Thermal and Compositional Analysis of Orange Essential Oil Obtained from Citrus Industry Waste

Gabriel Ferreira*, Louise Sobral, Daniel W. Barreto and Verônica Calado

Universidade Federal do Rio de Janeiro, Escola de Química, Bl. E, 21941-598, Rio de Janeiro, Brazil

Abstract: During the production of orange juice, more specifically after the commercial extraction of fruit juice, other waste materials are generated, consisting of peel, pieces of membranes, pulp bagasse, juice vesicles and seeds. In this way, the final destination of the waste can become a problem when not managed correctly. Therefore, there are several possibilities for using these solid residues, as they present substances of great commercial interest. In this perspective, the present work evaluates the recovery of orange essential oil from the citrus industry waste using hydrodistillation. The oil obtained was characterized by acidic index, FTIR, GC / MS, TGA and DSC. The results exhibited that oil isolated by hydrodistillation has a similarity with cold-pressed orange oil. The chemical constitution of oil obtained from waste was almost the same as the commercial orange oil analyzed. However, the thermal behaviour presents a few differences in thermal stability and vaporization temperature between analysed essential oils. Therefore, this work produces an alternative to obtain a product with quality, high yields and added value that can be used in cosmetic and pharmaceutical industries.

Key Words: Orange waste, Essential oil, Oil extraction, Chemical composition, Thermal behavior.

1. INTRODUCTION

Orange (Citrus sinensis L.) is a citrus fruit, with a flavor varying between sweet and acidic, and quite popular, ranking 5th among the most produced fruits in the world (about 49 million tons a year) [1,2]. Considering only its cultivation, Brazil ranks first in the world ranking, followed by China, the European Union, Mexico and the United States. [3,4]. According to Braddock (1999), the chemical composition of the orange constituents is distributed as follows: 85% water and 15% referring to the substantial portion. Of this small fraction, 10% refer to soluble sugars such as glucose, sucrose, fructose, rhamnose and xylose; 2% to the fibrous portion, formed by pectin, cellulose, hemicellulose and lignin; 1% to proteins and amino acids; 1% to organic acids, such as ascorbic, oxalic and citric; 0.7% to minerals, such as calcium, potassium, phosphorus and magnesium; and only 0.3% to terpenic oils and lipids [5-7].

Orange essential oil is the most valuable by-product of the orange juice industry [8]. The oil can be found in all plant tissues but is more concentrated in the husks. In general, it can be obtained in three ways: as a by-product of the orange juice industry, hydro-distillation of fruit components, or by cold pressing of the peels [2, 9-15]. The International Standards Organization (ISO) defines it as the product obtained from plant materials through distillation by steam vapor or by pressing citrus pericarps, with subsequent elimination of the aqueous phase by physical methods [16]. However, in this context, some more recent works stand out for obtaining essential oil through environmentally friendly alternatives. Some of the most innovative methods involve the use of microwave irradiation [17-20], supercritical fluids [21], extraction and isolation by ionic liquids [22, 23], or the use of sunlight as an energy source for the extraction [24, 25]. The essential oils obtained by these different methods can vary in quality, yield, and composition depending mainly on the citrus species used [26-28].

The orange essential oil is a complex mixture of different organic molecules. These molecules are divided into two fractions, the volatile, present in greater quantity, which may represent about 96% of the total oil, and the non-volatile [29]. The volatile fraction can contain more than 100 compounds, such as aldehydes, specifically octanal and decanal, esters, ketones, alcohols, such as linalool, and terpenic hydrocarbons, such as limonene, myrcene, and valencene [30-32]. Many of them are present only in traces. However, D-limonene can reach concentrations ranging from 90 to 96%, consolidating itself as the main component of the oil [33, 34]. This compound is approved as safe by the US Food and Drug Administration (FDA), and also, some studies report it as an anti-cancer tool in the diet in humans [35] and antifungal and antibacterial drug [2, 36]. Because it is considered one of the purest sources of monocyclic terpene, it is widely used in the manufacture of rubbers, paints, and adhesives as a

