to give ample time to maximise extraction for all tests. The flask with sample and solvent was shaken regularly to produce a gentle agitation. Five minutes before time the agitation was stopped to facilitate settling of the cake particles. After

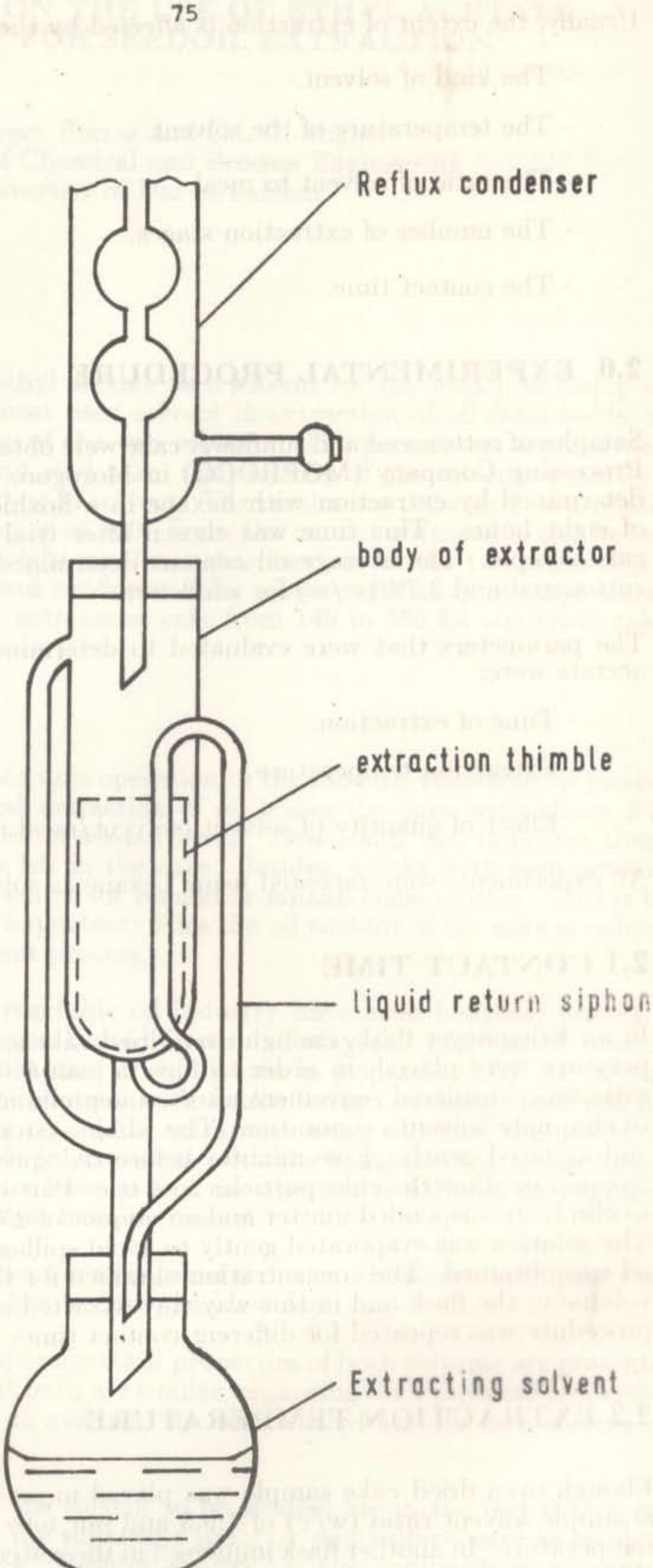

fig.1 SOXHLET EXTRACTOR

cooling the flask with chilled water, and filtering some of the liquid to remove suspended matter, an aliquot of 25 ml was withdrawn to determine total amount of oil extracted as above. The procedure was repeated for several temperatures.

2.3 QUANTITY OF SOLVENT

Enough oven-dried cake sample was placed in an Erlenmeyer flask and the same procedure as for the effect of temperature was followed. In this case the temperature was fixed at 50 °C and the contact time was fixed at 60 minutes. The procedure was repeated using different sample- solvent ratios.

2.4 TYPE OF SOLVENT

The purpose of this experiment was to compare ethyl acetate with other common solvents under similar conditions. The solvents chosen were hexane, trichloroethylene and benzene. For this experiment the following conditions were chosen: Time 4 hours, temperature 45 °C, and sample-solvent ratio 1:31 g:ml.

