Extraction of Cottonseed Oil Using Subcritical Water Technology

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This work represents the extraction of cottonseed oil using subcritical water. The extraction efficiencies of different range temperatures (180–280°C), having mean particle size range from 3 mm to less than 0.5 mm, water:seed ratios of 0.5:1, 1:1, and 2:1, and extraction times in the range of 5–60 min were all investigated. The composition of the extracted oil, using the subcritical water, was analyzed by gas-liquid chromatography and compared with that extracted using traditional hexane extraction. The results showed that the optimum temperature, mean particle size, water:seed ratio, and extraction time were 270°C, <0.5 mm, 2:1, and 30 min, respectively. In addition the extracted oil was identical to that extracted using the traditional hexane method.
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Keywords: extraction, cottonseed oil, subcritical water, oil extraction, water as a solvent

Introduction

Cotton plants are widely distributed and mainly cultivated for both their flowers (the cotton itself) and seeds in different countries, especially in Egypt where the soil and weather are most suitable for its cultivation.

In the past, the cottonseed oil extraction was done by applying manual powered mechanical pressure to squeeze the oil from the seed. This was very labor intensive and at best one half of the oil contained in the seed could be extracted. Nowadays, cottonseed oil is mostly extracted using the solvent extraction technique, mainly hexane is used as the solvent. The extraction process could be simply described as a leaching process in which solid or liquid components are removed and recovered from a solid mass by solvent extraction. Cottonseed oil extraction in modern factories involves a number of steps. These steps are tedious and incorporate many complicated procedures. Those include seed preparation, primer pressing, and steam cooking to facilitate the solvent extraction process. In addition, the extraction step itself takes a very long time approaching almost 8 h as an extraction residence time.

Lately, subcritical water technology has attracted many researchers for its versatile applications in the field of environment as a green alternative process than solvent extraction. On heating within the critical point of water (temperature <374°C, pressure 22.1 < MPa) under enough pressure to maintain the liquid state. Water (subcritical water in this state) was reported to have distinctive properties, such as a low dielectric constant and a high ion product.[1,2] Many extractable components from different biomass could be easily extracted under these conditions.

The development of such technique has passed over many periods. In 1950, Fred Zimmerman and his staff developed a completely new method of obtaining vanillin (a pleasant smelling aromatic compound) directly from pulping liquor.[3] Then in 1966, John Connolly of Standard Oil Corporation published remarkable data on hydrocarbon solubility in water at high temperatures and pressures.[4] In 1970 Gerhard

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Schneider suggested the extension of wet air oxidation to higher temperatures for disposal of organic materials.[5] In the early 1970s, the properties of super-critical fluids (e.g., changes in solubility and diffusivity with temperature and pressure) were discovered at Max Planck Institute.[6] Since 1982 many patents by General Atomics Company (GA) including reactor designs, solids handling, effluent quenching, reaction rate enhancers, heat transfer, and corrosion resistant materials have been developed.[7]

Authors of this article have carried out many extraction processes using the subcritical water technology as well as synthesis of new materials.[8–11]

Extraction of compounds from natural sources is the most important application of subcritical water. In 1999, Hiroyuki Yoshida, showed that a relatively large amount of oil, organic acids, and amino acids could be extracted from fish, squid entrails and meat wastes by subcritical water treatment.[12,13]

The essential oil from plants has been extracted by using subcritical water. Usually the oil in these plants is traditionally extracted either using steam distillation[5,6] or solvent extraction.[12–15] These techniques present some shortcomings, namely losses of volatile compounds, low extraction efficiency, long extraction time, degradation of unsaturated compounds, and toxic solvent residue. That encourages the use of alternative techniques for the extraction of essential oils.[16] Continuous subcritical water extraction presented a powerful alternative for solid sample extraction.[17–19] Its use in the field of essential oils is recent and seems to be very promising.[20,21]

The aim of this work was to investigate the use of subcritical water to extract oil from the cottonseed. With a typical weight of 10 g, the results were compared with those obtained by traditional techniques to study the advantages of using subcritical water method for the extraction of cottonseed oil.

