Innovative utilization of waste chocolate condensate as cocoa powder

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Abstract. The chocolate condensate, a side product of the roasting process in chocolate production, contains mostly volatiles and liquid chemical compounds similar to the cocoa beans. Currently, it is only considered as waste, although some valuable chemicals could be obtained by extraction. This study purposes of extracting valuably chemicals, such as pyrazine that has a strong aroma to chocolate, from chocolate condensate using three different solvents, i.e., n-hexane, toluene, and ethanol. Later, cocoa powder production from chocolate condensate was developed comparing two different drying methods (spray dryer and tray dryer) and analyzed using FTNIR, FTIR, and GC-MS.

1. Introduction
Cocoa plants are vastly cultivated in many tropical countries, such as Asia region (Indonesia, Malaysia, and Papua New Guinea), Western Africa region (Cote d'Ivoire, Ghana, Nigeria, and Cameroon), South America (Brazil and Ecuador). In 2017, the world production of cocoa reached 4.7 million tonnes, increased from 4.0 million tonnes in 2016 [1]. Cote d’Ivoire, Ghana, and Indonesia showed to be the three largest country producers of cocoa with percentage of 42%, 17%, and 7%, respectively. For every single tree, the production could reach 20 to 50 of cocoa pulp/fruit and harvesting time could be done through the year. The cocoa pulp consists of fruit peel, pulp, seed shell, and cocoa beans [2]. The most important part of the cocoa fruit is cocoa beans itself, while the other parts are only considered as waste.

Chocolate condensates were obtained by condensing the evaporated cocoa beans roasting process. Roasting involves complex chemical transformations, attributed to Maillard reactions, the caramelization of sugars, protein degradation, and other chemical reactions. During roasting, the volatile fraction is released from the bean and resulted in a liquid condensate when it is cooled. Currently, chocolate condensates were usually being dumped as it is considered as waste with no benefit to the production line. Several studies [3–9,13,15] mentioned that pyrazines had been
identified in chocolate condensate that plays an essential role in cocoa flavor or additives. It also has a rich content of ester groups that are classified as chocolate fats. Besides those two major components, the other compounds are aldehydes, ketones, alcohol, ethers, esters, and organic acids [10].

This study aims to thoroughly analyze the content of condensate and the possibility to utilize this side product as an additional side income for the chocolate industry. Based on the preliminary identification, pyrazine, one of the essential components responsible for strong cocoa flavor, was tried to be extracted. Then, pyrazines-free condensate was dried using spray dryer and tray dryer to produce commercial condensate powder similar to cocoa powder.

2. Experimental Setup
The raw material of chocolate condensate was obtained directly from PT. Papandayan, Bandung, an industrial chocolate plant located in West Java, Indonesia. The feed material consisted of liquid condensate and solid matter. At first, analysis of chocolate condensate by using GC-MS (Shimadzu GCMS-QP-2010 with Rtx-5MS capillary column) analyzer was conducted to obtain the composition and concentration of species in liquid and solid matter. The extraction process then was carried out using various solvents, i.e., n-hexane, toluene, and ethanol. The product from each extraction process was then analyzed using GC-MS as well as the acid number and saponification number. The pretreatment of the sample before GC-MS analysis consisted of dilution of sample in dichloromethane for 100 times. The condensate was also pretreated by filter and centrifuge to separate possible presence of solid.

After the extraction, chocolate condensate residue was dried to produce cocoa powder by evaporating the water or liquid using spray dryer and tray dryer at temperatures of 80°C, 90°C, 100°C, and 110°C. The analysis of fat content and moisture content of each sample was cone by FTNIR. FTIR was used to compare the spectrum of the resulted cocoa powder from the standard commercial cocoa powder.

2.1. Extraction
25 mL of chocolate condensate was mixed with a solvent at a volume ratio of 1 to 1 in separating funnel. The funnel was then shaken for 10 minutes and settled down for 5 minutes with the funnel was opened to release the accumulated vapor. The condensate and solvent mixture was then treated again for another 10 minutes of shaking and 5 minutes of settling down for two cycles to obtain the optimum extraction. The extract and raffinate then separated and contained in different bottles.

