HYDRO-DISTILLATION VERSUS STEAM DISTILLATION FOR CLOVE OIL PRODUCTION

Chavdar Chilev, Dimitar Peshev

Department of Chemical Engineering
University of Chemical Technology and Metallurgy
8 Kliment Ohridski Blvd., Sofia 1797, Bulgaria,
chavdar_chilev@uctm.edu (Ch.Ch.); d.peshev@uctm.edu (D.P.)

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ABSTRACT

The production of clove essential oil by hydro distillation and steam distillation has been experimentally investigated. The density of the oil was determined to be $\rho \approx 1.0648$ g cm^{-3}. By means of hydro-distillation, a higher yield of 9.714 mass % was obtained compared to the steam distillation - 4.986 mass %. This is due to the formation of a hard-to-break emulsion in the distillate when using the steam distillation technique.

Liquid-liquid extraction and gravity sedimentation were independently applied for the aim of separating the essential oil from the obtained distillate. The obtained yield of clove oil per distillate unit using liquid-liquid extraction was 9.714 mass % and its higher than that found by gravity sedimentation - 4.95 mass % using the same production method. However, considering the final cost per unit of produced oil and its intended use in foods, cosmetics and medicines, separation of the oil by gravity settling is more suitable.

Keywords: hydro-distillation, steam distillation, clove oil, eugenol.

INTRODUCTION

The clove (Syzygium aromaticum) essential oil is used as an anti-inflammatory agent, due to its high content of flavonoids [1 - 3]. It is also used to treat the symptoms of rheumatism and arthritis. A major component of clove oil is eugenol ($C_{10}H_{12}O_2$; phenylpropanoid). It constitutes 80 - 90 % of the oil [4]. Eugenol is a yellowish liquid, soluble in alcohol, chloroform and dichloromethane. The vapor pressure of eugenol is 10 mmHg at 123°C while boiling and flash point are 256°C and 104°C, respectively. It has antioxidant, analgesic, antimutagenic, antiplatelet, antiallergic, anti - edema and anti - inflammatory properties [5, 6]. Its prominent antibacterial potential is due to the free OH group in the structure [7]. Eugenol possesses a broad-spectrum antibacterial activity and non-drug resistance property [8]. Hong et al. proposed using of eugenol to prevent Staphylococcus aureus contamination and food poisoning in meat products [8]. Zhuofan et al. investigated the possibility of using eugenol for fruit-preservation applications [9]. The eugenol/citral emulsion with tuned physicochemical properties and antimicrobial activity was used in strawberries preservation.

Apart from purely pharmacological, medical and food applications, eugenol is also used in several other industries. Amnin et al. investigated the thermomechanical and antioxidant properties of an active film composed of carrageenan and cellulose nanofibers incorporating eugenol, intended for active packaging applications [10]. The results of the authors demonstrated the potential of this film as a biodegradable packaging solution that offers prolonged food shelf life. The eugenol was used for syntheses of tree new macrocyclic aromatic compounds which are porphyrin analogues [11]. These compounds have light absorbing ability, singlet oxygen production yield, fluorescence emission efficiency, excited triplet state formation properties, fluorescence lifetime length, and the application as hole transporting materials in metal halide perovskite solar cells.

A major concern in the clove oil manufacturing is the low product quality due to low content of eugenol and presence of brown - coloured impurities [12, 13]. The production of quality clove oil depends primarily on the method of its extraction. The most used methods for clove oil production are steam distillation and hydro-distillation.

In the steam distillation process, the separation of the essential oil present in the oil glands (cells) of the plant is due to destruction of the oil bearing cells walls caused by the increased pressure induced by thermal expansion of their content. The stream flow acts as a carrier for the essential oil molecules.

In the hydro - distillation method, the plant material is completely immersed in boiling water. Thus, the volatile components are extracted at a temperature slightly below 100°C by a diffusion mechanism. During the boiling process, the plant material absorbs water, and the oil contained in the oil-bearing cells diffuses through the cell walls by osmosis. The essential oil components are entrained by the boiling water vapor and directed to a condenser.

Both types of distillation processes have their advantages and disadvantages. The main advantage of steam distillation is that the amount of steam used, and its temperature can be easily controlled. In addition, the steam flow penetrates the pores of the solid plant material easier than water. On the other hand, during the steam distillation, it is possible to extract unwanted components, contaminate the essential oil, and change its quality and colour.

Therefore, the objective of this research was to experimentally determine optimal process conditions ensuring high product quality by using steam distillation or hydro - distillation.