3.0 RESULTS

The interest is in the comparison of ethyl acetate with hexane as a solvent for oil extraction from seeds. This is the reason why the results, with the exception of Tables 2 to 4, are presented in a relative scale in which, for each experiment, the values of hexane are given a basis of 100 and then the values of ethyl acetate are determined accordingly. The figures presented summarise the results obtained. Tables 2 and 3 present some values of the oil extracted with both solvents for the cakes at two different extraction times. The tables show that the extraction of cottonseed cake is easier than for sunflower cake for both solvents. This effect has important implications in the behaviour of the solvents with the different parameters studied. Table 4 shows the results for the different solvents in an absolute form and also in a relative scale in which hexane has been given a value of 100.

4.0 DISCUSSION

4.1 EFFECT OF CONTACT TIME

Bernardini (1973) made research on the influence of the several parameters that affect seed oil extraction and came to the conclusion that extraction time has a fundamental importance to the amount of oil recovered from oilseeds. The greatest amount of oil is extracted during the first thirty minutes of extraction. An extremely long extraction time (not quantified) is required to obtain a residual oil content below 1%. He also found out that every type of seed behaves differently during the extraction process.

The behaviour, in agreement with Benardini (1973), is quite different depending on the type of cake treated (Fig. 2). For cottonseed cake, at short contact times of less than 60 minutes, the efficiency of ethyl acetate is less than that of hexane, but as time increases, its efficiency approaches that of hexane. On the other hand, for sunflower cake, the efficiency of ethyl acetate is almost 2.5 times that of hexane at short contact times. This efficiency diminishes as the contact time increases.

The reason for this difference in behaviour lies in the degree of difficulty with which the oil is removed from the seeds. In tables 2 and 3 it is shown that the extraction of oil from cottonseed cake is relatively easier than in sunflower cake. Also, from these

