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Spent Bleaching Earth Treatment in a Pilot Scale Tubular Reactor using Subcritical Water Technology

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Abstract

This work represents the extraction of oilsand free fatty acids from the spent bleaching earth using sub-critical water as a solvent in pilot scale batch reactors. Prior to using the pilot scale reactors, the extraction conditions were optimized using laboratory small batch reactor of 34 cm³ volume. The optimization of the extraction condition showed that the optimum temperature, feed to solvent ratio, and extraction time were 270 °C, 1:3(the solvent is just water), 20 min. The obtained data were used to design tubularreactor with 7 Kg capacity heated with an electric heater. The extraction was carried out using 750 grams of the spent bleaching earth with 1:3 ratio. The results showed that more than 95% of the oil absorbed in the spent bleaching earth was recovered under 210 °C. The heating up period was 72 minutes with holding extraction time of 20 minutes at 210 °C and cooling down for 25 minutes.

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Introduction

Bleaching earths are natural or acid-activated bentonite clays that are extensively used for refining edible oils as they adsorb color and other impurities and improve the oil flavor and stability. Spent bleaching earth (SBE) usually contains between 17 and 28 weight (wt) % oil which is not removed during a final filter pressing process.

Edible-oils refining involves the treatment of degummed and neutralized oil with bleaching clay to eliminate dissolved coloring materials and to reduce the quantity of oxidizing matter. The oil content of the spent bleaching clays is in the range from 20 to 40 wt. %. This oil represents a large part of the cost of bleaching and it is important to be recovered [1]. The cost of the spent clay with its oil contents comprises a considerable portion of the total refining cost. The disposal of spent bleaching clays in landfills can cause environmental pollution problems in addition to being a source of odors and fire hazards. This problem can be solved by developing a process for the recovery of the oil entrained in the spent clay followed by the regeneration of the de-oiled clay for the reuse.

Solvent extraction processes for recovery of oil from bleaching residues have been suggested because they give higher yields and better quality of oil compared to other methods, provided that the process is carried out on fresh residues [1-5]. The extracted clays may be used in bleaching, either directly or after activation with acids. Solvent extraction followed by burning at 400°C is reported as a method which produces more active clay than the original [2-3]. A low molecular weight ketone was found to be the most effective solvent for bleaching powder [4]. Funayama[5] reported the removal of sorbed oil from the spent catalysts and other inorganic materials. Kheoh[6] studied the reactivation of spent bleaching clay. The reactivation process involves washing of the spent earth from edible oil bleaching with organic solvents to remove fats, colored compounds and organic impurities with subsequent solvent removal. The preferred solvents are acetone and methylethylketone (MEK). Sakakura[7], described a solvent extraction method to recover oil and fats which can be used for food. DeFilippi and Chung [8] studied the extraction of silicone oil and soybean oil from bleaching clays using halocarbon and hydrocarbon solvents. They also reported an economical evaluation of a plant based on critical fluid extraction for recovery of silicone oil from spent bleaching clay. They concluded that such a plant will pay out favorably due to the credits for recovered oil; however, in their economical evaluation they did not consider the possibility of a process in which both oil recovery and regeneration of the spent clay are carried out simultaneously.

The principles of green chemistry are critically important today, and pressurized hot water extraction, as a "solvent less" extraction technique fulfills the criteria of green chemistry well. According to definition, green chemistry involves approaches that reduce or eliminate the use or generation of hazardous substances in the design, manufacture and application of chemical products. Lately, subcritical water technology has attracted many researchers for its versatile applications in the field of environment as a green alternative process to 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. Many extractable components from different biomasses could be easily extracted under these conditions. Extraction of compounds from natural sources is the most important application of sub-critical 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 sub-critical water treatment [9, 10]. The essential oil from plants has been extracted by using sub-critical water. Usually the oil in these plants is traditionally extracted either using

steam distillation [11, 12] or solvent extraction [13–15]. 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 sub-critical 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].

At ambient conditions the relative permittivity, or dielectric constant, of water is high, about 80. Under these conditions water is a polar solvent and it can be applied for the extraction of polar compounds because “like dissolves like”. The relative permittivity of water drops when the temperature is increased with sufficient pressure to maintain the liquid state [9]. At 250°C (pressure 50 bar), for example, the relative permittivity of water is only about 27, which is comparable to the relative permittivity of ethanol at 25°C and 10 bar. Consequently, water at 250°C and above can be applied for the extraction of non-polar compounds.