*Address correspondence to this author at the Universidade Federal do Rio de Janeiro, Escola de Química, Bl. E, 21941-598, Rio de Janeiro, Brazil; Email: calado@eq.ufrj.br

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dispersing and wetting agent, and also as an industrial and resin solvent [37-39]. Besides, as it is the component responsible for the odor released by the fruit, it is also used by the pharmaceutical and food industry to give flavor and aroma to other products and foods [7, 9, 10, 34]. The non-volatile fraction, in turn, is composed of carotenoids, flavonoids, tocopherols, fatty acids, and coumarins [40].

Essential oil is widely used in the production of food, beverages, cosmetics, chemicals, and pharmaceuticals [31, 40, 41]. However, despite its versatility, the flavor industry still faces a severe problem of its use. Because of their unsaturated nature, terpenic compounds are more easily oxidized in the presence of air, heat, light, and moisture [42-44]. The main consequence of this oxidation is the loss of the organoleptic qualities of the oil, resulting in undesirable flavors. Therefore, to protect them, micro or nano-encapsulation and other techniques are being used today [45-47].

The present work aimed at investigating compositional and thermal characteristics of an orange essential oil obtained by hydrodistillation of the citrus industry waste. The characterization was performed in order to evaluate the application viability of using a recovered essential oil from orange juice production waste. For this purpose, the essential oil isolated by hydrodistillation was compared with a commercial cold-pressed orange essential oil in search of compositional differences. In addition, the thermal behavior was determined to establish the oil differences under usual processing conditions.

2. EXPERIMENTAL SECTION

2.1. Materials

A sample of oily residue from the winterization stage of orange essential oil and of cold-pressed orange oil was kindly provided by local industry, (Cutrale, SP). The waste material consisted of mainly oil, waxes, and solid particles.

2.2. Methods

2.2.1. Orange Essential Oil Extraction

In a stainless steel tank with a maximum capacity of approximately 4.5 liters and adapted to only have an outlet for the steam generated, a certain amount of oily residue and enough distilled water were placed so that feeding is not required during the process. A condenser and a graduated distillation head were attached to this tank and, after assembling this apparatus, this system was subjected to constant heating. The vapors generated in the tank, when leaving the essential oil in the residue, were liquefied in the condenser and were retained in the distillation head, forming two phases: the lightest, rich in essential oil, and the heaviest, rich in water, being adequately collected.

2.2.2. Compositional Analysis

The samples of orange essential oil obtained by hydrodistillation and cold pressing were subjected to the determination of the acidity index according to the methodology proposed by Warth (1956). According to the method used, the acidity index is obtained using 0.1N potassium hydroxide alcoholic solution (methanol) as titrant and phenolphthalein as an indicator. The solvent solution, used in the solubilization of the samples, consisted of a mixture of toluene and methanol (1: 1), and the solubilization temperature used was 60ºC. The amount of the sample used in each test was approximately two grams. After solubilization and cooling to room temperature, the samples solubilized in the solvent were titrated. The volumes used for the titrant, in each analysis, were discounted in 0.2 mL, referring to the amount of titrant used to titrate the blank. The test was performed in triplicate.

FTIR spectra of the samples were obtained using a Shimadzu IR affinity-1 spectrometer using the ATR method. The analysis was carried out in the spectral range of 500–4000 cm-1 with 4 cm-1 resolution.

The oil constituent identification was performed with a Gas Chromatography using an Agilent 7890A Gas chromatograph (GC) equipped with an HP 7673 auto-sampler and coupled to a flame ionization detector (FID) and a quadrupole mass spectrometer (MS) Agilent. The identities of the diterpenes were assigned by GC–MS with standards characterized by IST/EPA/NIH Mass Spectral Library databases (2002 version). The samples were diluted in a ratio of 1:100 of sample/solvent with dichloromethane. The polar chromatography column used was Carbowax type. Mass spectrometer conditions include ion source temperature at 230ºC, quadrupole at 200ºC, an acceleration voltage of 200 eV above the set, and ionization voltage of 70 eV.