Materials and Methods

Materials

All chemicals and materials used in this work were locally manufactured in Egypt, where the extraction processes pass through many steps that use different materials. The cottonseeds used in this study were obtained from Henderson factory (Elminia, Egypt), which were the same as those used in the traditional solvent extraction process employed in the factory. Hexane used for measuring the extracted oil in water is produced by El-Nasr Chemical (Cairo, Egypt). Distilled water, prepared at Elminia University in Egypt, was used as an extracting solvent in subcritical water extraction. A mixture of edible oil (sunflower oil) and paraffin wax was used as the heating medium for subcritical water extraction. This mixture could reach up to 290°C without boiling. Both compounds were obtained from local markets in Elminia, Egypt.

Sample Preparation. Fresh seeds were stored in polyethylene bags at room temperature and samples of 10 g of seed were used for the extraction process. Before the seeds were used they underwent many procedures such as dehulling and cleaning to remove impurities.

Methods

Hexane Extraction. Before starting the experiments, the amount of oil contained in the seeds was measured. Dried cottonseeds used in this study were dehulled and the oil was extracted by hexane. Ten grams of dehulled seeds were contained in a 50-ml plastic container and 40 ml of hexane were added to the seeds. The plastic container was then tightly closed and mixed using a rotating mixing machine, which was put inside an oven adjusted at 45°C.

Subcritical Water Extraction. The subcritical water extraction was carried out in laboratory–built apparatus consists of a heating bath installed with agitator. After the preparation step, the subcritical water extraction was carried out in stainless steel pipes SUS 316, i.d. 0.0168×0.15 m^2 (with a reactor volume of 34×10^{-6} m^3) with Swadgelok caps. The seeds and estimated amount of water were then charged into the reactor tube. The reactor was then sealed and immersed in a preheated oil-paraffin bath (Thomas Kagaku). It is very important to note here as a safety comment that the sealed tube should not be overfilled to prevent hydrolytic pressure of the expanding liquid from the fracturing the tube vessel The extraction was carried out in the range of 180–280°C, and the pressure inside the reactor was estimated from the steam table for the subcritical conditions (saturated steam). After the desired reaction time, the reactor was immediately cooled down by immersing it into a cold-water bath. The extraction product was separated into three phases, the oil phase, the aqueous phase (including oil and water), and the solid phase, using a centrifuge and filter to separate the oil phase from the aqueous phase and the solid phase.

For the separated aqueous phase, recovery of all oil produced from the water layer was done by adding hexane to extract any oil that could be emulsified into the water. Then, the hexane was evaporated by heating in a furnace at 80°C. The extracted oil was then weighed and the data was recorded. The experiments were done in some cases in double or triple to avoid any uncertainty.

Analyzing the extracted Oil

The composition of the extracted oil using, using the subcritical water, was analyzed by gas liquid chromatograph model HP 6890, equipped with a BD-23 column(60 m $\times$ 0.32 mm $\times$ 0.23 μm) using carrier gases of H_2, N_2, and air with flow rates of 40, 3, 450 ml/min, respectively. The detector was operating at 250°C, with injector at 230°C.

Results and Discussion

The first step was to measure the amount of oil contained in the cottonseeds used in the study. Following the procedures described in the materials and methods, it was found that the oil content represents 15% by weight based on the dry weight of the dehulled seeds. This percent was taken as the maximum oil content of the used cottonseed. The yield of oil extraction using subcritical water was based on this oil content and is calculated as:

$$\text{Yield } \% = \frac{\text{The weight of extracted oil}}{\text{The weight of dehulled seed used in the experiment} \times 0.15} \times 100$$

