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A SNAPSHOT ON THE IRON CONTENT IN MALAYSIAN CRUDE PALM OIL

(Tinjauan Mengenai Kandungan Ferum dalam Minyak Sawit Mentah Malaysia)

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Abstract

This study reported the iron content in crude palm oil (CPO) and selected secondary oils collected at the Malaysian palm oil mills through national surveys that were carried out in 2015, 2016, and 2019. Data from these surveys provided an indicative average iron content in the CPO produced by Malaysian palm oil millers. It was found that the average iron content (11.1 ppm) was higher than the result obtained from the previous national survey. To this finding, this study aimed to investigate the effect of filtration using filter paper on the potential type of iron found in CPO. Analysis of iron was conducted using an inductively coupled plasma - mass spectrometry (ICP-MS) instrument. Another quality parameter that might accelerate the iron content such as free fatty acid was also deliberated. The possible factors that might contribute to the high iron content in CPO and recommendations on the control of iron contamination were also discussed.

Keywords: iron, survey, crude palm oil, quality

Abstrak

Kajian ini melaporkan kandungan ferum dalam minyak sawit mentah (MSM) dan beberapa jenis minyak sekunder di kilang sawit Malaysia yang diperolehi daripada kaji selidik di peringkat nasional yang telah dijalankan pada tahun 2015, 2016, dan 2019. Data yang diperolehi daripada kaji selidik ini menunjukkan nilai purata kandungan ferum dalam MSM yang dihasilkan oleh pekilang di Malaysia. Nilai purata kandungan ferum (11.1 ppm) didapati lebih tinggi berbanding hasil kaji selidik yang telah dilaporkan sebelum ini. Analisis kandungan ferum telah dijalankan menggunakan instrumen spektrometri jisim - plasma gandingan aruhan (ICP-MS). Satu kajian awal telah dijalankan bagi meneroka kesan penapisan menggunakan kertas turas kepada jenis ferum yang mungkin terdapat dalam MSM. Parameter kualiti yang mungkin menjadi pemangkin kepada kandungan ferum seperti nilai asid bebas lemak dihuraikan. Faktor-faktor yang berkemungkinan menyumbang kepada kandungan ferum serta cadangan-cadangan bagi mengawal pencemaran ferum ke dalam MSM juga dibincangkan.

Kata kunci: ferum, kaji selidik, minyak sawit mentah, kualiti

Introduction

Crude palm oil (CPO) is extracted from the mesocarp of oil palm fruit under several milling processes. After refining process, refined palm oil undergoes further fractionation process producing liquid fraction namely palm olein and solid fraction namely palm stearin. Secondary oils are the oils recovered from empty palm fruit bunches by double pressing and palm fibre using solvent extraction technique. These secondary palm oils are sold as technical oil after undergoing a certain refining process for non-edible purposes.

Palm oil is widely exported as either in its crude or processed forms. In 2019, the total export of palm oil and its products were up to 27.98 million tonnes with total revenue of MYR 64.84 billion [1]. Being the second largest palm oil exporter in the world, Malaysia has set the goal to provide premium quality palm oil. Quality is an important aspect of palm oil products as well as from the trade point of view. Generally, the palm oil quality is evaluated based on parameters such as free fatty acid (FFA), deterioration of bleachability index (DOBI), and moisture and impurities (M&I). The quality requirements for palm oil trading are also based on the business-to-business contract, which the Palm Oil Refineries Association Members (PORAM) trading specifications are often referred to as the quality guidelines. Apart from that, the details on the quality of palm oil are specified in several specification documents such as Malaysian Standard, MS 814:2007, and Codex Stan CXS 210-1999 [2,3].

Quality of palm oil may deteriorate as a result of hydrolysis and oxidation reactions affected by certain factors such as excessive heat, water contamination, acidity, light, presence of oxygen, air, and pro-oxidant metals such as copper (Cu) and iron (Fe) [4]. The hydrolysis reaction resulted from the splitting of triacylglycerols (TAG) to FFA and partial glycerides will lead to an increase in the refining loss. Meanwhile, oxidation happened due to the attack of unsaturation by oxygen to form first peroxides and then secondary products by subsequent reactions, which gives a rancid smell and creates problems during the bleaching process. Quality deterioration may also occur if the oil is not handled and stored properly. In general palm oil milling practices, only the analyses of FFA, DOBI, and M&I are carried out as a tool to monitor the quality of CPO produced. Fe content is rarely measured since it is not a contractual specification despite its detrimental effect on the oil quality.