2.2.3. Thermal Characterization

Thermogravimetry analysis (TGA) was performed using 10 mg of oil samples and was carried out on a Perkin Elmer instrument, model Pyris 1. The samples

were heated from 20 to 350 °C at a heating rate of 10 ºC min-1 under a nitrogen atmosphere flow of 30 mL min-1. The aim of this analysis was to determine the volatilization temperature of the oils and compare them based on thermal stability.

The thermal behaviour of orange essential oils was analyzed in a DSC Q500 (TA Instruments Inc.). Approximately 7 mg of each oil was added in hermetically sealed aluminium sample holders that were heated from 30 to 250 °C at 10 °C/min rate, using an empty pan as reference. The evaporation temperature range (Tonset, Tend, and Tpeak) and evaporation enthalpy (ΔH) were determined using TA Instruments Universal Analysis Software.

3. RESULTS AND DISCUSSION

The residue was adequately treated by hydrodistillation in order to separate the essential oil from the substantial residual portion [20]. The majority composition of winterization tanks waste is an essential oil and the yield obtained for essential oil recovery was around 95%. This yield value is superior to other hydrodistillation processes exhibited in literature due to residue nature since the works mainly seek the essential oil recovery from orange peels [2,9]. Figure (**1a**) shows the cold-pressed oil provided by Cutrale, while Figure (**1b**) shows the oil obtained by hydrodistillation. It is observed that the cold-pressed oil presents an intense yellow color marked by the significant presence of flavonoids and carotenoids, while the hydrodistilled oil is colorless because of obtaining pathway. In addition to the visual difference, the oils stand out with different characteristics in various properties. The acidity index for cold-pressed oil was calculated to be around 2.24 mg KOH/ g of oil, while hydrodistilled oil was 1.12 mg KOH/ g of oil. Therefore, there are considerable differences between the samples analyzed.

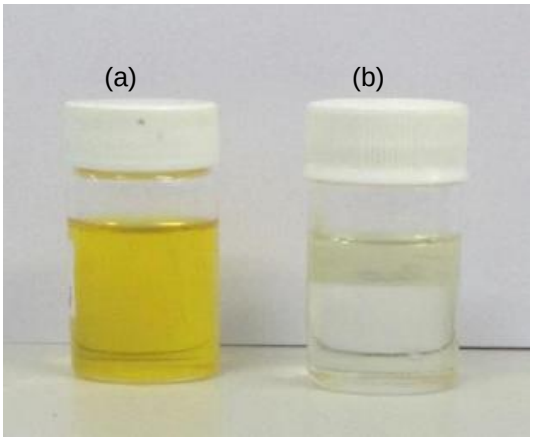


Figure 1: Digital photos of (a) commercial cold-pressed orange essential oil and (b) hydro-distilled orange essential oil samples.

FTIR analyzes were performed in order to indicate some compositional difference among oil samples. Figure **2** shows the FTIR spectra of oil samples. By analyzing the data, the principal peaks of oil essential constituents can be observed. Both oils, hydro-distilled and cold-pressed, exhibit the same vibrational modes. The limonene has a peak with pronounced intensity around 1650 cm−1, which is assigned to the stretching of the double bonds (C=C) found in the endocyclic and exocyclic positions of the structure [48]. The peaks at 2850 to 3100 cm-1 were assigned to hydrocarbon bonds (C-H) [49]. Specifically, the cold-pressed oil spectra show more intense peaks, mainly around 1650 and 890cm-1. This behaviour, possibly, can be attributed to the significant flavonoids and carotenoids concentration in this oil since his colouration.

