Physicochemical Characterization of Crude Palm Oil (CPO) in Sumatra and Non Sumatra Region

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Crude palm oil (CPO) is a strategic commodity for Indonesia. The locations of palm oil plantation and mill Abstract: in Indonesia are almost spread evenly in almost all regions of Indonesia. This condition leads to variations in CPO processing which may yield in varied physicochemical characteristics of CPO. Physicochemical characteristics of CPO will determine the final quality of CPO for trade. This study was aimed to investigate the physicochemical characterizations of CPO (i.e., acylglycerol fraction, free fatty acid, moisture content, deterioration of bleachability index (DOBI), and total carotene) especially those produced in Sumatra and non Sumatra region (Kalimantan and Sulawesi). These locations were selected based on the productivity value of CPO. The results showed that physicochemical characteristics of CPO in Sumatra and non Sumatra were very varied in terms of those parameters. Most of the free fatty acid, moisture content, DOBI, and total carotene from those regions met the requirements of national and international standards. However, the physicochemical characteristics of CPO were not found to be fulfilled by all the observed CPOs, so that the preparation guidelines for production systems and management of CPO processing was needed. Furthermore, diacylglycerol levels as part of acylglycerol fractions were considerably high with an average of 6.73% (3.18 - 13.64%). A higher portion of diacylglycerol in CPO must be mitigated as this compound is the precursor of a processing contaminants, such as 3-MCPDE and GE. These compounds have the potential to cause cancer. Therefore, it requires further mitigation regarding the potential formation of 3-MCPDE and GE in crude palm oil.

1 INTRODUCTION

Utilization of crude palm oil (CPO) is currently very broad, including as raw material for the production of various types of food and non-food products (Ayustaningwarno 2012). The need of CPO in this world increasing every year (Abdullah 2011) and Indonesia is one of the largest CPO producer countries in the world (Nasution et al. 2015) with production value in 2017 reaching 34.47 million tons produced in almost all regions of Indonesia, especially in The regions of Sumatra, Kalimantan and Sulawesi are the largest CPO production areas (BPS 2018). The exports of Indonesia's CPO is quite high, in 2017 reaching 29.07 million tons (84.33% of total production). Asian and European are the biggest export destinations (BPS 2018). This shows that CPO is one of the strategic trading commodities for Indonesia besides oil and gas (Widyaningtyas and Widodo 2016).

However, Indonesia's CPO exports still have obstacles, especially to European countries, several factors including environmental issues and contaminants in palm oil (GAPKI 2017). Today concern of contaminants in palm oil are 3monochloropropane-1,2-diol ester (3-MCPDE) and glycidyl ester (GE) (Lanovia et al. 2014). 3-MCPDE and GE compounds are potential carcinogenic contaminants (Habermeyer et al. 2011). Matthäus and Pudel (2013) reported that Indonesian palm oil contains 3-MCPD and GE (calculated as free 3-MCPD) between 8 - 10 mg/kg. This value is quite high because European countries have set a tolerable daily intake limit (TDI) of 3-MCPD is 2 µg/kg body weight/day (Freudenstein et al. 2013). In regulation in Europe, the maximum limit of GE content in palm oil for consumption is set at 1,000 µg/kg and as raw material for formula milk and baby food is 500 µg/kg (EC 2018).

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Several studies have shown that 3-MCPDE and GE are produced in the oil refining process, specifically in the deodorization process (Craft et al. 2012). The formation of 3-MCPDE and GE is also supported by the precursors contained in CPO namely monoacylglycerol (MAG) and diacylglycerol (DAG) (Chai et al. 2018) as a result of hydrolysis of triacylglycerol (TAG) (Ab Kadir et al. 2017) in palm oil. However DAG has more potential to produce 3-MCPDE and GE than MAG (Šmidrkal et al. 2016). Handling of palm fruit is one of the crucial factors triggering the formation of DAG. Differences in the source of oil palm plantations and the production process of each palm oil mill (PKS) will result in different physicochemical characteristics in CPO (Matthäus and Pudel 2014). Based on that information this study aimed to identification physicochemical characterization of CPO was carried out in Sumatra, Kalimantan, and Sulawesi as the largest CPO production area in Indonesia on several characteristics including the acylglycerol fraction to determine the DAG content in CPO which has the potential to form 3-MCPDE and GE compounds. In addition, the physicochemical characteristics of CPO were made as a requirement in trade including moisture content, free fatty acid (FFA) (Šmidrkal et al. 2016), deterioration of bleachability index (DOBI), total carotene (Sim et al. 2018; Zulkurnain et al. 2012), and density (Wulandari et al. 2011).