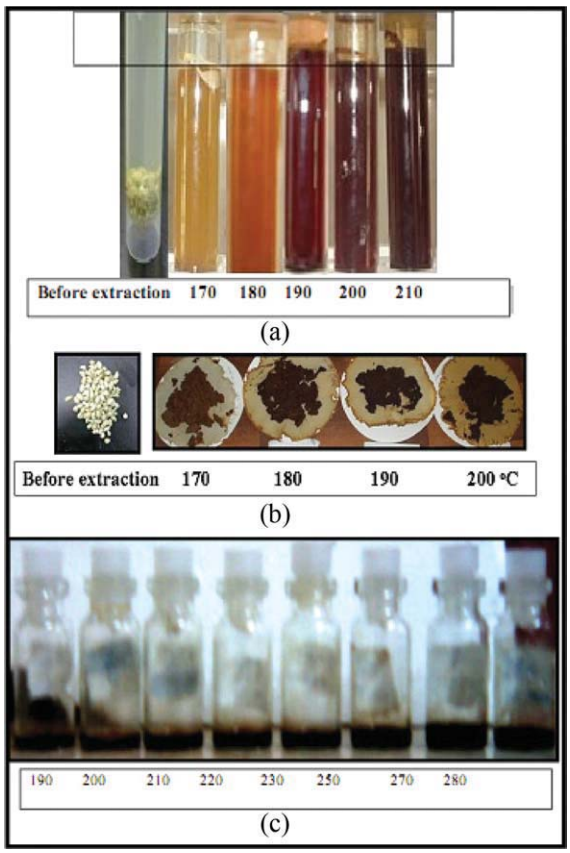


Figure 1. (a) Photographs of the extraction products of the cottonseed extraction at different temperatures in the range of 170–210°C, (b) the solid residual, and (c) the final extracted oil in the range of 190–280°C.

[Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Now to discuss the extraction conditions, the extraction process was carried out under different operating conditions to find the optimum conditions as shown in Figure 1, so in each time only one parameter changed while the other extraction parameters were kept constant. The extraction parameters were classified as temperature of extraction, extraction time, solvent (water) to seed ratio, particle size, and seeds pretreatment.

First, the effect of temperature on the extraction process by changing the extraction temperature and keeping other parameters constant. The temperatures tested were: 180–280°C. Figures 2a, b show the effect of extraction temperature on the overall yield of extracted oil and the total solid residual for 10 min of extraction time using 10 g of dehulled and uncrushed seed (with 3 mm diameter). The separation of oil was done through a filtration procedure to measure the extracted oil content accurately. The calculations were done based on a maximum extraction yield of 15% oil content. The results showed that the maximum yield of extraction could be obtained at 270°C. The maximum value was 0.33 g of extracted oil (which represents 21.7% of the maximum oil content of 1.5 g). However, the measurements of solid residual during the extraction course showed a linear reduction in the solid residual content when increasing the temperature.

Second was to determine the optimum extraction time by changing the extraction time. The extraction was carried out at temperature 190, 200, 210, 230, 250, and 270°C, only the figures represent the results of 190, 250, and 270°C are shown to minimized the number of presented data, and water to seed ratio of 2:1 (optimum extraction temperature and water to seed ratio, respectively). Extraction times were tested in the range of 5–60 min while keeping other parameters constant. Based on these conditions, the experiments were accomplished and the optimum extraction time and solid residue were determined. The results in Figures 3a, 4a, and 5a show that when increasing the extraction temperature, the yield of oil extracted increased while the residual solid decreased. Also, the peak (maximum yield at applied temperature) is reached earlier as the temperature increases. However, it was observed that the yield of oil extracted increased up to a maximum value then it started to decrease