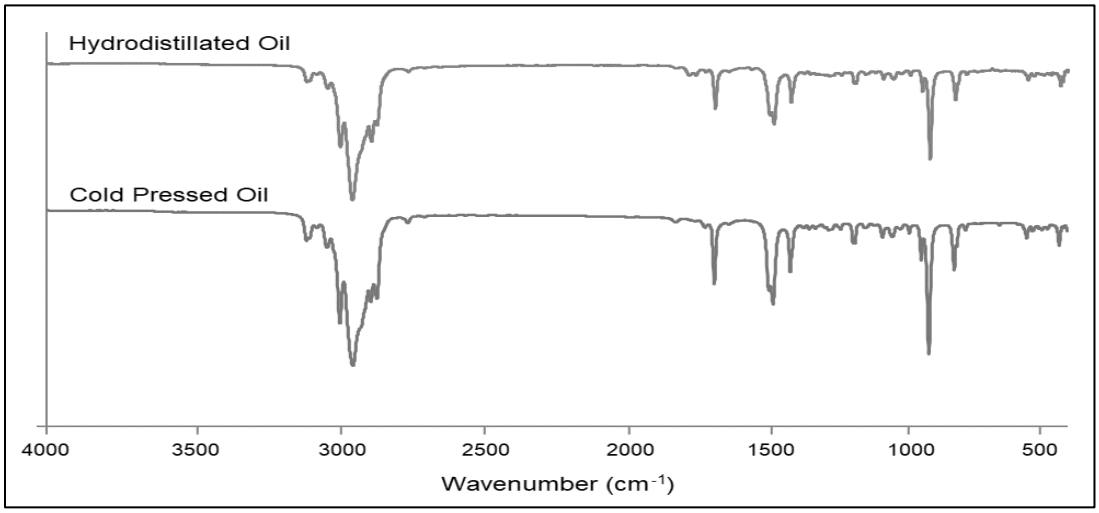
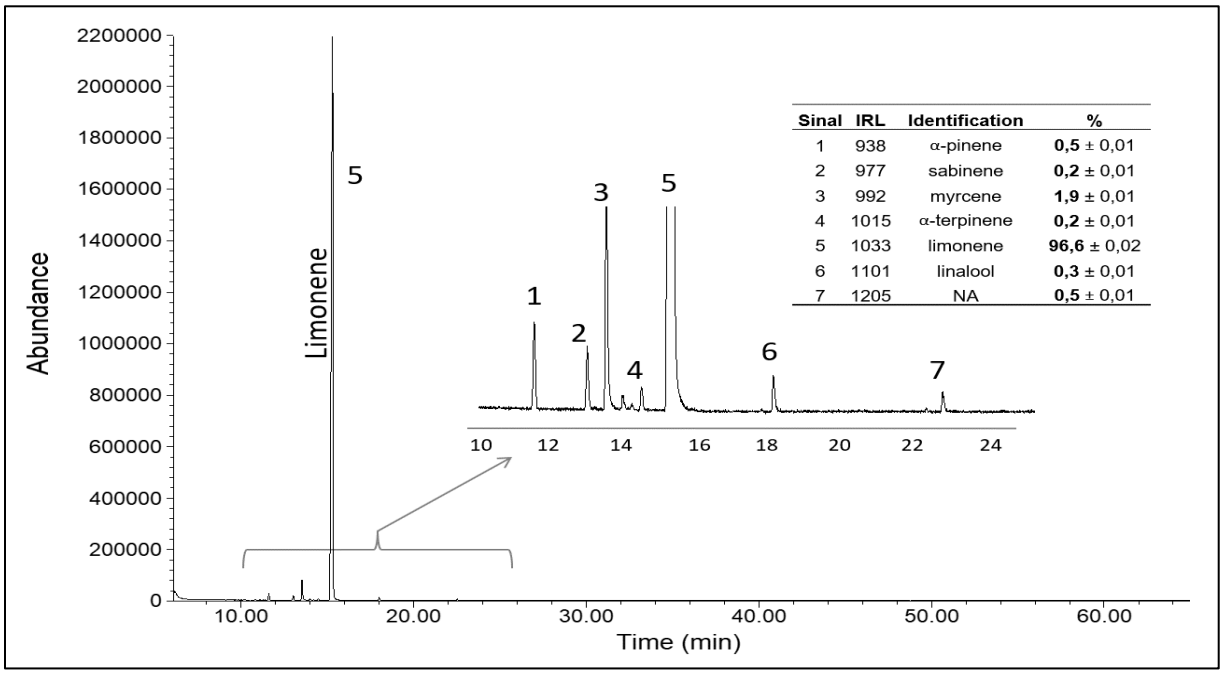


