

## Application of Rubber (*Hevea Brasiliensis*) Seeds Oil Extracted using Supercritical Carbon Dioxide in Cosmetics

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### Article history

Received :4 October 2013

Received in revised form :

15 May 2014

Accepted :22 May 2014

### Graphical abstract



### Abstract

Synthetic oil is often the choice of commercial for use in cosmetics especially lipsticks due to the lower cost of production. Meanwhile, the natural oil in comparison with synthetic oil is non-toxic and safe to apply in cosmetic. In addition, polyunsaturated fatty acids (PUFAs) play an important role in lipsticks by giving the smooth feels when apply to the lips and also help to repair the dry lips. In this study, rubber (*Hevea brasiliensis*) seeds which are abundant and discarded as waste in Malaysia had been discovered to contain a significant value of alpha-linolenic acid (ALA). The method used to extract rubber seeds oil (RSO) is supercritical carbon dioxide (SC-CO<sub>2</sub>), a green technique to ensure the extracted RSO is free from organic solvent with better quality and safe to be consumed. Furthermore, the effect of temperature and pressure of the extraction was studied to obtain the optimum yield of rubber seeds oil. Lastly, the experiments of Fourier Transform Infrared (FTIR) were performed to samples of lipsticks with or without RSO. The results obtained show that the presence of polyunsaturated fatty acids is stable in the lipmoist samples after 8 weeks of storage.

**Keywords:** Natural oil; polyunsaturated fatty acids; rubber seeds oil; supercritical carbon dioxide; Fourier Transform Infrared

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### 1.0 INTRODUCTION

Lipstick contains a variety of waxes, oil, emollients, emulsifiers, preservative, binders and pigments [1]. The mixture of waxes from different origin, nature and different oils forms the white base which gives the structure of lipstick. The base of a lipstick also determines the physical properties of a lipstick for example the melting point, stability, solubility and strength of lipstick. Besides this, oil gives a smooth and creamy feel when apply on the lips, enhance the easy application quality and give shiny look to lipstick. Synthetic oil is often the choice of commercial for use in lip moist due to the lower cost of production. The examples of synthetic oils that always found in lipsticks formulation are mineral oil and petrolatum which are saturated paraffinic and naphthenic fatty acids. Therefore, synthetic oil used is not act as moisturizer but barrier which can block pores and may seals the moisture into lips causing the lips become dry. Furthermore, the synthetic oil especially petrolatum usually contaminated with polycyclic aromatic hydrocarbons which can cause cancer or harmful to human health. Natural oil acts as non-toxic botanical base ingredients which are

compatible with the skin's natural oils (sebum) which can enhance the natural beauty and care for the skin.

In view of the statement above, exploring new source of natural oil used in cosmetics become very crucial. Plant derived omega-3 fatty acids can avoid allergic, unpleasant smell and contamination of mercury. Rubber (*Hevea brasiliensis*) seeds had been identified contained significant values of polyunsaturated acids especially omega-3 fatty acid. As reported by Jumat and Bashir [2], the rubber seeds oil (RSO) contains significant value of alpha-linolenic acid (ALA) which is  $19.22 \pm 0.21\%$ . ALA is one of the omega-3 fatty acids which is important in human health development and also reduces the risk of cardiovascular [3].

According to the Association of Natural Rubber Producing Countries, Kuala Lumpur, Malaysia has an estimated average of 1,229,940 hectares of rubber plantation in 2007 (Malaysian Rubber Board, 2009). Hence, it means that 1.2 million metric tons of rubber seeds being annually produced.

These rubber seeds are abundant and wasted because they are not currently uses in daily life. Therefore, rubber seeds considered as the neglected source of natural oil.

Supercritical fluid extraction (SFE) with supercritical carbon dioxide (SC-CO<sub>2</sub>) represents an alternative method for the extraction of oils from natural product and has received considerable attention [4]. SFEs have been used as solvents for wide varieties of applications such as essential oil extraction [5]. Hence, in the study the SC-CO<sub>2</sub> had been used to extract RSO. The solvent used for this technique is carbon dioxide, which is inert, non toxic, non flammable and environmental acceptable. The oils obtained using SC-CO<sub>2</sub> extraction were of outstanding quality and the yield were comparable with those extracted using organic solvent extraction technique [6].

In this study, the effects of temperature and pressure on the extraction of RSO were investigated in order to obtain the optimum oil yield. In addition, the potential of RSO as the natural oil using in cosmetics had been studied by adding RSO into the lipmoist samples. The lipmoist samples were tested using Fourier Transform Infrared (FTIR).