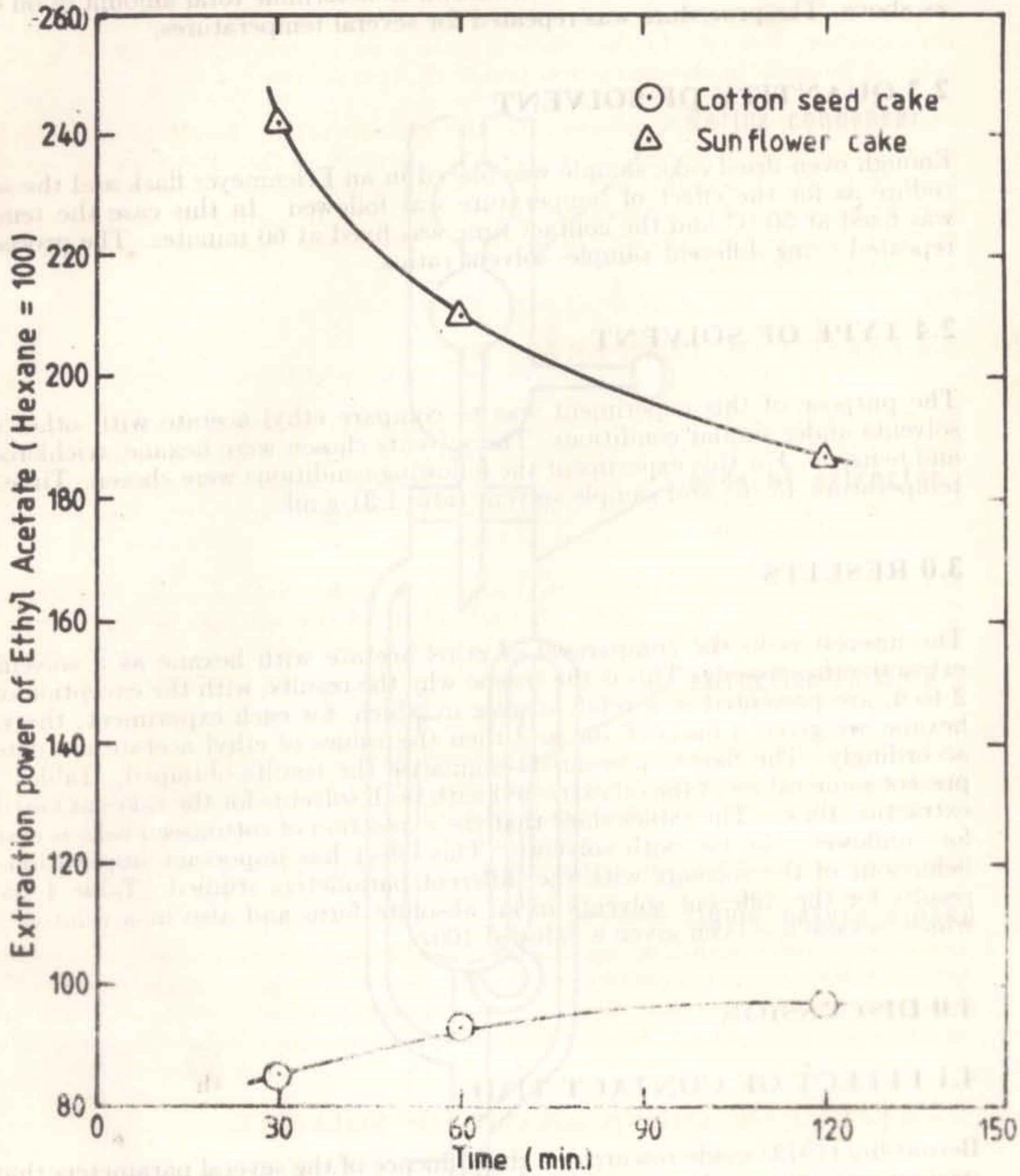

Fig. 2—Effect of contract time on the relative extraction power of Ethyl Acetate [temp. = 25 °C, solvent = 1.9·3 (g/ml)

Tables it is seen that ethyl acetate extracts a higher proportion of the oil in sunflower cake than in cotton seed cake. It is therefore clear that for the cotton seed cake, the hexane is becoming saturated before ethyl acetate as time increases, extracting, by consequence, less oil. In the relative scale used in figure 2 this effect is shown as a relative increase in the extraction power of ethyl acetate.

On the other hand, for sunflower cake, the opposite is true, and if the relative extraction power basis were reversed, it will show an increase in the extraction power of hexane relative to ethyl acetate; but as the hexane is the basis, the result is a decrease in the effectiveness of ethyl acetate; nevertheless the reduction in the efficiency of ethyl acetate changes from about 240 to about 190 for the time span evaluated, leaving it, still, as a better solvent.

4.2 EFFECT OF TEMPERATURE

In studying the influence of temperature in seed oil extraction, Bernardini (1973) found that the increase of solvent temperature, maintaining the extraction time and solvent to meal ratio constant, increased the extraction efficiency of oil from the seeds. However, for some of the seeds studied, a decrease in dissolving power was also observed when a temperature of 50 °C was exceeded.

For the selected contact time, ethyl acetate is more efficient as an extracting solvent than hexane (Fig. 3). Again, the behaviour of the solvents is very different from one type of seed cake to the other. For cottonseed cake, the " relative efficiency" of ethyl acetate increases as temperature increases, but for sunflower cake, it decreases as temperature increases.

In the case of cottonseed cake ethyl acetate becomes a better solvent than hexane as the temperature increases, extracting more oil per increment and as a consequence its " relative efficiency" increases above that of hexane.

For sunflower cake, as the extraction is more difficult and ethyl acetate is a much better solvent than hexane, it becomes relatively saturated faster than hexane and for this reason the increment in extraction is less than for hexane. Again if the relative extraction power could be reversed, it would show an increase in the efficiency of hexane relative to ethyl acetate; but as the case is the opposite, the effect is to show a reduction of the extraction efficiency of ethyl acetate relative to hexane. The reduction in efficiency, from about 200 to 180, however leaves ethyl acetate a better solvent.

4.3 EFFECT OF THE QUANTITY OF SOLVENT

When extraction time and temperature are constant, the amount of solvent influences the extraction of oil from a seed, up to a seed-solvent ratio (w/v) of 1:18 (Bernardini, 1973). With increase of this ratio, the oil yield increases only slightly. Beyond the ratio 1:88, there is no increase in the oil yield. The amount of solvent required to reduce the oil content of different seeds to the same value varies according to the type of seed. Oil seeds with a ligneous structure, such as grape or olive pomace, require a larger amount of solvent to attain the same residual oil as the other materials.