EXPERIMENTAL

Materials

To obtain essential oil, clove tree buds of Madagascar origin, purchased from Pimenta Bulgaria Ltd., were used.

The solvents used were ethanol (p.a. 99.9 %, Valerus Ltd.), water (ChromaAR HPLC - from Macron fine chemicals), sodium sulfate anhydride (p.a. 99.9 %, Valerus Ltd.), dichloromethane (p.a. 99.8 %, Valerus Ltd.). Filter paper (Valerus Ltd.) with a pore size of 5 μm and a filtration rate of 10 ml for 40 s was used.

Methods for the clove oil separation

When using both types of distillation processes (hydro - distillation and steam distillation) the obtained condensate is a water - oil emulsion. To separate the essential oil, this emulsion must be broken. This can be done by direct gravity sedimentation of the emulsion in a separatory funnel or by preliminary liquid-liquid extraction of the oil with a second organic phase. In the second case, the liquid-liquid extraction is followed by sedimentation and separation of the organic from the aqueous phase in a separation funnel. Finally, the essential oil is recovered by vacuum evaporation of the extraction solvent.

Gravity settling

One of the most used in industry methods for separating the essential oils from the condensate emulsion is by gravity settling.

Clove oil is heavier than water and separates as the bottom fraction (Fig. 1a). The obtained emulsion has a certain stability, and separating the clove oil immediately after obtaining the emulsion is inappropriate due to incomplete sedimentation of the emulsion. A prerequisite for complete separation is cooling down the emulsion and standing it for at least 24 h.

Due to the small amount of obtained oil, it cannot

a)

b)

Fig. 1. Formation of emulsions in the distillate: (a) freshly prepared emulsion; (b) gravitationally broken emulsion.

be quantitatively and precisely separated from the water in the separatory funnel alone. To minimize the loss of oil in the separatory funnel, unavoidably a small amount of water was passed through with the oil. The resulting mixture is placed in a special test tube with a conical bottom (Fig. 1b). After another 24 h standing, the oil is precisely separated by a medical syringe with a needle from the bottom of the tube and weighed on an electronic scale.

Liquid-liquid extraction

Due to the relatively high solubility of eugenol in water, a portion of the essential oil remains in the aqueous fraction after the sedimentation. To minimize the loss of oil, it can be isolated more completely from the aqueous phase by liquid-liquid extraction. In the present work dichloromethane was selected as an extractant. Dichloromethane is practically insoluble in water and does not form a stable emulsion with it. This means that when dichloromethane is added to water, two distinct layers are formed. Upper layer of water and heavy (lower) layer - dichloromethane. Dichloromethane has a low boiling point, i.e. it is volatile and after the extraction process is easily regenerated by evaporation under vacuum.

The obtained distillate is transferred to a separatory funnel and 15 mL of dichloromethane is added per 125 mL of distillate. The mixture is shaken well to allow the extraction of the oil to proceed. It is then left still for five min and the lower liquid layer is collected. This layer is a mixture of dichloromethane and clove oil. The extraction procedure is repeated three times, i.e. a three-stage cross-current extraction is performed. The same amount of fresh extractant (dichloromethane) is added in each step.

Drying with anhydrous sodium sulfate

The lower liquid layer of the broken aqueous emulsion is a mixture of oil and dichloromethane containing a certain amount of water. Therefore, this mixture is an emulsion consisting of a polar liquid (water) dispersed in a non-polar medium (dichloromethane + oil). To break this emulsion the liquid mixture is dried using Na_2SO_4 (anhydrous). The added anhydrous Na_2SO_4 in the form of insoluble in dichloromethane powder, binds and hence removes the water from the liquid phase. When the water is removed, the initially opalescent emulsion is broken, and the organic liquid mixture is clarified. Sodium sulfate is added in excess until the liquid becomes clear. The dehydrated mixture of dichloromethane and essential oil is separated from Na_2SO_4 by gravity filtration using filter paper.

Production of pure oil and regeneration of dichloromethane

The dried mixture of oil and dichloromethane is subjected to evaporation in a rotary evaporator at an atmospheric pressure. The dichloromethane, being more volatile, is evaporated, while the remaining liquid phase is the obtained pure oil. The boiling point of dichloromethane at operating pressure is 39.6^{o}C. The liquid mixture is heated to 40^{o}C during the evaporation, which warrants complete removal of the solvent. Evaporation continues until no condensate (dichloromethane) is observed in the cooler of the evaporator.