In the present work, the extraction of oils and free fatty acids from the spent bleaching earth using sub-critical water as a solvent in a pilot scale tubular reactor to validate the scalability of the process for industrial application.

2. Materials and Methods

2.1 Materials

The bleaching earth used in this work was supplied by EL MANAR plant, El-Nobareyya city, El-Beheya governorate (province), Egypt. Distilled water produced in the Chemical Engineering department, Minia University, was used as an extracting solvent in subcritical water extraction. Ethanol was used (as solvent) for titration to determine free fatty acids. Methanol was used as solvent for Thin Layer Chromatography (TLC) analysis to determine mono-, di-, and triglycerides, chloroform was used as solvent for TLC analysis to prove the existence of the mono-, di-, and triglycerides; and NaOH was used as a catalyst and in titration of the free fatty acid. The TLC plates (Kieselgel 60 F254 precoated plates) E. Merck, Darmstadt, Germany.

2.2.1 Measuring of Oil Content in the Bleaching Earth

Before starting the experiments, the amount of oil contained in the spent bleaching earth (SBE) was measured. SBE as delivered from EL MANAR plant was extracted by petroleum ether. Five grams of SBE were contained in a 500-ml container with a sealed cap and 200 ml of petroleum ether were added to the SBE. The container was then tightly closed and mixed using a magnetic stirrer over a hotplate adjusted at 45. The SBE was separated from the extraction mixture by filtration. Then, the extracted oil was recovered by evaporating the solvent.

2.2.2. Subcritical Water Extraction (SCWE) Using Bench Scale Reactor

The SCWE was carried out in a laboratory-built apparatus as shown in figure 1. It was carried out in stainless steel pipes SUS 316, 1.68 cm inner diameter and 15 cm height (with a reactor volume of 34 cm³) with Swagelok caps. The bleaching earth was charged into the reactor tube, then distilled water was added as an extraction solvent. The reactor was sealed and immersed in a heating bath (Thomas Kagaku Co. Ltd.). The extraction was carried out in the range of 180°C - 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 water bath at normal ambient temperature of about 20-25 °C. The extraction product was separated into three phases: the oil phase, the aqueous phase (including oil and water), and the solid phase. The three phases were

separated through simple centrifugation and vacuum filtration processes. To recover any traces of oil from the aqueous phase, petroleum ether was added to extract any oil that could be emulsified into the water phase. Then, the petroleum ether was evaporated at 80°C. The extracted oil was then weighed.

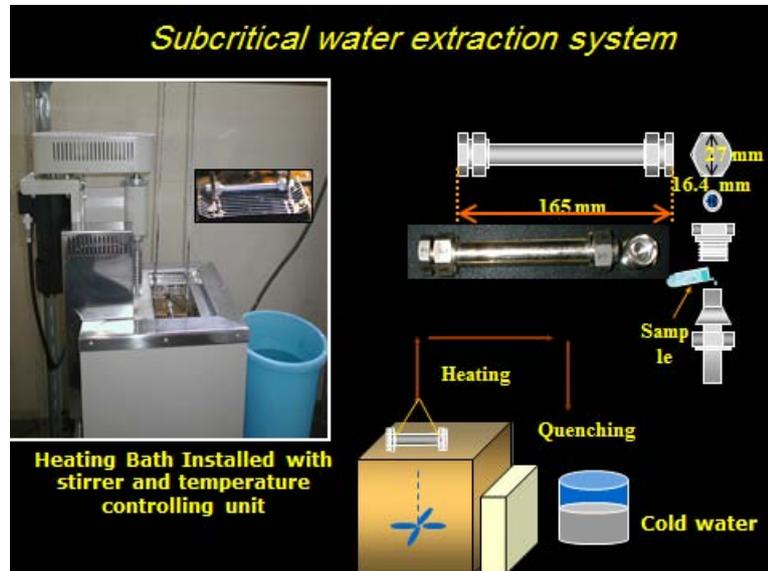


Figure 1: The experimental set of the SCWE using bench scale reactor.