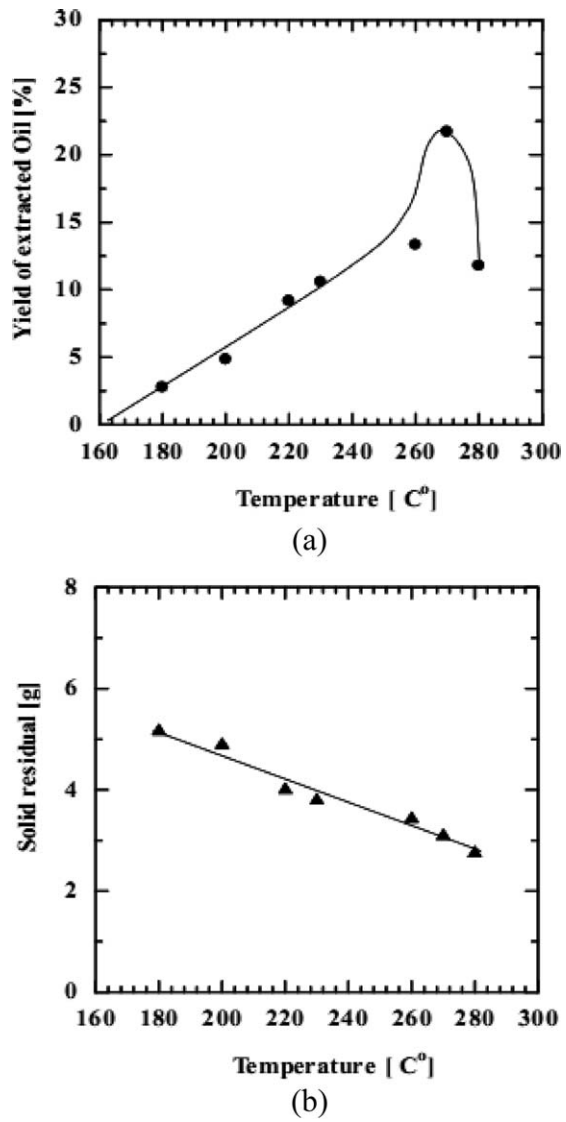


Figure 2. Effect of extraction temperature on the oil extraction (a) and the solid residual (b) at 10 min, water:seed ratio 2:1, using 10 g of seed within 3 mm diameter.

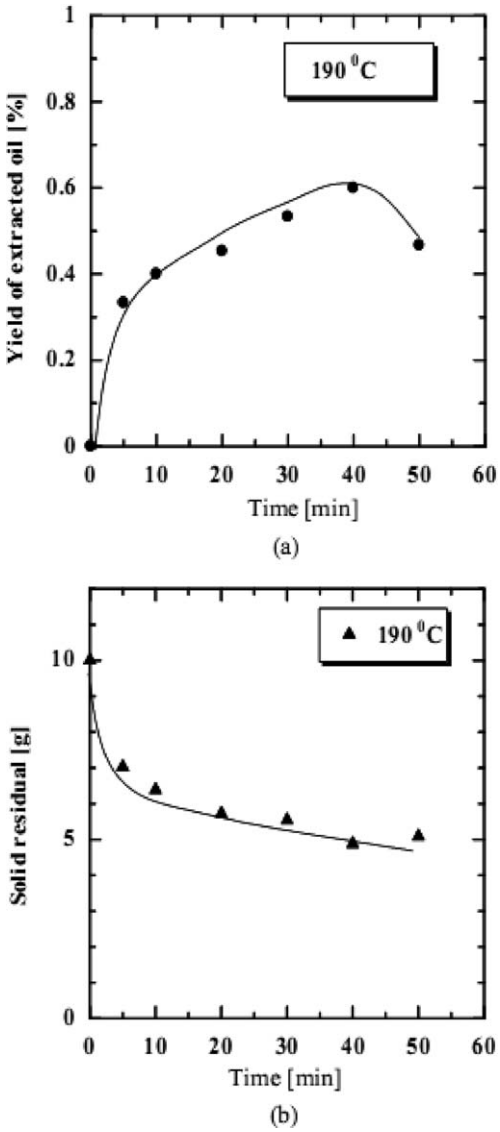


Figure 3. Effect of extraction time on the oil extraction (a) and solid residual (b) at 190°C, water:seed ratio 2:1, using 10 g of seed within 3 mm diameter.

by increasing the extraction time. Such reduction in oil yields by increasing the extraction time is due to the decomposition of some extracted oil. Also, it was observed that increasing the yield is done through increasing the extraction temperature. Maximum extraction yield was in the range of 20–40 min and recorded 0.6, 19, and 56%, for extraction temperatures of 190, 250, and 270°C, respectively. It is important to note here that the extraction time was longer at extraction temperature of 270°C than other temperatures. It is important to note here that for extraction temperature of 270°C, the optimum extraction time was different from that of other temperatures, which it was longer. This could be explained in the bases of transformation of the fat into the oil phase as a free fatty acid due to the higher temperature and extraction time in this case. Moreover, it was not possible to measure the solid residual after reaction time of 20 min because the solid became very fine and very law in its content.