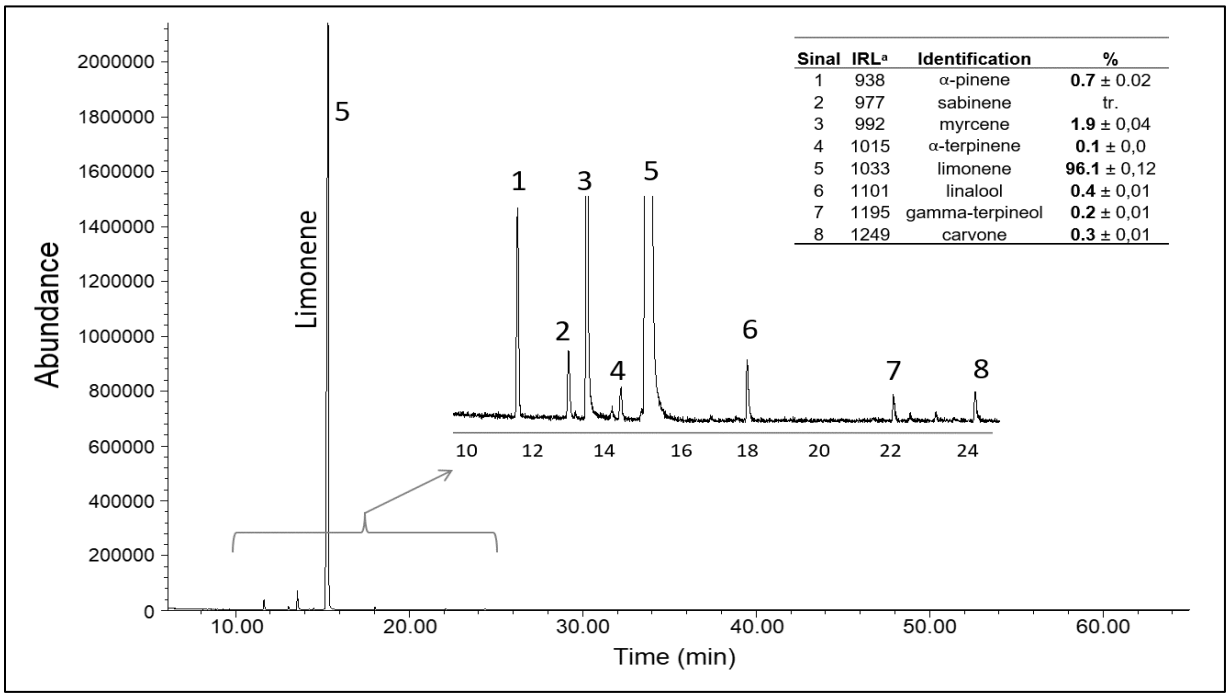
Figure 2: FTIR spectra of oil samples.