2.2.2. Subcritical Water Extraction using Pilot Scale

For testing the validity of the obtained results in the bench scale, two different batch reactors were designed and manufactured. The first design based on large tank reactor with bottom heating. The reactor was manufactured using a cylindrical stainless steel SUS 316, 50 cm inner diameter and height of 70 cm with 30 liter total volume. **Figure 2** shows an image of the reactor. For the second design, tubular type batch reactor with was manufactured using stainless steel SUS 316, 13.2 cm inner diameter and 56.8 cm height with 7 liter total volume. The reactor was heated through a wound electrical heater as shown in **Figure 3**.

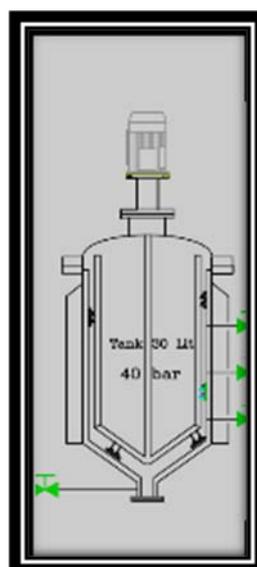


Figure 2: The tank batch reactor

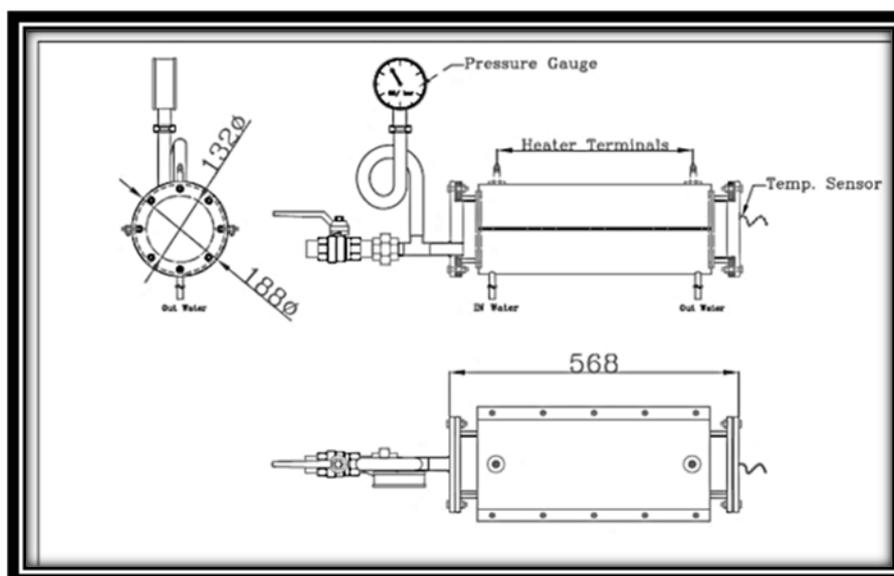


Figure 3: The tubular batch reactor.

Running the batch reactors

In both different reactor, 750gm of the bleaching earth was charged into the reactor tube and tap water was added with 1:3 ratio (2.250 L) then the temperature were raised gradually until reaching the target temperature. For the tankbatch reactor, the maximum obtained temperature was 130 °C and the tank batch reactor electrical coil was damaged in addition, the heating period took more than 70 minutes. Accordingly, the tubular reactor was designed and used to overcome such technical problem. The maximum reach temperature was 210 °C. The bleaching powder was mixed with hot water at 79 °C and charged to the reactor.

Through a control unit, the temperature and time were followed. For the tubular reactor the extraction was carried out in a batch mode using 750 gram of the spent bleaching earth with 1:3 ratio, (the solvent is just water). More than 95% of the oil absorbed in the spent bleaching earth was recovered under 210 °C. The heating up period was 72 minutes with holding extraction time of 20 minutes at 210 °C and cooling down was 25 minutes.

3. Results and Discussion

The first step was to estimate the amount of oil contained in the bleaching earth used in the study. The oil content in SBE was easily measured according to the method described and found to be 25% by weight based on the dry weight of the bleaching earth. This percentage was taken as the maximum oil content of the used earth. The yield of oil extraction using subcritical water was based on this oil content and was calculated as in the following equation:

$$\text{Yield \%} = \frac{\text{The weight of extracted oil}}{\text{The weight of bleaching earth used in the experiment} \times 0.25} \times 100$$

To find out the optimum extraction conditions, the extraction process was carried out under different conditions. The tested parameters were the temperature, time of extraction and the feed-to-solvent ratio. To study the effect of temperature on the extraction process, the subcritical water extraction process was carried out by changing the extraction temperature while keeping other parameters constant. The temperatures tested were in the range of 180°C - 280°C. The extraction time was in the range of 5 to 50 minutes while keeping other parameters constant. Based on these conditions, the experiments were accomplished and the optimum extraction time and solid residue were determined. The tested feed-to-solvent ratios were 1:1, 1:2, 1:3, 1:4 and 1:5 to get its optimum value. Figures 4-6 show the effect of the studied parameters on the overall extraction yield.