However, Figures 3b, 4b, and 5b showed that the solid residual values were decreasing with the increase in the extraction time until it almost reached a plateau. Also, the rate of reduction in the solid residual was increasing by the increase in extraction temperatures.

The optimum extraction temperature and time have been determined. Now, the effect of solvent-feed ratio on the extraction yield was studied, where the solvent is water and the feed is the cottonseed. Accordingly, the extraction process was carried out under different water:seed ratios and the extraction yields were compared. Figure 6 shows the effect of the water:seed ratio on the yield of oil in the range of 0.5:1 to 2:1. Experiments were carried out at 270°C for 10 min extraction time using dehulled-uncrushed seeds. It was

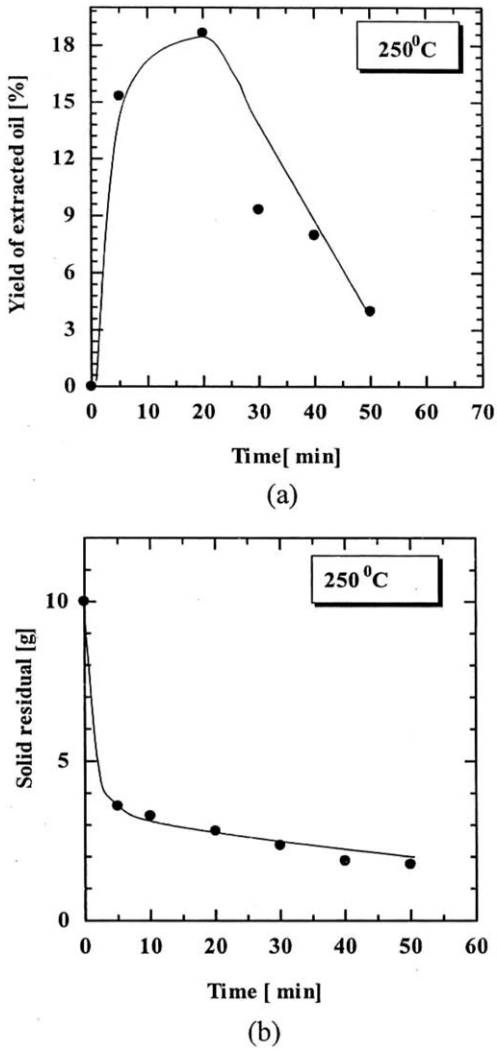
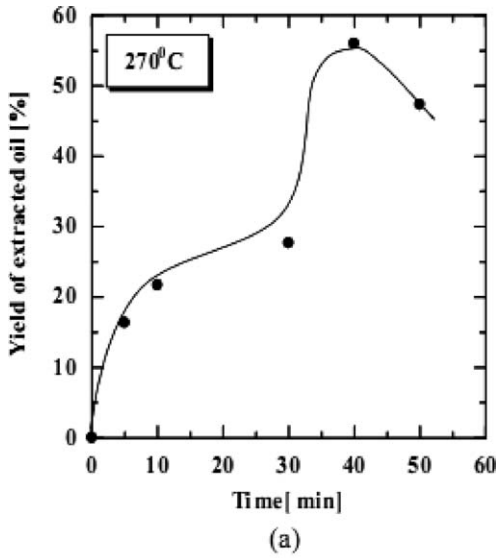


Figure 4. Effect of extraction time on the oil extraction (a) and solid residual (b) at 250°C, water:seed ratio 2:1, using 10 g of seed within 3 mm diameter.