Since FTIR data do not show significant differences among oil samples, GC-MS analyses were performed to verify oil composition. The GC–MS chromatograms of essential oils are exhibited in Figures **3** and **4**. The chromatogram data showed that the major component in oil samples is limonene (up 96%) in both oils. Besides that, there are other molecules present in both oils: α-pinene, myrcene, sabinene, linalool, α-terpinene. However, compared to cold-pressed oil, the hydrodistilled oil presents carvone and γ-terpineol in its composition. Instead of that, the concentration of the main components is very similar, indicating a composition similarity between the oils. It is possible that two different substances have the same retention time and may have been counted as a single substance [24]. Comparing the composition of analysed oils with recovery essential oils reported in the literature, it can be observed that cold-pressed oil and hydrodistilled oil agree with previously reported results [24, 50].



Sinal	IRL	Identification	%
1	938	α-pinene	**0,5** ± 0,01
2	977	sabinene	**0,2** ± 0,01
3	992	myrcene	**1,9** ± 0,01
4	1015	α-terpinene	**0,2** ± 0,01
5	1033	limonene	**96,6** ± 0,02
6	1101	linalool	**0,3** ± 0,01
7	1205	NA	**0,5** ± 0,01

Figure 3: GC–MS chromatogram of the cold-pressed essential oil.



Sinal	IRL[a]	Identification	%
1	938	α-pinene	**0.7** ± 0.02
2	977	sabinene	tr.
3	992	myrcene	**1.9** ± 0,04
4	1015	α-terpinene	**0.1** ± 0,0
5	1033	limonene	**96.1** ± 0,12
6	1101	linalool	**0.4** ± 0,01
7	1195	gamma-terpineol	**0.2** ± 0,01
8	1249	carvone	**0.3** ± 0,01

Figure 4: GC–MS chromatogram of the hydro-distilled essential oil.

The TGA curves are exposed in Figure **5**. It is observed that the essential oils presented a single thermal degradation event with very similarity. The Tonset and Tmax were 56°C and 111,7°C for hydro-distilled oil, respectively, and 46°C and 108,7°C for cold-pressed oil, respectively, which indicate their thermal stability. These results are consistent with literature observations since essential oils are quite volatile and have D-limonene as the principal constituent [51]. It can be observed that hydro-distilled essential oil has a bit bigger thermal stability than cold-pressed oils and this, possibly, occurs due to the processing of hydrodistilled oil which involves high temperatures and eliminate some constituents that are more volatile [24].

The thermogram obtained by DSC analysis of orange essential oils is shown in Figure **6**. A single thermal event for both oils is observed under the analyzed temperature sweep. This endothermic event is associated with vaporization of the volatile fraction of oils, and the Tmax was 236°C and 217°C for hydrodistilled oil and cold-pressed oil, respectively. As essential oils are constituted by a mixture of varied chemical compounds, vaporization does not occur at a specific temperature, but over a temperature range [45]. The evaporation temperatures of the volatile fraction, mostly D-limonene, of hydrodistilled orange essential oil and cold-pressed oil was observed in the range between 235°C and 241°C, and 218°C and 227°C, respectively. Those changes in Tmax and evaporation temperature range can be assigned to the sesquiterpenes concentration, which has higher evaporation temperatures. The evaporation enthalpy was calculated around 87,7 J/g for hydro-distilled essential oil and around 156,4 J/g for cold-pressed oil. This behaviour could be attributed to the minor compositional differences between the samples, which could change the interactions in the samples, i.e. probably, the cold-pressed oil presents primary evaporation energy due to the greater purity [52].