For the two types of seed cake studied (Fig. 4), the extraction power of ethyl acetate is higher than that of hexane. For cottonseed cake, at low solvent quantities the efficiency of ethyl acetate is high and as the cake-solvent ratio is increased the efficiencies of the two solvents tend to approach each other. For sunflower cake, the opposite phenomenon is observed; the efficiency of ethyl acetate increases as the quantity of solvent increases. Since ethyl acetate is a better solvent than hexane, as more of it is used to extract oil from a given weight of sunflower cake, it extracts relatively more oil than the equivalent quantity of hexane, hence a higher efficiency as the quantity of

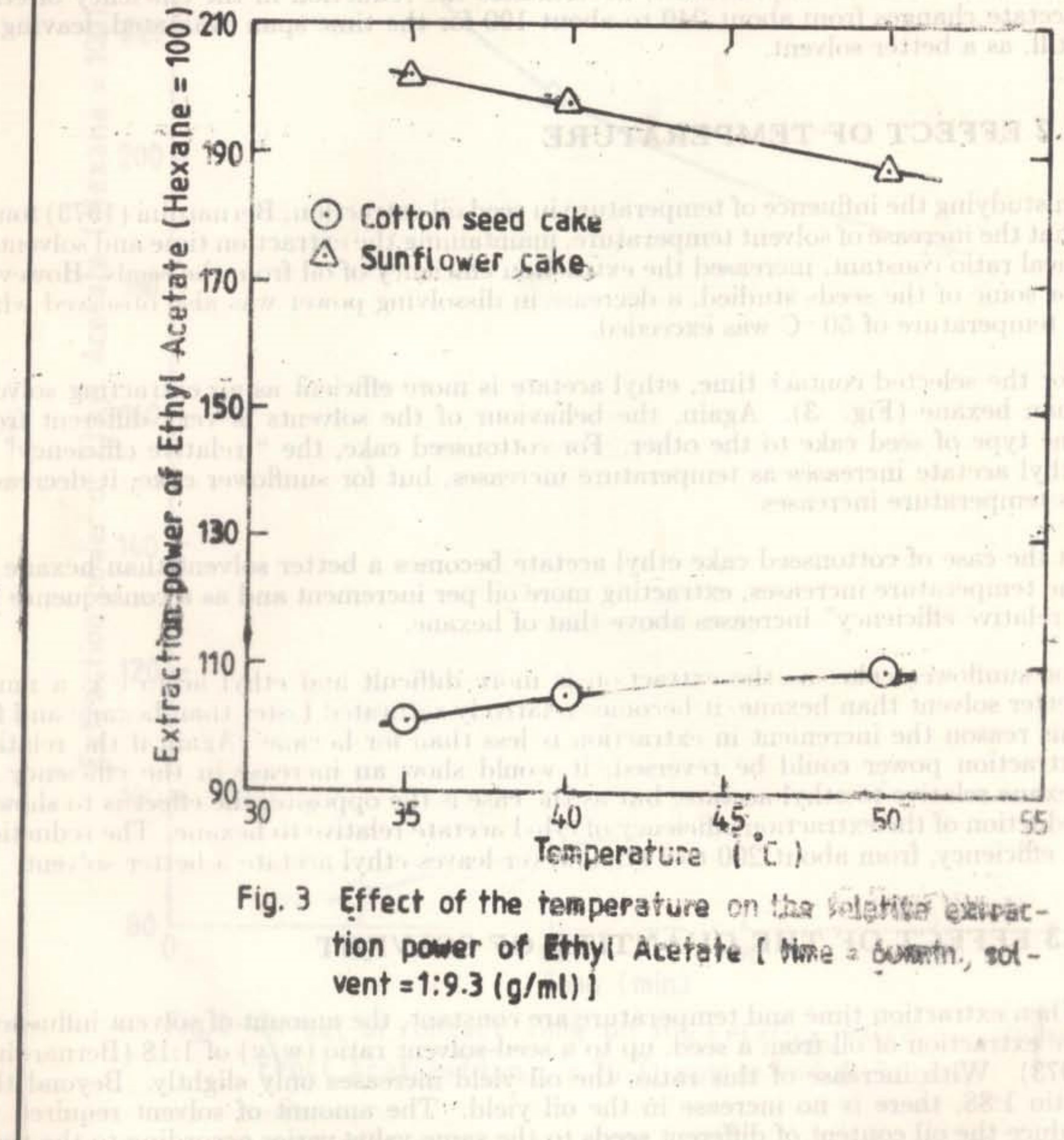

Fig. 3 Effect of the temperature on the relative extraction power of Ethyl Acetate (time = 60min., solvent =1:9.3 (g/ml))