2 MATERIALS AND METHODS

2.1 Materials

This study was conducted at the Seafast Center Chemical Laboratory, IPB and palm oil mill (POM) in Sumatra, Kalimantan and Sulawesi. The materials used in this study were 62 CPO samples from 19 POM in Sumatra region, and 11 POM in non Sumatra region including 10 POM in Kalimantan, and 1 POM in Sulawesi.

Materials for analysis include distilled water, NaOH 0.25 N, indicator phenolphthalein 1%, alcohol 95% (Mallinckrodt), hexane (Merck), tetrahydrofuran (Merck), N-methyl-N-trimethylsilyltrifluoroacetamide (Sigma), heptane (Merck).

The apparatus for analysis include 250 mL high density polyethylene (HDPE) plastic bottle, 50 mL amber bottle, beaker glass, erlenmeyer, burette, hot plate, analytical balance, oven (Memmert), desiccator, porcelain crucible, waterbath (NAPCO model 220 A), 25 mL volumetric flask, UV-Vis spectrophotometer (Shimadzu), vial tube, vortex, micropipet, gas chromatography instrument with flame ionization detector (GC-FID) (Agilent 7820A).

2.2 Sampling and Sample Preparation

Sampling of CPO was carried out in Sumatra (Nangroe Aceh Darussalam, North Sumatra, West Sumatra, Jambi, South Sumatra, Bengkulu, Riau, Lampung and Bangka Belitung), Kalimantan (West Kalimantan, East Kalimantan, Central Kalimantan and South Kalimantan), and Sulawesi (West Sulawesi).

The number and location of POM being the target of CPO sampling is determined by stratified purposive sampling by taking into value of total production, number of POM, location, and availability of access to take samples at the POM. Samples were taken in 2 different storage tanks in one POM. Samples were taken randomly from the top, middle and bottom of each storage tank and then homogenized in a container. At each storage tank \pm 500 mL sample was taken which was divided into 2 containers (as replications) and then taken to the laboratory.

When arrived at the laboratory, the sample was poured into a glass cup and then heated to a temperature of \pm 50 °C and homogenized. After the sample is homogeneous and a temperature of 50 °C is reached, the sample is put into a 50 mL amber bottle. Before storing, nitrogen gas is blown on the headspace for 1 minute. Samples are stored at 4 °C.

2.3 Analysis of Moisture Content, Free Fatty Acid, Total Carotene, Density, and Acylgliserol Fraction

CPO samples that have been obtained are then analyzed by physicochemical characterization, namely moisture content with SNI 01-2901-2006 test method, free fatty acid levels (FFA) with official Ca 5a-40 2009 AOCS test method, deterioration of bleachability index (DOBI) with MPOB test method (2004), total carotene with MPOB test method (2004), and acylglyserol fraction using AOCS official test method modification Cd 11b-91 2017.

3 RESULTS AND DISCUSSION

The physicochemical characteristics of CPO including FFA, moisture content, DOBI, total carotene, and the fraction of acylgliserol (diacylglycerol (DAG) and triacylglycerol (TAG)) in

the regions of Sumatra, and non Sumatra is vary greatly. Some of physicochemical characterization CPO have fullfiled of standard specification that applies nationally and internationally, namely the Indonesian National Standard (SNI), Malaysian standard, and Codex (BSN 2006; Malaysian Standard 2007; Codex 2017). The standard is used as a control of CPO production.

The physicochemical characterization of FFA, moisture content, and DOBI are mostly below (FFA and moisture content) and above (DOBI) of the standards specifications (Figures 1, 2, and 3). However, some CPOs have values that are outside the specifications. High FFA indicates a decrease in quality due to the hydrolysis of triglycerides in CPO (Matthäus and Pudel 2013). This is due to the condition of oil palm fruit that is not fresh and the waiting time for oil palm fruit to be processed too long (Hudori 2017). These conditions can be controlled through good handling of oil palm fruit. The high moisture content in CPO will also accelerate the hydrolysis reaction (Ab Kadir et al. 2017). DOBI values in CPO indicate an increase in secondary oxidation product content. This is caused by several factors in the processing of oil palm fruit, such as the level of fruit maturity, the time and condition of the processing, distribution process, and storage and contamination that occurs in CPO (Hasibuan 2016). The results showed that relatively much CPO contained carotenoids under standard specifications (Figure 4). The influencing factors are varieties and fruit maturity level (Syahputra et al. 2008) as well as the processing, due to excessive temperature, light, pressure, and time which will cause the carotene content in CPO to decrease (Hasibuan and Harjanto 2009).