The obtained extract then diluted using the same solvent by 1:20 volume. The diluted extract then filtered using filter paper and injected to centrifuge for 10 minutes by 500 rpm. The extract from centrifuge then re-filtered using filter paper before injected to GC-MS for the analysis.

2.2. Condensate Drying
Evaporation of water from chocolate condensate was carried out to produce cocoa powder by utilizing two different processes, i.e., spray dryer (EYELA Spray Dryers SD-1) and tray dryer, at temperatures of 80°C, 90°C, 100°C, and 110°C. In every run, 200 mL of condensate was used, and 5%-wt dextrin was added to the feed. The drying process carried out at an airflow rate of 1.67 mL/min for 2 hours.

In the case of the tray drying process, the experiments were done at a similar temperature used in the previous cases of spray drying. The drying residence times in the tray dryer were varied for 30, 60, 120, and 180 minutes. The weight fluctuation was recorded online, and the drying process was stopped at desired drying period. In the end, the moisture content of the samples at various drying time was measured.
3. Result and Discussions

3.1. Analysis of raw condensate

In all experiment works, the obtained raw condensates from industrial chocolate plants were used directly without any further pretreatment. The GC-MS result of raw chocolate condensate shows that some chemical groups are present in the sample, as shown in Figure 1.

![Figure 1. The GC-MS analysis of chocolate condensate.](image)

The obtained raw condensate has similar compound variation and distribution, mentioned in the references [9,10], such as alcohols, aldehydes, ketones, esters, organic acids, and pyrazine compounds. Pyrazine, the compound that gives chocolate flavor could be found both in raw and stable condensates. It was expected that the pyrazine would be most likely to be found in stable condensate (9%) due to its melting point of 53°C. While the solubility of pyrazine in water is relatively high (ca. 300 g/L), it is also expected to be found in the liquid condensate. Nevertheless, the value was too low to be detected by our analytical instrument. In general, it did not require high concentration of pyrazine to give a flavor of chocolate as food additive. Among other compounds, alcohol group was found to be dominant, with the concentration 40-95%.

3.2. Extraction method

Pyrazine is a valuable compound that should be extracted from chocolate condensate using the extraction method. The extraction process was carried out by varying solvents (n-hexane, toluene, and ethanol). The variation of solvent was considered as aimed to get the most effective one in extracting pyrazine from condensate.

The extraction process using ethanol resulted in a single-phase mixture. It indicates that all compounds were dissolved in ethanol as a polar solvent, including the pyrazine. On the other hand, two-phase liquid occurred when n-hexane and toluene were employed as solvent. The use of ethanol as solvent was applied to examine whether the formed solid in chocolate condensate could be dissolved in a high polarity solvent. The extraction process by n-hexane and toluene were then analyzed using GC-MS, and the results are shown in figure 2. The extraction using ethanol was not analyzed further as all compounds were dissolved in the solvent, it means the aim of extraction was not achieved as pyrazine was still in the same liquid phase with others.
As shown in Figure 2, the pyrazine could be extracted using n-hexane solvent but not in toluene. Pyrazines should be dissolved in polar solvent as it was completely dissolved in water or ethanol as mentioned above. Toluene has a higher polarity compared to n-hexane. Therefore, the pyrazine was predicted to be more favorable in toluene than in n-hexane solvent. The analysis using GC-MS shows different results, there is no pyrazine identified in extracted products by toluene, but it was found in n-hexane solvent. This phenomenon could be caused by the extreme dilution of toluene extract sample before it was injected to GC-MS to obtain a clear visibility sample, and it could lead GC-MS unable to detect the pyrazine in the sample. On the other hand, it shows that the polarity of pyrazine is low or semi-polar, that it could be dissolved in n-hexane, a non-polar solvent.

In addition to GC-MS analysis, the obtained samples, which are raw condensate, liquid condensate, stable condensate, the mixture of condensate and ethanol, the extract and raffinate of each n-hexane and toluene were analyzed for their acid number and saponification number. The acid number, which was converted to propionate acid content and saponification number, is shown in Figure 3 and Figure 4.