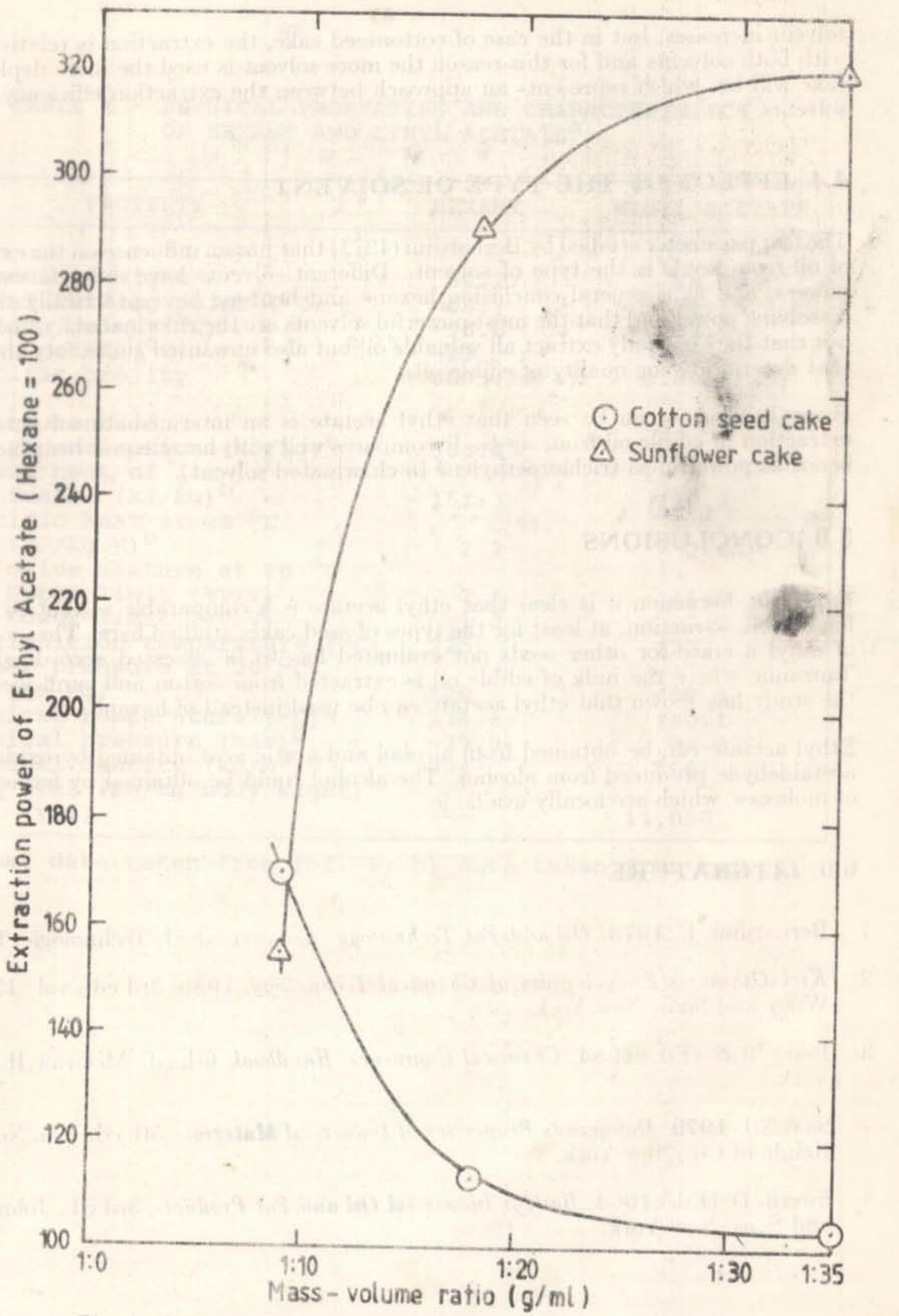

Fig. 4 – Effect of the quantity of solvent on the relative extraction power of Ethyl Acetate [time = 60 min., temp. = 50 °C]

solvent increases; but in the case of cottonseed cake, the extraction is relatively easy with both solvents and for this reason the more solvent is used the more depleted the cake will be, which represents an approach between the extraction efficiency of both solvents.

4.4 EFFECT OF THE TYPE OF SOLVENT

The last parameter studied by Bernardini (1973) that has an influence on the extraction of oil from seeds is the type of solvent. Different solvents have different extraction powers, and as a general conclusion hexane and benzene have practically the same dissolving power and that the most powerful solvents are the chlorinated hydrocarbons, but that they not only extract all valuable oil but also unwanted gums, fats and waxes that deteriorate the quality of edible oils.