Experimental setups

To obtain essential oil in laboratory conditions were assembled installations for both steam distillation and hydro-distillation. To separate clove oil from the water-oil emulsion (hydrosol), the liquid-liquid extraction process with dichloromethane described above was used. To prove the reproducibility of the methodology, all experiments were performed at least twice, and the average error between individual experiments was less than 5 %.

Hydro-distillation

The experimental set-up shown in Fig. 2 was used to conduct the hydro - distillation of cloves.

Initially, 50 g of the clove buds were weighed and placed together with 1L of distilled water in the glass flask 1, equipped with an electric heater 2 (Fig. 2). The heating flask 1 is connected to a distillation unit consisting of a reflux condenser 4 and a separatory funnel 5 where the distillate was collected. The heat necessary to boil the water is supplied by indirect heating using an electric heater, integrated into the distillation flask. The main components of clove oil are poorly soluble in water. These components are entrained with the water vapours during the boiling and enter the condenser 4 (Fig. 2). Cooling in the condenser is provided by counter current flow of cold water. The resulting condensate was collected in the form of hydrosol in the separatory funnel 5. To maintain constant volume of the liquid phase into the distillation flask, distilled water from tank 3 (Fig. 2) was continuously added to compensate for the evaporation.

Steam distillation

In steam distillation, the essential oil was extracted from pre-generated steam that passes through a fixed bed of the raw material. Fig. 3 illustrates the constructed laboratory experimental setup.

At the beginning of the process, 50 g of solid phase was placed in the feed tank 1 shown in Fig. 3. The flow rate of the steam, generated in the steam generator 4, was adjusted by controlling the power supplied to the heater through the rheostat 5. The generated steam was fed to the bottom of the feed tank 1 and passed through a layer of the raw plant material 3. The heat and the steam penetrated the plant material, partially destroying its cell structures and thus releasing the enclosed essential oil. The essential oil molecules, together with the carrier vapours, passed through the condenser 7 and their condensate was collected in the product tank 8.

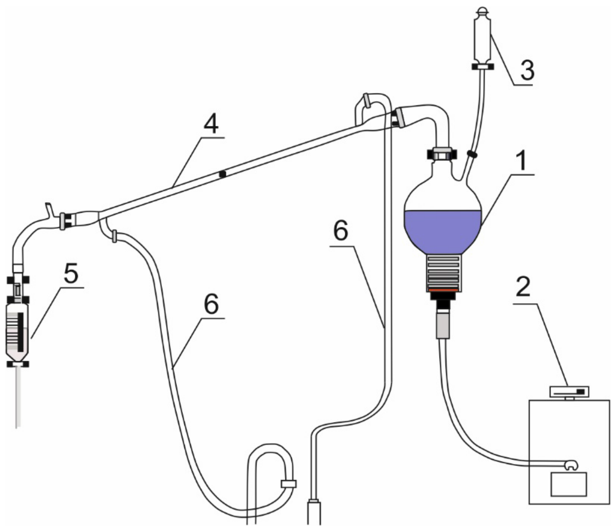

Fig. 2. Scheme of an experimental set-up for obtaining essential oil by hydro - distillation. 1- distillation flask; 2 - rheostat; 3 - tank of distilled water; 4 - heat exchanger (condenser); 5 - separatory funnel; 6 - cooling water line.

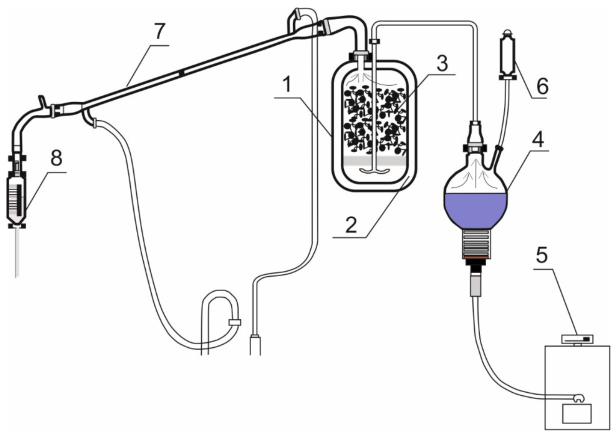

Fig. 3. Scheme of an experimental set-up for production of essential oil by steam distillation.1 - insulated feed tank; 2 - heating jacket; 3 - cloves; 4 - boiler; 5 - rheostat; 6 - tank of distilled water; 7 - heat exchanger (condenser); 8 - separatory funnel.