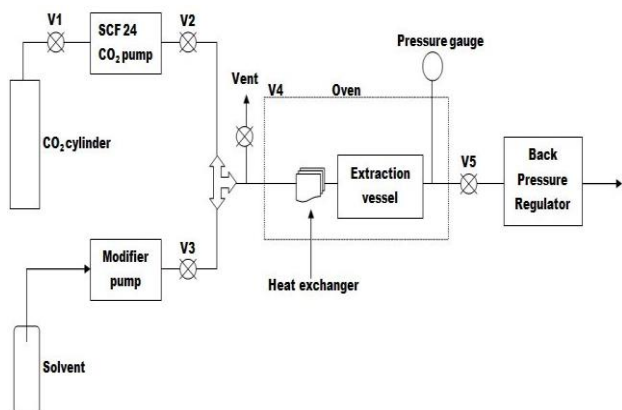
## 2.0 MATERIALS AND METHODS

### 2.1 Raw Material

The fresh rubber seeds were purchased from Malaysia local company. The rubber seeds were separated from the shell and cut into small pieces after rinsed with distilled water. The seeds were oven dried before grinding process. The grinded seeds were stored in air tight container and kept in the freezer at temperature about -20°C for extraction used.

### 2.2 Extraction using Supercritical Carbon Dioxide (SC-CO<sub>2</sub>)

The extraction of RSO was performed using lab-scale supercritical fluid extraction which consist Supercritical 24 fluid extractor (SSI, State College Pennsylvania, US), constant flow pump, a carbon dioxide cylinder and programmable back pressure regulator (Model BP-2080, JASCO, Japan). In this study, carbon dioxide was used as the solvent in the extraction of RSO at a pressure range of 20 to 30 MPa and temperatures between 40 to 80°C. The Figure 1 shows the schematic diagram of lab-scale supercritical fluid extraction instrument.



**Figure 1** The schematic diagram of lab-scale supercritical fluid extraction instrument

An approximately 5 g of ground rubber seeds used for every extraction process. The extract of RSO was collected at various interval of time for 3 hours. After the extraction, the extract was relaxed in the vial that attached to the restrictor valve. The Figure 1 shows the schematic diagram of lab-scale supercritical fluid extraction instrument.

The oil yield was calculated using the following equation:

$$\text{Oil Yield (g)} = (m_2 - m_1) / m_0 \quad (1)$$

Where the  $m_2$  is the weight of extracted RSO in gram,  $m_1$  is the weight of bottle sample in gram and the  $m_0$  is the weight of rubber seeds sample in gram.

### 2.3 Gel-Based Lipmoist Preparation

Lip moist samples were prepared in gel form with several main lip moist ingredients. Table 1 show the percentage of composition in each gel-based lip moist samples which sample (A) contains all the ingredients, sample (B) contains only major lip moist compounds (wax & oil) and sample (C) without adding RSO as a control sample. The wax and oil were melted and heated separately to the temperature of 90 °C, and then both of the ingredients were mixed with continuously stirring. The temperature was adjusted to lower temperature of 60 to 75 °C. The mixture was left to cool down in room temperature after the mixture was totally mixed well.

**Table 1** Composition of gel-based lip moist samples

	Sample (A)	Sample (B)	Sample (C)
Beeswax	7%	10%	7%
Castor oil	60%	60%	75%
Lemon oil	0.5%	-	0.5%
Oleyl alcohol	12%	-	12%
Isopropyl palmitate	7.5%	-	7.5%
Rubber seeds oil	15%	30%	-
Total	100%	100%	100%

### 2.4 Fourier Transform Infrared (FTIR) Spectroscopy

In a FTIR instrument, a beam of radiation is divided into two beams by means of beam splitter. A path difference between the beams is introduced whereupon they are allowed to combine. Therefore, the interference between the beams is obtained and the intensity of the output beam can be monitored as a function of path difference using an appropriate detector [7]. In this study, Perkin Elmer Spectrum 2000 Explorer FTIR spectrometer was used for analysis of samples. Spectrum was calculated from 4000 cm<sup>-1</sup> to 450 cm<sup>-1</sup> at 4 cm<sup>-1</sup> spectral resolution. A thin film of gel sample was spread on the potassium bromide (KBr) disk and placed under the microscope. The samples of lipmoist were kept at 45°C for 8 weeks and ready for analysis.

### 3.0 RESULT AND DISCUSSION

#### 3.1 Extracted Rubber Seeds Oil

Figure 2 shows the extracted rubber seeds oil. The color of the RSO is golden-yellowish color with very pleasant peanut smell. The rubber seeds used was stored at room temperature for around 3 months before extraction and being dried using oven. This is because according to the study by Narahari and Kothandaraman [8] the hydrogen cyanide (HCN) in the rubber seeds will be reduced effectively when stored at room temperature for a minimum period of two months. Furthermore, the rubber seeds go through the process of boiling and draining is eaten by Indians in the Amazon Valley of South America without any side effect [9].