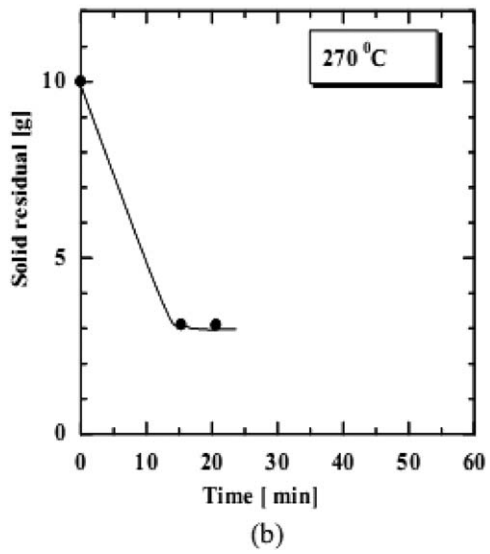


Figure 5. Effect of extraction time on the oil extraction (a) and solid residual (b) at 270°C, water:seed ratio 2:1, using 10 g of seed within 3 mm diameter.

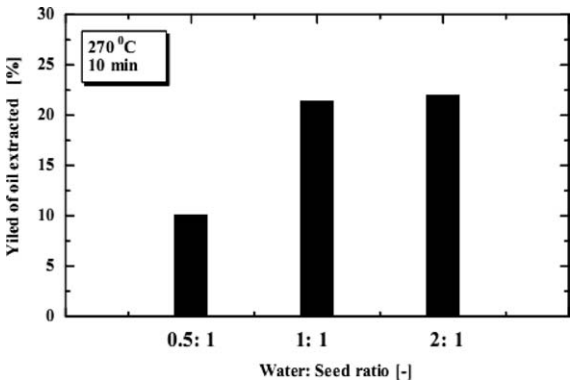


Figure 6. Effect of the water:seed ratio on the yield of the oil extraction at 270°C for 10 min extraction time and using 10 g of seed within 3 mm diameter.

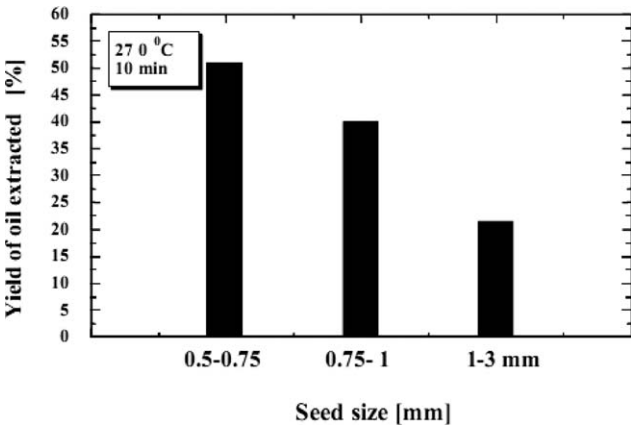


Figure 7. The effect of the particle size on the yield of the oil extraction at 270°C for 10 min extraction time and water:seed ratio 2:1.

clearly found that by increasing the ratio of water (the solvent) to seed the yield of extraction increased too. The maximum extraction yield was 22% at water:seed ratio of 2:1. It was found that there was no significant difference between the results of 1:1 and 2:1 ratios. In addition, it is very important to note that increasing the amount of water above 2:1 could not happen, because of the dramatic increase of the pressure inside the reactor which hindered the easy opening of the reactor and led to explosion-like performance during the opening of the reactor to recover the extraction product.

Regarding the previous optimum data, now the effect of the particle size of the seeds on extraction yield will be discussed. It is considered as an important parameter in oil extraction due to its effect in minimizing the diffusion limitations during the extraction process. The extraction process was done at 270°C using water to seed ratio of 2:1 for 10 min for three different particle sizes. The results in Figure 7 show that the extraction yield increases with the decrease in the particle size, where a maximum yield of 51% was obtained from seeds with particle size of 0.5–0.75 mm.

Finally, it is important to obtain the maximum oil yield, where the extraction process was followed under the optimum conditions. Figure 8 shows the effect of the extracting

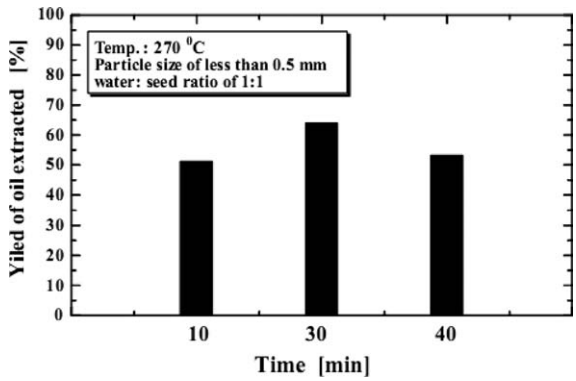


Figure 8. The effect of extraction time on the yield of the oil extraction under the obtained optimum conditions.