RESULTS AND DISCUSSION

Firstly, the results of clove oil production by steam distillation and hydro-distillation are presented (Fig. 2). With both distillation methods, the oil is extracted from the water-oil emulsion by liquid-liquid extraction to ensure complete essential oil recovery from the emulsion as well as equal conditions for assessment of the impact of the distillation method on the product yield and quality of the obtained oil.

Secondly, the results for clove oil production by hydro-distillation, but when the oil is separated by either gravity settling or liquid - liquid extraction, are then presented and analysed.

Selection of distillation method

The purpose of the conducted experiments was to compare the two methods for clove oil production in terms of yield, rather than a study on the composition and characteristics of the obtained oil. To characterize the latter, its density, ρ, was measured and reported in Table 1.

The density of the oils obtained in the individual experiments was practically the same with an average value of 1.0648 g cm^{-3}, which is in good agreement with available literature data [4].

The experiments were performed at two different distillation rates. The distillation rate was regulated via the power supply to the heater of the distillation flask or of the boiler respectively. Two levels of supply voltage were used, 160 and 180 V, providing different intensity of heating. The obtained results showed that at equal other conditions, approximately the same amounts of

Table 1. Results obtained by both distillation methods.

Type of distillation	Initial amount, g	Amount of distillate, mL	Cloves/Distillate ratio	% mass	ρ, g cm^{-3}
Hydro distillation	50	250	0.2	5.302	1.0641
Hydro distillation	50	300	0.167	9.714	1.0625
Hydro distillation	50	400	0.125	8.62	1.0631
Steam distillation	100	400	0.4	2.331	1.0668
Steam distillation	100	600	0.6	4.986	1.0675

oil are obtained with both hydro-distillation and steam distillation, independently on the distillation rates. It was established that at the lower distillation speed, the process is conducted in a more stable and reproducible way and facilitated the distillate separation. When performing the steam distillation at the high rate, in the initial stage of the process, along with the essential oil, the steam extracted also significant amounts of contaminants, which lead to colouring of the obtained oil. Therefore, in the case of steam distillation, only the slow distillation rate was feasible.

Another process parameter, which impacts the yield of essential oil in both the hydro-distillation and the steam distillation is the ratio between the amount of initial raw plant material to the amount of the collected distillate [g (initial raw material)/mL (collected distillate)]. In Table 1, this parameter is denoted as Clove/Distillate ratio. In the present experimental study this ratio was varied from 0.125 to 0.2 g mL^{-1} for hydro-distillation and from 0.4 to 0.6 g mL^{-1} for steam distillation. Obviously, variations of the Clove/Distillate ratio resulted in variable total yield of essential oil expressed as the percentage of the produced oil from the mass of the feed raw plant material. The results demonstrate that the optimum Clove/Distillate ratio is 0.167 g mL^{-1} for the hydro-distillation and 0.6 g mL^{-1} for the steam distillation process. At the optimal value for the ratio, in the present work was obtained a yield of 9.714 wt. % by hydro-distillation, which is in good agreement with the literature data [14].

In the case of steam distillation, the achieved yield was significantly lower - 4.986 wt. %. This can be explained with a pure efficiency of the essential oil recovery via liquid-liquid extraction of the distillate. When the steam and heat penetrate the raw plant material, a number of other substances besides the essential oil components are extracted with the steam. These include various tanning substances, higher molecular weight alcohols, etc. which causes the brown colour of the distillate, shown in Fig. 4

When trying to separate the oil from the water-oil emulsion shown in Fig. 4 by a liquid - liquid extraction process, the three - layered liquid system shown in Fig. 5 was obtained.

The bottom layer was composed of dichloromethane and clove oil. This layer was separated from the remaining liquid and then pure clove oil was obtained by evaporation of the dichloromethane as detailed in section 2.2.2. The middle layer most likely contained a significant amount of clove oil, dichloromethane and some of the extracted by-products. The attempts to recover pure clove oil from this layer via further liquid-liquid extraction with dichloromethane were unsuccessful. The upper layer is believed to contain mostly water and the by-product substances extracted

Fig. 4. Distillate obtained by steam distillation of clove buds.

Fig. 5. Broken three - layer multicomponent liquid system.

with the steam. It probably contains vary small almost of clove oil. Therefore, pure oil can be obtained only from the bottom layer of the semi-broken emulsion. Perhaps a large part of the essential oil remains in the middle layer and cannot be recovered in pure form, which may explain the nearly twice lower yield of essential oil compared to the one achieved by hydro-distillation. Clearly, hydro-distillation is a more practical process for production of cloves essential oil, which allows for up to 9.714 mass % yield.