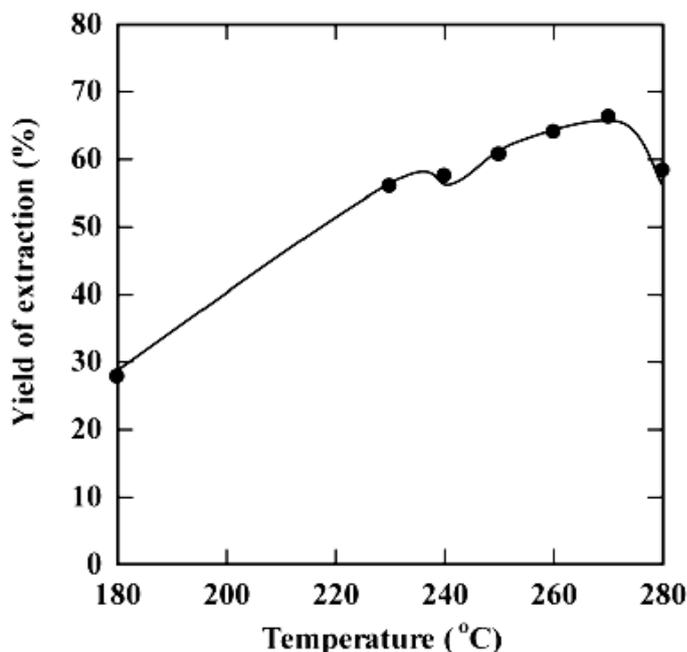


Figure 4: Effect of the temperature on the yield of extraction, using feed to solvent of 1:3 and for 30 min extraction time.

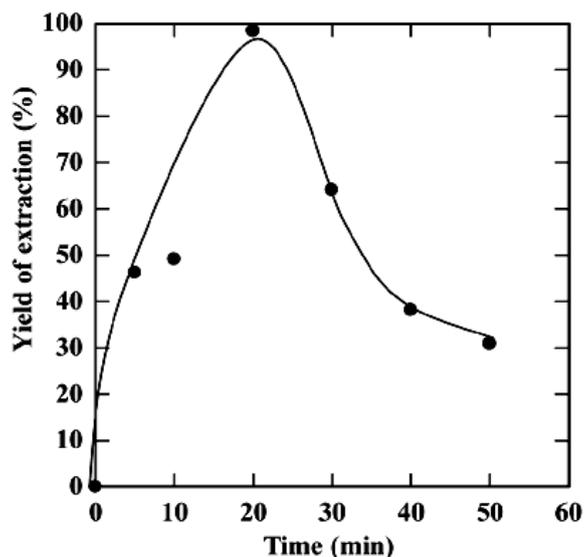


Figure 5: Effect of time on the extraction yield using feed to solvent ratio of 1:3 at 270 °C.

Figure 4 shows the effect of the extraction temperature on the overall yield of extracted oil. The extraction proceeded for 30 min. of extraction time using 5 g of bleaching earth and 15 gm of distilled water as a solvent (feed-to-solvent ratio of 1:3). The results showed that the yield of extraction increased with increasing temperature to a certain level, and then it decreased due to the thermal decomposition of the extracted oil. The maximum yield was 66.32% at 270°C (which represents 0.829 grams of oil from a maximum containing value of 1.25 grams present originally in the SBE). However, the measurements of solid residual during the extraction process showed a linear reduction in the solid residual content when increasing the temperature. The second studied parameter was the optimum extraction time. In this part of the study, the extraction was carried at 270°C, feed-to-solvent ratio 1:3. The extraction time was in the range of 5 to 50 minutes while keeping other parameters constant the results showed in figure 5. It was observed that the yield of oil extracted increased up to a maximum value, and then reduced by increasing the extraction time. Such reduction is due to the decomposition of some extracted oil into degradable products such as organic acids that settled and separated from the floated oil phase into the water phase.