Figure 2 The extracted rubber seeds oil (RSO)

#### 3.2 Effect of Temperature on the Extraction of RSO

As shown in the Figure 3, the oil yield increase with the increasing of temperature and the maximum oil yield was obtained when the extraction process was performed at 60°C with constant carbon dioxide flow rate at 4 ml/min. However, the continuous increasing of temperature resulting the decrease in oil yield attained. This is because solvent density is being reduced once the temperature is increased. Therefore, the solubility of the RSO in the carbon dioxide was decreased and this reduces the oil yield. The extraction temperature should be controlled in order to prevent the structure alteration of the interest compounds and the risk being destroyed at high temperature.

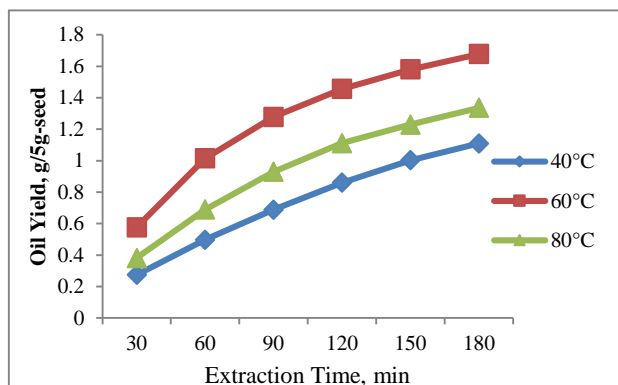


Figure 3 Effect of temperature on the extraction efficiency at fixed pressure of 30 MPa and constant flow rate of 4 ml/min

#### 3.3 Effect of Pressure on the Extraction of RSO

The effect of pressure on the oil yield was shown in Figure 4. The experiment was performed at various pressures at the temperature of 60°C and the carbon dioxide flow rate fixed at 4 ml/min. It can be observed that the oil yield increased with the increasing of operating pressure. The phenomenon is due to the solvent density increased when pressure is increased at constant temperature. Hence, the greater solvating power produced causing the solubility of oil become higher and this give the higher yield of extracted oil. Therefore, there will be more oil will be transported to the surface of the seeds giving higher yield of extracted oil during high pressure because the solvent, CO<sub>2</sub> can dissolve the oils at the surface easily.

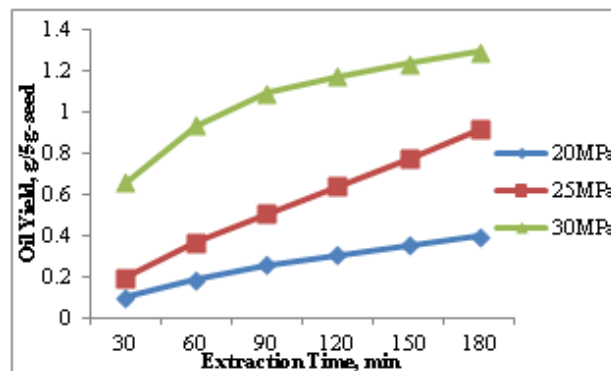


Figure 4 Effect of pressure on the extraction efficiency at 60°C and carbon dioxide flow rate at 4 ml/min

#### 3.4 The Composition of Polyunsaturated Fatty Acids in RSO

As shown in the Table 2, RSO contains  $19.22 \pm 0.21\%$  of alpha-linolenic acid (ALA) which is higher than palm oil and soybean oil. Alpha-linolenic acid is one of the important elements of omega-3 fatty acids which play important roles in human metabolism, not only playing structural roles in phospholipid bilayers but also acting as precursors to bioactive molecules [12]. Omega-3 fatty acids which also categorized as polyunsaturated fatty acid is easily absorbed by the skin and exerts its effect of speed up healing process in the body due to its ability of angiogenesis [13]. There is study also found that unsaturated fatty acid increase the cytokines and growth factors that regulate local cellular responses to injury [14].