Figure 1: Free fatty acid levels of CPO in Sumatra and non Sumatra region.



Figure 2: Moisture content of CPO in Sumatra and non Sumatra region.



Figure 3: DOBI of CPO in Sumatra and non Sumatra region.



Figure 4: Total carotene of CPO in Sumatra and non Sumatra region.

DAG fraction is a precursor that has the potential to form 3-MCPDE and GE compounds (Šmidrkal et al. 2016) during the process of refining palm oil, especially the deodorization process, where the process undergoes a heating process at a temperature of 240 °C for 2 hours (Matthäus et al. 2011). According to Rahn and Yaylayan (2011) the formation of 3-MCPDE is produced through the reaction of chloride ions in lipid through the formation of acyloxonium ions. Based on the research results, the average DAG content in CPO in Sumatra, and non Sumatra region is 6.73% (3.18 - 13.64 %) (Figure 5). These results are relatively high, according to Greyt (2012) if the DAG content in palm



Figure 5: Diacylglycerol content of CPO in Sumatra and non Sumatra region.

oil is more than 4%, then the 3-MCPDE content in the oil is greater than 5 ppm. A high enough DAG component in CPO has the potential to form 3-MCPDE contaminants in the presence of chloride ions supported under suitable conditions. Franke et al. (2009) have reported that chloride ion levels in CPO are below 1 mg/kg and total chlorine is 2 mg/kg.

The conformity of the physicochemical characterization of CPO (FFA, moisture content, DOBI, and total carotene) in Sumatra and non Sumatra region to SNI, Malaysia Standard, and Codex standards is quite good (Figure 6). However, the physicochemical characteristics of CPO were not found to be fulfilled by all the observed CPOs, several things need attention including some critical points in the process of CPO processing such as the selection and handling of oil palm which will result in a decrease in the quality of CPO. Therefore preparation of guidelines for production systems and management of CPO processing was needed.



Figure 6: The conformity of the physicochemical characterization of CPO in Sumatra and non Sumatra region against several standards (SNI, Malaysia Standard, and Codex).

Based on the ANOVA test, physicochemical characterization CPO produced in Sumatra and non Sumatra did not have significant differences in FFA values, moisture content and DOBI, but there were significant in total carotene and DAG content (Table 1). So that CPO originating from Sumatra and non Sumatra tends to have different physicochemical characteristics. Characteristics of land conditions, soil physicochemistry, and climate are important factors in palm oil production (Hasriyanti et al. 2017). In addition, the CPO production process will also

affect variations in the physicochemical characteristics of CPO.

Table 1: Variation of physicochemical characterizationCPO in Sumatra and non Sumatra region.

Physicochemical characterization CPO	Region	
	Sumatra	Non Sumatra
Free fatty acid (%)	4.51 ± 1.72 ª	4.40 ± 1.92 ^a
Moisture content (%)	0.22 ± 0.12 ^a	0.19 ± 0.15 ^a
DOBI (-)	2.50 ± 0.39 ^a	2.30 ± 0.43 ^a
Total carotene (mg/kg)	477.64 ± 52.61 ^a	$518.09 \pm 48.57 \ ^{\rm b}$
Diacylgliserol (%)	6.36 ± 0.83 ^a	$7.31 \pm 2.07 \ ^{b}$

Note : (a,b) different letters above the value of physicochemical characterization in each region showed significant difference (p < 0.05)

4 CONCLUSION

The physicochemical characterization of CPO in Sumatra and non Sumatra region varies greatly in all physicochemical characteristics studied (FFA, moisture content, DOBI, total carotene, and diacylglycerol) but for some physicochemical some regions did not differ characteristics significantly. Some of physicochemical characteristics of CPO in Sumatra and non Sumatra have met the requirements of SNI, Malaysia standards, and Codex for FFA parameters, moisture content, total carotene, DOBI, and density. However, the physicochemical characteristics of CPO were not found to be fulfilled by all the observed CPOs. The DAG content of CPO in Sumatra, Kalimantan and Sulawesi is relatively high so that further mitigation is needed regarding the cause so that the potential formation of 3-MCPDE and GE in the next process can be minimized. The results of this study are expected to be followed up as recommendations for the authorities in the preparation of CPO production management and management system guidelines in order to obtain quality and competitive CPO. In addition it is necessary to further mitigate the causes of high DAG content and its potential in the formation of 3-MCPDE and GE in the next process.

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