From Table 4 it can be seen that ethyl acetate is an intermediate solvent for the extraction of edible oil from seeds. It compares well with hexane and benzene, but it is not as powerful as trichloroethylene (a chlorinated solvent).

5.0 CONCLUSIONS

From the discussion it is clear that ethyl acetate is a comparable solvent to hexane for seedoil extraction, at least for the types of seed cakes studied here. The suitability of ethyl acetate for other seeds not evaluated has to be assessed accordingly. For Tanzania, where the bulk of edible oil is extracted from cotton and sunflower seeds the study has shown that ethyl acetate can be used instead of hexane.

Ethyl acetate can be obtained from alcohol and acetic acid obtained by oxidation of acetaldehyde produced from alcohol. The alcohol could be obtained by fermentation of molasses, which are locally available.

6.0 LITERATURE

1. Bernardini, E., 1973. *Oil and Fat Technology*, 2nd revised ed., Technologie, Rome.

2. *Kirk-Othmer's Encyclopedia of Chemical Technology*, 1980. 3rd ed., vol. 12. John Wiley and Sons, New York.

3. Perry, R.H. (Ed.) 1984. *Chemical Engineers' Handbook*. 6th ed., McGraw Hill, New York.

4. Sax, N.I. 1979. *Dangerous Properties of Industrial Material*, 5th ed., Van Nostrand Reinhold Co., New York.

5. Swern, D. (Ed.), 1964. *Baileys Industrial Oil and Fat Products*, 3rd ed., John Wiley and Sons, New York.

TABLE 1 - PHYSICAL PROPERTIES AND CHARACTERISTICS OF HEXANE AND ETHYL ACETATE[a]

PROPERTY	HEXANE	ETHYL ACETATE
Molecular weight	86.17	88.10
Normal boiling point (°C)	68.7	77.15
Melting point (°C)	-95.6	-83.6
Flash point (°C)	-22	-5
Specific gravity	0.6603(20/4)	0.8946(25)
Latent heat of vapourization (kJ/kg)[b]	366.4	427.1
Latent heat of fusion (kJ/kg)[b]	151.3	119.2
Specific heat at 20 °C (kJ/kg.K)[b]	2.2	2.0
Explosive mixture at 20 °C		
Upper limit (%V/V)	7.5	11.0
Lower limit (%V/V)	1.2	2.2
Autoignition temperature (°C)	225	427
Vapour pressure at 20 °C (mm Hg)[b]	120	72.5
Critical temperature (°C)[b]	234.8	250.1
Critical pressure (bar)[b]	29.9	38.3
Critical density (kg/m^3)[b]	234	308
LD_{50} Oral (mg/kg body wight) (rat)	---	11,000

a) most data taken from ref. 5; b) data taken from ref. 4

TABLE 2- OIL EXTRACTED AFTER THE FIRST 30 MINUTES OF CONTACT

	HEXANE		ETHYL ACETATE	
	Cottonseed cake	Sunflower cake	Cottonseed cake	Sunflower cake
Weight of sample (g)	92.78	93.10	92.66	92.30
Oil content in sample (g)	9.26	3.47	9.25	3.44
Oil extracted (g)	7.91	0.55	6.70	1.32
Percent extracted (%)	85.4	15.8	72.4	38.4

TABLE 3 - OIL EXTRACTED AFTER 120 MINUTES OF CONTACT

	HEXANE		ETHYL ACETATE	
	Cottonseed cake	Sunflower cake	Cottonseed cake	Sunflower cake
Weight of sample (g)	94.26	93.60	94.40	93.50
Oil content in sample (g)	9.41	3.49	9.42	3.49
Oil extracted (g)	8.85	0.78	8.56	1.45
Percent extracted (%)	94.1	22.4	90.8	41.6

TABLE 4 - DISSOLVING POWER OF SOME COMMON SOLVENTS
(Time: 4 hrs; Temperature: 45 ^{o}; Solvent: 465 ml)

	HEXANE		ETHYL ACETATE	
	Cottonseed cake	Sunflower cake	Cottonseed cake	Sunflower cake
Percent extracted	7.5	2.4	7.8	3.7
Relative extraction	100	100	104	154
	TRICHLOROETHYLENE		BENZENE	
	Cottonseed cake	Sunflower cake	Cottonseed cake	Sunflower cake
Percent extracted	8.7	3.7	7.6	2.5
Relative extraction	115	155	102	103