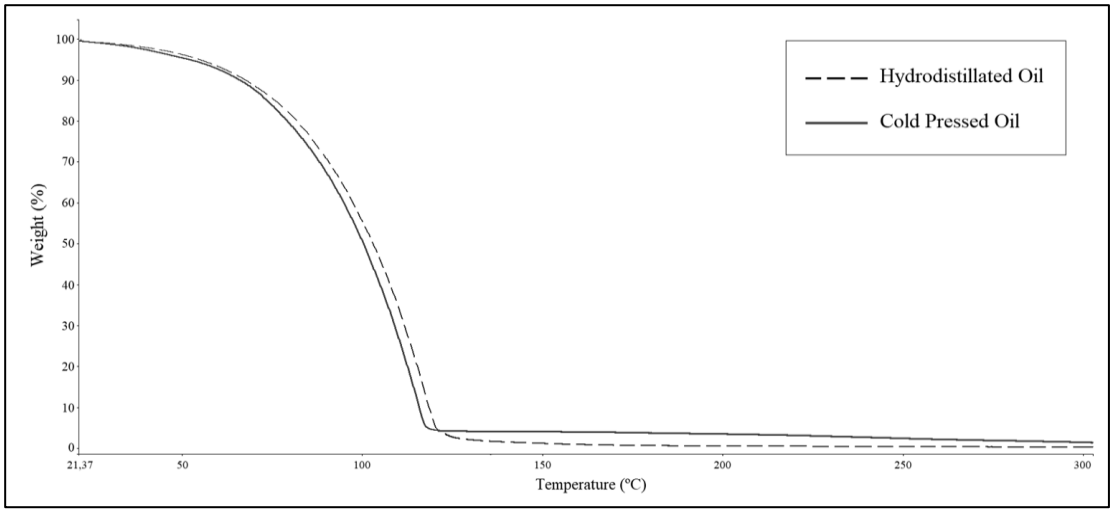


Figure 5: TGA curves of hydro-distilled essential oil and cold-pressed oil.

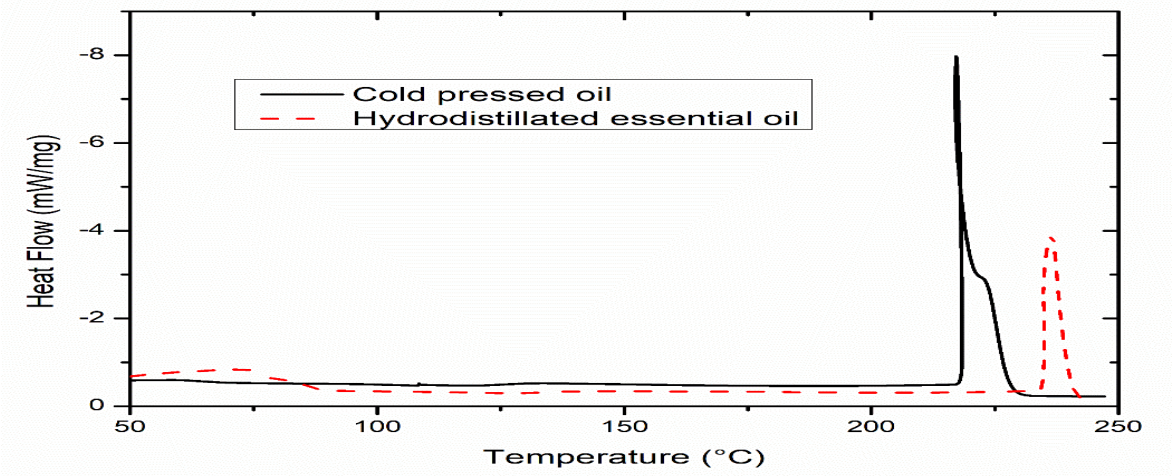


Figure 6: DSC curves of hydro-distilled essential oil and cold-pressed oil.

4. CONCLUSIONS

The orange essential oil was successfully recovered from winterization tanks waste with high yields. That essential oil obtained by hydrodistillation of the oily residue has similarity in chemical composition and the thermal treatment with the orange essential oil obtained by cold pressing. The compositional analysis showed that both oils contain D-limonene as the major compound. The TGA analyses do not show significant changes in the degradation profile of the samples, and the DSC shows an increase in the vaporization temperature of the hydrodistilled oil, which probably could be assigned to little constitutional differences among samples.

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DATA AVAILABILITY STATEMENT

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

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