Now let us discuss the feed-to-solvent ratio to get its optimum value. The tested feed-to-solvent ratios were 1:1, 1:2, 1:3, 1:4 and 1:5. **Figure 6** shows the effect of the feed-to-solvent ratio on the yield of extracted oil. Experiments were carried out at 270°C for 20 minutes of extraction time. It was clearly found that by increasing the ratio of the feed to the solvent the yield of extraction increased too. The maximum extraction yield was 66.32% at a feed to solvent ratio of 1:3.

By compromising all the results we can get that the maximum yield was 98.4% from the oil originally contained in the bleaching earth. Accordingly, the optimum conditions of subcritical water extraction of oil from SBE would be as follows:

- Extraction temperature: 270°C
- Time: 20 min.
- Feed-to-solvent ratio: 1:3

Comparing the obtained results with those obtained for the cottonseed and jojoba oil extraction, some interesting conclusions could be obtained. In the case of cottonseed oil, temperature was the same as that obtained in the present work for the SBE. But in the case of jojoba oil extraction, the optimum temperature needed for extraction was 240°C which is lower than that in the case of cottonseed and SBE. This may be explained based on the oil content. The oil content in cottonseed, SBE, and jojoba is 15%, 25% and 48%, respectively. The optimum extraction time was the same in all cases [20,21].

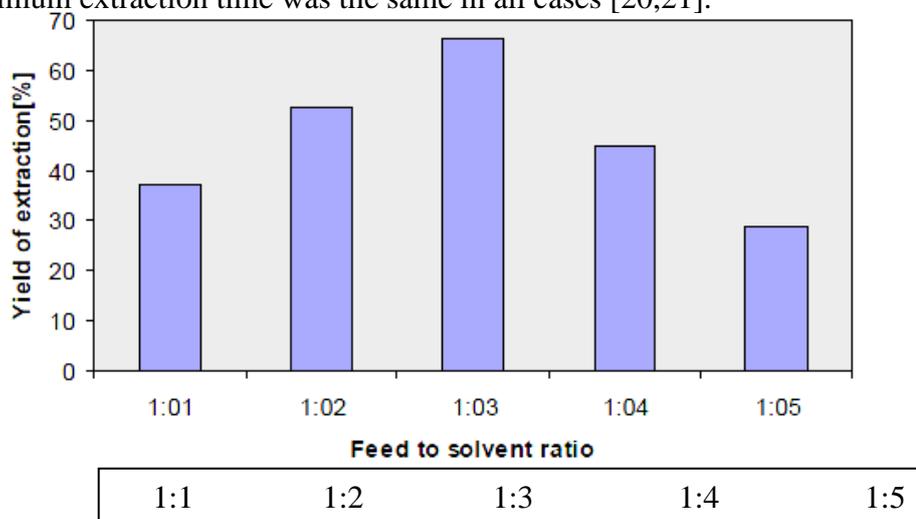


Figure 6: Effect of feed to solvent of on the yield of extraction at 270 °C for 30 min.

Results of the Pilot Scale Running

Based on these results, the extraction was carried out in the pilot scale batch reactors. It is very important to note here that the optimized data obtained using the small batch reactor cannot be applied directly to the pilot scale, since to get 20 min extraction time in a pilot scale reactor we need more time for heating up the reactor to reach the needed extraction temperature. Figure 7 shows the results of the extraction products after around 40 min at 130 °C. For the tank batch reactor, as shown in the figure, the results were not satisfactory, since no oil could be extracted under such operating conditions of low extraction temperature. This is due to the damaged took place in the electrical heater with also the long heating up period needed to heat up the reactor. For the tubular reactor, the situation was much better. Figure 7 shows the heating profile of the tubular reactor. As could be seen, the maximum reached temperature was 210 C. It took 72 min to reach this temperature. The reactor was kept at this temperature for another 20 minutes then the heating was stopped directly after reaching this temperature using sudden cooling with cold water. The extraction products were discharged from the reactor and the oil yield was measured. It was found that around 95% of the already existed oil has been extracted. As shown in the figure 7 (b), 139 ml was extracted from 528 ml of the original powder. Such results validate the employed method and it strongly advised to go for more large scale experiments with using more powerful electric heaters to shorten the heating up period.