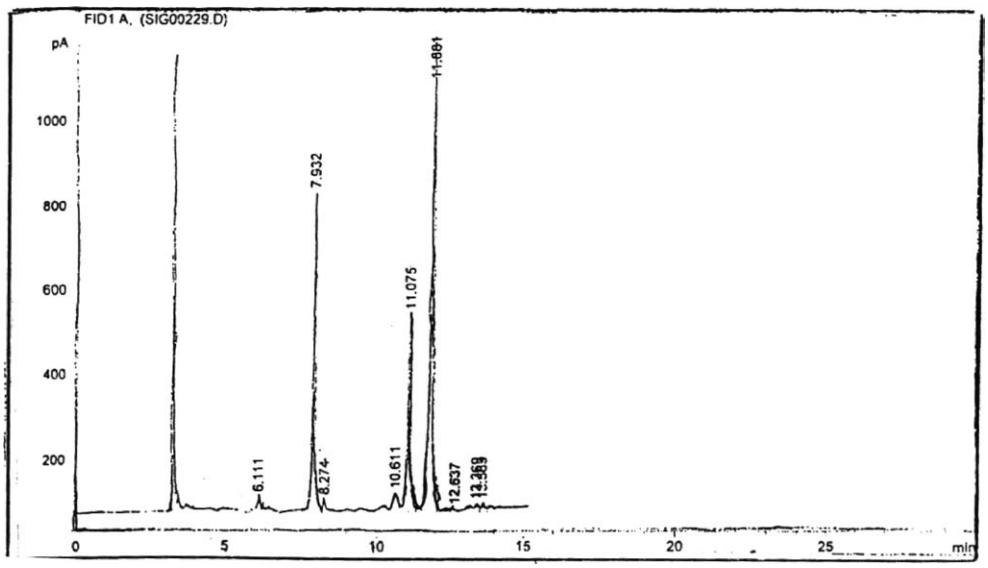


Figure 9. The gas-liquid chromatographic of the extracted cottonseed oil using subcritical water.

time on the yield of extraction at 270°C using powdered seeds (<0.5 mm) and water:seed ratio of 1:1. The results showed that the maximum yield was 64% from the oil contained originally in the seeds. Accordingly, the optimum conditions of subcritical water extraction of cottonseed oil would be as follows:

- Extraction temperature: 270°C
- Time: 30 min.
- Water:seed ratio: 1:1
- Particle size: <0.5 mm

Analysis of the extracted oil

The last step in this research was to make sure that the obtained oil was not decomposed during the extraction process as well as it being safe to be used as edible oil. The result of the gas-liquid chromatograph is shown in Figure 9.

Table 1 shows a comparison between the fatty acid compositions for cottonseed oil extracted with hexane and subcritical water. The obtained results indicated practically no difference in the fatty acid compositions of the cottonseed oil extracted with the subcritical water method with that extracted by hexane.

Conclusion

In this work subcritical water has been used as a new pathway for cottonseed oil extraction. The main conclusions from this work are that the optimum oil extraction temperature is 270°C, the optimum extraction time is 30 min, the optimum solvent: feed ratio is 1:1, and the optimum particle size is <0.5 mm.

Comparing this technique with the traditional hexane extraction method, it is found that the new technique has a shorter time of extraction providing an environmentally friendly proceeding, since it uses water as the solvent and no organic solvents are involved.

Table 1. Comparision Between the Compositions of the Oil Extracted by Hexane and Subcritical Water

Fatty acid	Linoleic	Palmatic	Oleic	Stearic	Myristic
Heaxane extraction	47–50	25–28	22–22.7	0–0.4	0.8–0.9
Subcritical water Extraction	47	25	21	0.3	0.9

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