Selection of a method to separate the clove oil

In Fig. 6 is shown a comparison between the obtained results for separation of clove oil from the hydrosols by liquid-liquid extraction or direct gravity sedimentation.

It can be seen from the Fig. 5 that for equal amounts of collected distillate, the yield of oil extracted by dichloromethane extraction is nearly twice higher than the one by gravity sedimentation. This experimental finding can be explained with the relatively high solubility of eugenol in water of approximately 0.68 g L^{-1} at 30^{o}C [15]. Due to the latter, a significant part of the oil remains dissolved in the aqueous distillate (hydrosol) and cannot be separated.

Apparently, based on the laboratory scale results, the liquid-liquid extraction process with dichloromethane as an extraction solvent is a more reasonable choice. However, carrying out liquid-liquid extraction in industrial scale is associated with additional equipment and maintenance and thus additional capital and operational costs. Moreover, the costs for regeneration of dichloromethane and sodium sulfate must be added.

During the extraction process, the oil is contacted with additional chemicals - dichloromethane (or another extracting agent) and anhydrous sodium sulfate. Its leads to contamination of the final product with these substances. Although dichloromethane is separated and regenerated by distillation, and sodium sulfate is removed by filtration, small amounts of these substances remain in the oil.

According to the international standards the clove oil obtained via liquid-liquid extraction is forbidden for food applications, which lowers its price. This type of oil, if compliant with certain requirements, is permitted in cosmetics (creams, ointments). The oil obtained without the use of chemicals, by means of direct gravity settling, is a functional ingredient in several food supplements and medicines.

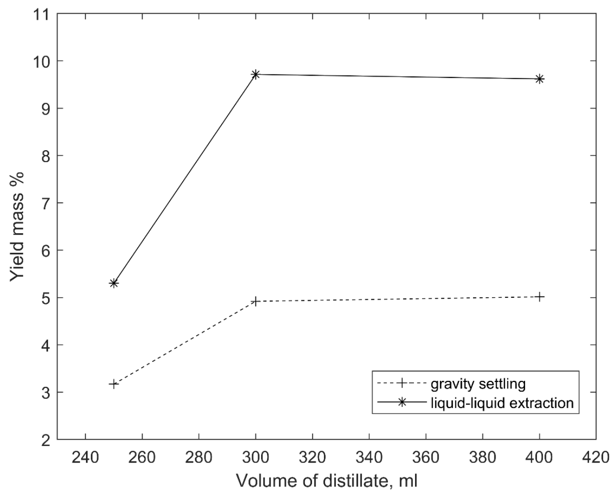

Fig. 6. Comparison between the obtained results for clove oil separation from the hydrosols by liquid-liquid extraction and gravity settling.

All the above considerations are in favour of choosing direct gravitational sedimentation when the aim is to produce high quality essential oil without traces of organic solvents and other impurities in industrial scale.

CONCLUSIONS

Two methods of producing clove oil, hydro-distillation and steam distillation, are investigated and compared. For this aim, laboratory installations for hydro - distillation and steam distillation have been assembled and successfully used for distillation experiments to obtain essential oil from clove flower buds.

The density of the produced essential oil was determined to be $\rho \approx 1.0648$ g cm^{-3}, which is in good agreement with available literature data. The results demonstrated that the steam distillation is unfeasible due to the obtaining of hard-to-break emulsions as a distillate, leading to a significant decrease in the oil yield. The mass yield of oil achieved by steam distillation per unit raw plant material was found 4.986 wt. %, while the one by hydro-distillation was 9.714 wt. %. Thus, the experiments clearly showed that it is more practical to produce clove oil via hydro - distillation process.

Two methods for separating the essential oil from the resulting water-oil emulsion, direct gravity sedimentation and liquid-liquid extraction, were experimentally investigated and compared. Recovery of the oil by liquid-liquid extraction resulted in a nearly twice higher yield in comparison with the direct gravity sedimentation. However, in industrial scale applications the liquid-liquid extraction would require additional equipment and maintenance and thus additional capital and operational costs. Moreover, the contemporary stringent regulatory restrictions for use of products, contaminated with organic solvents and other chemical impurities, are in favour of choosing the hydro-distillation method, especially when the produced clove essential oil is aimed for application in foods and medicines. Based on the present investigation is concluded that a technology combining hydro - distillation with direct gravity sedimentation shall be chosen for the most efficient production of high - quality clove essential oil.

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