The free fatty acid content of cocoa butter is of interest to both producers and chocolate manufacturers since higher acid percentage leads to the reduction of quality in fermented cocoa beans as well as decrease in hardness of the cocoa butter [11]. The free fatty acid considered in this analysis is fatty acid that was not attached as form of triglyceride. The acid number shown in Figure 3 is fatty acid numbers counted as propionate acid in the sample. The determination of fatty acid number considered as propionate acid was the acid that found in all of the analyzed samples by GC-MS. The total summation of acid number from liquid condensate and stable condensate are expected to have similar content to acid number of initial condensate, but in this study, the acid number from both liquid and stable condensate has more significant acid number than initial condensate. This could be caused by a large number of acids in liquid condensate, as supported by the GC-MS analysis result for liquid condensate that has a lot of acids.

The smallest acid number is from the sample of n-hexane extract, due to its property as a non-polar solvent. The acids dissolved in n-hexane are few. On the other hand, n-hexane raffinate has a higher acid number, as it was mainly comprised of chocolate condensate, and the amount of acid number from extract and raffinate of n-hexane has an equal amount of acid number content in the first condenser. The result of GC-MS analysis shows that acid in initial condensate has high amount of acids.
A different result of acid number was observed for the toluene extract and raffinate. The toluene raffinate has a higher acid number compared to raw condensate. The raffinate has the highest acid number among all of the samples. The high acid content in the toluene raffinate is suspected due to the occurrence of fatty acid degradation in the raffinate. Therefore, the acid number is increased.

![Figure 3. Analysis of propionate acid content.](image)

![Figure 4. Analysis of saponification number.](image)

The saponification number form initial condensate should be equal to the summation of the saponification number from both liquid and stable condensate. Saponification number measures the
mean molecular weight of the fatty acids present in the oil or fat [12]. In this study, it was observed that stable condensate has the highest saponification number. It indicates that the triglyceride in the condensate is the majority contained in the solid condensate. The saponification number of each extract has lower number compared to its respective raffinate. This could be affected by the volume used for extraction. The volume ratio of condensate and solvent is 1:1. Therefore the triglyceride that could be extracted from the condensate is only a few.

3.3. Drying method

As known from previous analyzes there are no dangerous compounds in the chocolate condensate, and the pyrazine is challenging to be analyzed and extracted. Besides, the resulted FTIR spectrum of dried condensate at 100°C oven has similarities with commercial cocoa powder. Therefore, the chocolate condensate is then being dried to a product that could be consumed as cocoa powder.

The drying process was conducted by using a spray dryer and a tray dryer. This variation in drying method was carried out to obtain which method is more effective in making the cocoa powder from chocolate condensate. The resulted powder from spray and tray dryer then analyzed using FTNIR, FTIR, and CG-MS to get data about the contained components, as well the moisture content analysis by weighing the condensate at before and after the drying. Drying time in try dyer was varied by 30, 60, 120, 280, and 240 minutes. The cocoa powder that was taken for further analysis are powders that have similar moisture content to cocoa powder from spray dryer at same temperature. The comparison of moisture content of cocoa powder from spray and tray dryer shown in Figure 5.

As shown in Figure 5 above, the moisture content of cocoa powder from 180 minutes of drying is comparable to powder from the spray dryer. It can be deducted that samples of 180 minutes drying in a tray dryer would have similar cocoa powder with spray dryer; therefore, it was chosen for further analysis. The other way to measure the moisture content in the powder is by analyzing it using FTNIR as well as its fat content analysis. The analysis result of FTNIR for cocoa powder from spray and tray dryer is shown in Figure 6.

From the graphic of FTNIR results in Figure 6, fat and moisture content of cocoa powder are significantly different compared to the commercial cocoa powder. The lower fat content in the condensate can be caused by the injected sample to spray dryer has been separated from its stable, as it is required that the sample entering the spray dryer should be solid-free. The same sample is also injected into the tray dryer. It was expected that most of fat in the condensate is contained in solid
phase rather than in liquid condensate. Due to its high melting point, the fat will be in solid phase while stored at room temperature. Therefore the cocoa powder from liquid condensate will have lower fat content than in the commercial cocoa powder, while higher moisture content in cocoa powder from condensate could be caused by an incomplete drying process.