Naturally, CPO contains a small amount of Fe in the form of complexes, surrounded by proteins and phospholipids that rarely exceed 0.7 ppm [5]. The presence of Fe in CPO will exacerbate the oxidation reaction through its catalytic property that decomposes the hydroperoxides to form free radicals. High Fe content in CPO resulted in poor bleachability and oil stability [4, 6]. Fe presents in CPO is usually originated from the pick-up of machinery wear and tear, and also from fibre of the palm fruits which are contaminated with soil particles picked up during fresh fruit bunches (FFB) harvesting. A study on the CPO extracted from oil palm planted in laterite soil showed that the type of soil where the palms were planted contributed to high Fe content compared to those planted in alluvial soil [7, 8]. Fe content in palm oil is made up of two types, *i.e.* soluble and insoluble. The insoluble or particulate Fe often can be removed using a magnetic trap while soluble Fe is difficult to be removed by physical means.

In 2015, a one-year national CPO survey was conducted to gather information about the current status of palm oil quality. Based on the specifications, the overall quality performance of Malaysian CPO was satisfactory except for the high level of Fe. To this finding, further investigation is required to identify the nature of Fe in CPO during the national survey as Fe is one of the metals that is known to be pro-oxidant.

Recycling of oil residues derived from sterilizer condensate during CPO processing and empty fruit bunch liquor (EFBO) from the pressing of empty fruit bunches is a well-known practice in current CPO production [9,10] despite its negative effect on the overall quality of CPO. The recent introduction of new secondary oil namely palm pressed fibre oil (PPFO) [11, 12] has attracted our attention. The PPFO is obtained via the hexane extraction of palm pressed fibre and aimed for the application in the production of high value phytonutrients. However, there is a concern about the possibility of re-mixing PPFO into CPO by certain irresponsible CPO traders as the CPO price is high.

Therefore, this study reported the results of Fe content obtained from the recent CPO and secondary palm oils surveys as an update for the national survey of the Malaysian palm oil industry. The type of Fe found in the CPO was investigated by measuring the Fe content before and after filtration with filter paper. The factors that may contribute to the Fe traces in CPO and the potential ways to control Fe content were also discussed.

Materials and Methods

Sampling

A total of 240 CPO samples were obtained from the production mills located at Peninsular Malaysia, Sabah, and Sarawak for the CPO survey study. Two types of secondary oils, namely PPFO and EFBO were collected from 8 producing mills in Sabah, Johor, Pahang, and Perak. For the filtration study, a total of 32 CPO samples were obtained from different production mills in Negeri Sembilan, Selangor, Johor, and Sabah. All collected samples were kept in opaque bottles (250 mL) and stored at 5 °C upon receiving prior to analysis.

Filtration of Insoluble Iron

For the filtration study, CPO samples were heated in the oven at 55 °C to ensure all samples were melted and well homogenized before the filtration process. The initial CPO sample was collected in the scintillation vial (20 mL) and labelled as “before filter”. The remaining sample was filtered using filter paper Whatman No. 4, 185 mm diameter (Sigma Aldrich, Darmstadt, Germany), collected in another scintillation vial and labelled as “after filter”. The purpose of filtering the CPO was to remove the filterable coarse, impurities precipitate, and probably insoluble Fe residues in the CPO. Both samples were then analysed for Fe content.

Quality analysis

FFA analysis was conducted by a titration method defined in the AOCS Official Method Ca-5a 40:2007 and expressed as a percentage of palmitic acid.

Analysis of iron content in palm oil

A homogenized CPO sample (0.5 g) was digested with concentrated nitric acid (65%) and hydrogen peroxide (30%) in a close system microwave digestion (NovaWAVE SA, SCP Science) apparatus. The digested CPO sample was diluted and analysed using inductively coupled plasma - mass spectrometry NexION 2000 ICP-MS (Perkin Elmer, California, USA).

Statistical analysis

The overall means and error bars of all data in the figures and tables were calculated from the individual mean of each state. Samples were analysed in duplicate. The statistical analysis was done using Microsoft Office Excel 2007 (Microsoft Corporation, Redmond, WA).