#### 3.5 Analysis of Fourier Transform Infrared (FTIR) Spectroscopy

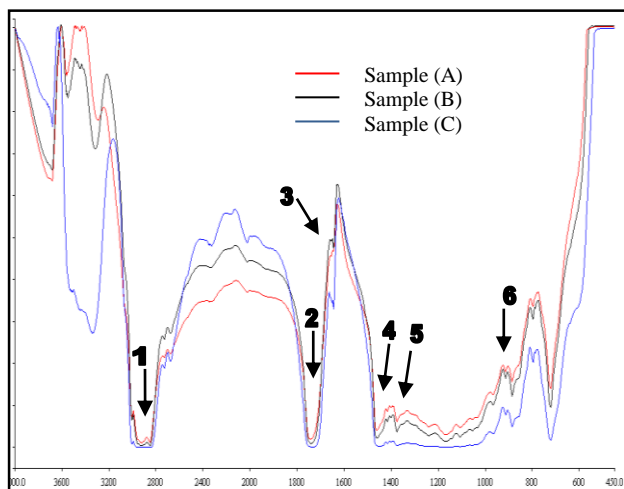
The infrared (IR) spectrum obtained from FTIR of the three gel-based lip moist displayed a number of absorption peaks. The assignments of IR bands were determined by reference to previous works [15,16,17,18].

The FTIR result for the three different compositions of gel-based lip moist samples as shown in the Figure 5 while Table 3 shows the functional groups and modes of vibration in gel-based lip moist with rubber seed oil enhancement. There were interactions detected in the wave range numbers between 1736–1743 cm<sup>-1</sup> and 1455–1463 cm<sup>-1</sup>. These two zones are the known vibration zone of carbonyl (C=O) functional group and CH<sub>3</sub> and CH<sub>2</sub> bending vibration zone. This interaction is found in all of

the three samples due to the presence of carbonyl groups, CH<sub>2</sub> and methyl groups in fatty acids of oils and wax used for lip moist production.

**Table 2** Comparison of Polyunsaturated fatty acids composition (%) of rubber seeds oil [2] with palm oil [10] and soybean oil [11]

Polyunsaturated fatty acid	Rubber seeds oil [2]	Palm Oil [10]	Soybean Oil [11]
Linoleic acid	37.18±0.10	0.73±0.01	50.17±0.83
γ-Linoleic acid	-	10.92±0.00	-
α-Linoleic acid	19.22±0.21	0.27±0.02	8.18±0.53



**Figure 5** FTIR results of 3 gel-based lip moist samples

**Table 3** Functional groups and modes of vibration in gel-based Lipmoist

No.	Frequency (cm <sup>-1</sup> )	Assignment
1	3005-3009	stretching vibration of the cis-double bond (=CH)
2	1736-1743	Carbonyl (C=O) functional group
3	1645-1650	Cis C=C
4	1455-1463	Bending vibration of CH <sub>3</sub> and CH <sub>2</sub> aliphatic groups
5	1376	Symmetric bending vibration of CH <sub>3</sub>
6	914	Bending vibration of cis-double bond (=CH)

There are variations of wave range between 3005–3009 cm<sup>-1</sup> which can be found in sample (A) and sample (B) but absent in sample (C) which without rubber seed oil enhancement. This is the zone known for cis-double bond stretching. Therefore, it shows that the polyunsaturated fatty acid (omega-3 fatty acids) presence in the lip moist samples added with RSO contain due to the vibration found in the wave range which is absent in the sample without RSO. According to cosmetics analysis in term of shelf life, the cosmetic samples will be kept at 45°C for 8 weeks to represent 2 years shelf life and used for analysis. From the FTIR results, it shows that the polyunsaturated fatty acids in RSO are stable in the ingredient base of lipmoist after 8 weeks.

#### 4.0 CONCLUSION

The extraction of rubber seeds oil (RSO) using supercritical carbon dioxide (SC-CO<sub>2</sub>) gave the better quality of oil because the extracted RSO is free from organic solvent and the study of Banana (2005) showed that at the pressure of 20.68 MPa and temperature 50°C, the bacteria or undesired microorganism will be eliminated. Hence, the end product produced meets the basic requirement of safety. In this study, the best oil yield obtained at the temperature of 60°C and pressure of 30MPa at constant flow rate of carbon dioxide, 4 ml/min. The FTIR results show that RSO can be mixed well with the ingredient base of lipmoist and remain stable after 8 weeks of storage at 45°C. Hence, RSO has the potential to be a new source of natural oil to be applied in lipmoist as the added value because it can increase the nutritional value of lipmoist.

#### Acknowledgement

Authors gratefully acknowledge support from Universiti Teknologi Malaysia and the Centre of Lipid Engineering and Applied Research (CLEAR) laboratory. Acknowledgement also extended to Ministry of Higher Education (MOHE) provided the research grant of ERGS (Vot 4L110) and MyPhD via MyBrain 15 Program under 10<sup>th</sup> Malaysia Plan for the financial support.

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