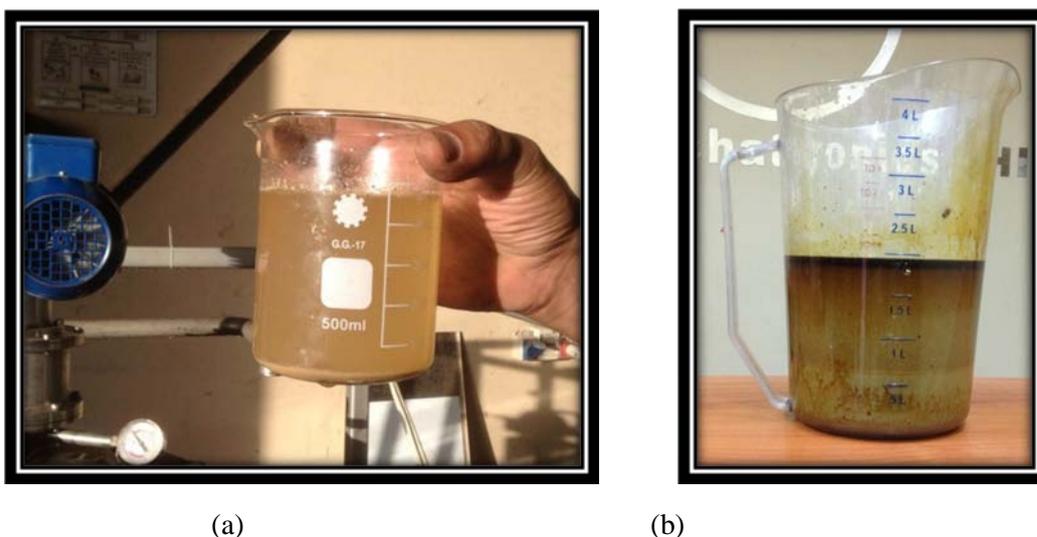


Figure 7: The extraction products from the pilot reactors, (a) the tank reactor and (b) the tubular reactor.

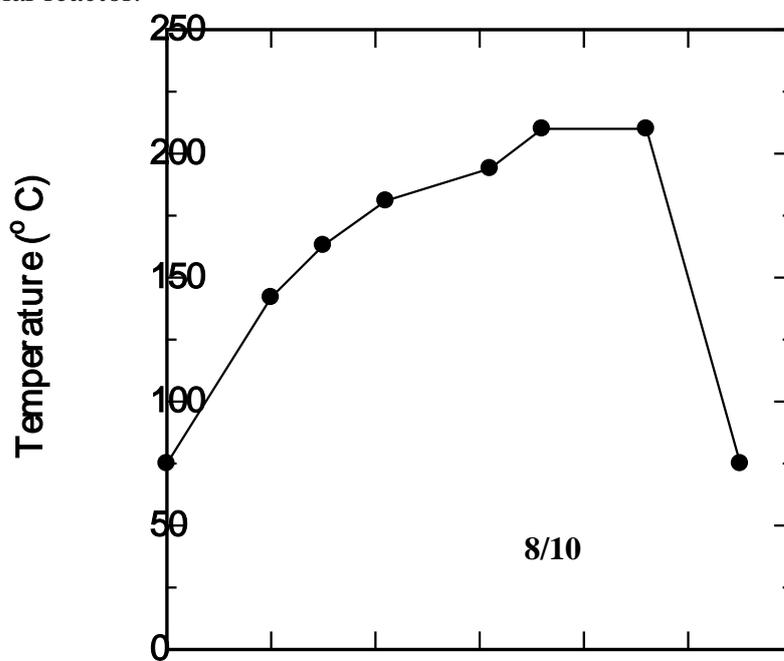


Figure 8: the heating profile of the tubular reactor.

Conclusions

In this work the validation of utilizing SCWE technology for the recovery of oils and fatty acids from the SBE was carried out. The result showed that at 270 °C and for 20 minutes using 1: 3 feed to solvent ratio it was possible to extract more than 94% of oil absorbed in the SBE. Two types of batch reactors, tank and tubular batch reactors, were used for the extraction of oil from the SBE. The results obtained using the tubular reactor showed its advantages over the tank batch reactor. The tubular reactor was more reliable due to its easy temperature control with homogenous distribution along its length. Using the tubular reactor, more than 95 % of oil was extracted from the SBE.

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