Results and Discussion

Overview of CPO surveys data

The average of total Fe content from 240 CPO samples obtained in the 2015 CPO survey was 11.1 ppm with a standard deviation of ± 5.1 ppm. This average Fe content was way higher as compared to the values recorded during previous national surveys in 1974, 1986, and 1997 with the average value of 3.76, 5.6, 4.89, respectively [13-15]. Figure 1 shows the distribution of average Fe content from different states in Malaysia, which exceeded the maximum acceptable level stipulated in the CODEX standard [3]. Further investigation revealed that all samples were collected from palm oil mills which have been operating for more than 10 years and some of them could be half-century old palm oil mills. High Fe content observed in the CPO from these mills may be attributed to the leaching of Fe from milling machinery, *i.e.* moving parts of milling machinery due to wear and tear suggested by Gee [8].

A previous study suggested that Fe leaching was indirectly caused by FFA content in CPO that corroded some of the Fe from the mild steel parts of machinery (*i.e.* screw press) in the mill [8]. Since the average FFA content distribution of all states in the current national survey was below 5%, hence no conclusive evidence can be drawn to support the effect of FFA on Fe content as reported.

The characteristics of secondary oils

A preliminary result of the Fe content measured in PPFO and EFBO samples are compared to CPO and shown in Table 1.

Fe content in the PPFO sample was the highest as compared to EFBO. PPFO is known to contain a high level of phosphorus and carotene, as the oil is solvent extracted from the pressed palm fibre. Another type of secondary oils, namely sterilizer condensate oil (SCO) and sludge palm oil (SPO) were reported to contain Fe up to 24.27 ppm and 9.5 ppm, respectively [16].

This clearly shows that secondary oils, *i.e.* PPFO and SCO contained higher amounts of Fe compared to CPO. Secondary oils are known to be low in quality and contain higher amounts of Fe picked up from their sources. For that reason, mixing of the secondary palm oils with freshly production CPO has caused an increase of Fe contamination during storage and transportation, forming oil at a highly oxidized state [17]. The mixing of production CPO with secondary palm oils must be totally avoided because this practice will degrade the quality of CPO produced. By not recycling these secondary palm oils into the standard CPO production helps to control the level of Fe content in CPO.

Filtration of CPO – Potential solution for particulate iron removal

The results from CPO filtration study showed that the Fe content was reduced after filtration, which proved that the particulate Fe can be removed from CPO by filtration step using Whatman No. 4 filter paper. The reduction percentage was up to 98% of the initial Fe content. There were two classes of Fe compounds found; one was soluble in CPO at temperature of 55 °C and passed through Whatman No. 4 filter paper, while the remainder was filterable Fe. The average of particulate Fe measured was 18.4 ppm with a standard deviation of 12.5 ppm, and surprisingly, the soluble Fe measured in the CPO was 5.6 ppm with a standard deviation of 3.8 ppm. This finding indicated that most Fe found in CPO was in the form of non-soluble particulates.

Over the past decades, several solutions at palm oil mills were identified for the reduction and removal of Fe in palm oil. A study on the removal of suspended impurities in CPO by centrifugation was shown to reduce the Fe content in the CPO. The Fe content measured from the residue of dried impurities samples was tremendously high (6155 ppm), indicated that most of the Fe were presented as dirt in CPO [18]. Impurities such as mineral fragments of soil and stone picked up during contact of fresh fruit bunches (FFB) or loose fruits with the ground at the plantations could be found in the oil and brought over for processing [19]. Therefore, the removal and minimization of the impurities content to a level as low as 0.05% (w/w) should be practiced reducing the Fe content in CPO. Apart from that, the installation of a magnetic trap at the end of the milling process was proven as an effective technique of removing particulate Fe from CPO [20]. However, this magnetic trap was not very effective for low level of Fe.

Instead, washing of CPO that is currently being practiced for chloride removal in order to minimize the formation of 3-MCPD esters has been a potential technique for removing a substantial amount of Fe [8]. This technique was supported by the earlier reported study on the effect of washing CPO with warm water and un-washed CPO as a control, which resulted in a 50% reduction of Fe content in washed CPO compared to unwashed [18].

In the chemical refining process, Fe can also be reduced during the settling of suspended impurities at the neutralisation stage [21]. The Fe is trapped by the installation of a magnetic trap and simultaneous removal of heavy metals with the precipitation of gum by caustic soda. At the degumming and bleaching stages, the formation of phospholipid-metal complex facilitated by the addition of calcium carbonate could remove the Fe complex associated with the phospholipid [18, 21]. This is due to the enclosure of the Fe complex into the precipitate. Besides that, the usage of non-acid activated clay with neutral and natural adsorbents during the bleaching process was found to be useful for the removal of Fe in incoming CPO [22]. Fe also can be removed by adsorption during the pre-treatment step using silica in physical refining [23].

Recommendation for controlling iron contamination in CPO

There was no significant correlation between Fe content and FFA found in this study. Regardless of the finding, the most feasible and economical way to control the quality of CPO is by regular checking on the quality of the FFB received and ensuring that only acceptable quality FFB is processed in a timely manner, preferably within 24 hours post-harvesting. This practice is not only to guarantee that the FFB is not overripe and bruised during handling, but also to minimize enzyme activity in FFB which results in high acidity of palm oil.

At the mills and refineries, important machineries that come into contact with FFB and the oil *i.e.* screw press, digesters, vacuum dryers, pumps and pipelines are recommended to be made of stainless steel materials, and with organic or epoxy coatings in tanks and pipes. This acts as a preventive measure to avoid Fe pick-up during the processes. The storage tanks should be cleaned prior to loading in order to preserve the quality of the oil, as well as to avoid any potential cross-contamination [24]. The contact between palm oil with mild steel should be minimized especially at high temperatures. Regular cleaning of palm oil processing line purifiers may also help to reduce the amount of dirt presence in oil and subsequently, the Fe content.

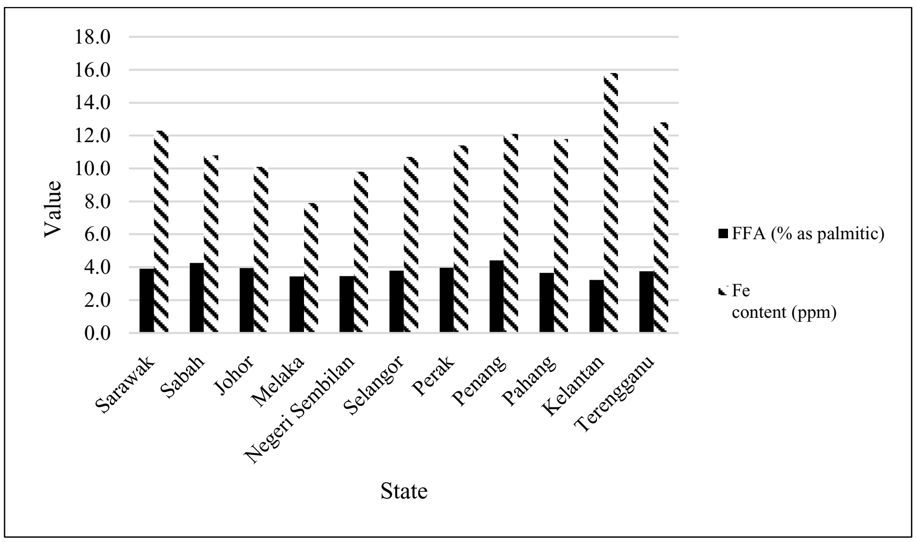

Figure 1. Average of free fatty acids and iron content in CPO from different states in Malaysia

Table 1. Iron content in CPO and secondary oils

Type of Oils	Iron Content (ppm)
PPFO	70.8 ± 44.64
EFBO (n=1)	3.9
CPO	11.1 ± 5.1

Conclusion

The increase in Fe content of CPO from the recent national survey was probably caused by particulate Fe that can be removed by filtration. This is supported by laboratory results on the findings of Fe content in CPO before and after filtration. Presently, mill and refinery already installed some devices to remove this particulate Fe. As the secondary palm oils were observed to contain high amounts of Fe, the mixing of these secondary oils into the fresh CPO should be totally avoided and prohibited. Nevertheless, preventing Fe contamination during milling, storage and transportation are crucial to safeguard the quality and safety of palm oil. High Fe content in CPO may cause a deterioration in the oil oxidative stability and subsequently affecting its keeping quality and bleachability. Further study on the effect of purifier in palm oil processing to the Fe content is necessary, in view of fact that some of the palm oil mills already omitted the usage of purifiers in their normal operation, the effect of this purifier exemption remains unknown at this point.

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