![FTNIR analysis results.](image)

**Figure 6.** FTNIR analysis results.

### 3.4. FTIR

Condensate cocoa powder resulted from spray and tray dryer were analyzed using FTIR to compare the similarity of its spectrum to commercial cocoa powder. The FTIR analysis result for cocoa powder at 80°C, 90°C, 100°C, and 110°C was shown in Figure 7, Figure 8, Figure 9, and Figure 10.

![FTIR spectrums for commercial cocoa powder (red), spray dryer (violet), and tray dryer (blue) at 80°C.](image)

**Figure 7.** FTIR spectrums for commercial cocoa powder (red), spray dryer (violet), and tray dryer (blue) at 80°C.
Figure 8. FTIR spectrums for commercial cocoa powder (red), spray dryer (violet), and tray dryer (blue) at 90°C.

Figure 9. FTIR spectrums for commercial cocoa powder (red), spray dryer (violet), and tray dryer (blue) at 100°C.
Figure 10. FTIR spectrums for commercial cocoa powder (red), spray dryer (violet), and tray dryer (blue) at 110°C.

Among the FTIR results for various temperatures (80 to 110°C), the spectrum that has the most similarity to commercial cocoa powder is spectrum cocoa powder from 90°C condensate drying for both tray and spray drying. Therefore, a suitable temperature for spray drying is 90°C.

The first peak at 3200 cm⁻¹ in Figure 8 is corresponding to the alcohol bond [17,18]. Among all three samples, the cocoa powder that has the highest alcohol content qualitatively is powder obtained from tray dryer method. Theoretically, powder that will have highest content of alcohol should be sample from spray dryer due to its drying time using spray drying method is the shortest one. The less strong peak of alcohol in powder from spray dryer could be caused by the addition of dextrin to the spray dryer sample, and then it would cover up the alcohol bond in the sample. The second peak is indicating the aldehyde bound in powder sample. Based on analysis using GC-MS, the highest aldehyde is contained in cocoa powder from spray dryer.

The third peak at 1500 – 1600 cm⁻¹ shows that there are alkene-aromatic compounds [17,18]. It is suspected that the absorbed spectrum in this region is corresponding to pyrazine. The smallest %transmittance peak among the three samples is powder from tray dryer, although it was not significantly different from spray dryer powder. Therefore, the pyrazines are still contained in the condensate sample, although it has been dried became to cocoa powder.

The presence of ester, ether, and carbocyclic acid was indicated by the absorbance in the 1300-1400 cm⁻¹ spectrum [17,18]. These compounds can be found most in powder from tray dryer, even it is only slightly higher than spray dryer powder, while the content in commercial cocoa powder is the lowest one. The difference of compounds in each powder could be caused by the source of the cocoa powder each itself. Commercial cocoa powder is obtained from liquor chocolate, while the others came from chocolate condensates, which are the by-product of cocoa bean roasting.

Figure 11 shows the comparison of several components from GC-MS analysis in each powder. Cocoa powder condensates are chosen by comparing the samples obtained from the tray and spray drying, which has the closest FTIR spectrum to commercial cocoa powder, i.e., 90°C.
Some components such as alcohol, ester, and ketone are found less in tray dryer cocoa powder than in the powder from spray dryer. It was affected by the longer drying time in the tray drying method compared to the spray dryer. These volatile components would be evaporated more in tray drying than in spray drying. Another factor that could affect these components is the addition of dextrin in spray drying method. The added dextrin would reduce or prevent additional evaporation of volatile components. Moreover, the analyzed component in powder from the spray dryer has a close similarity to commercial cocoa powder. Therefore the suitable method to produce cocoa powder from chocolate condensate is spray dryer.

4. Conclusions
The production of cocoa powder from chocolate condensate has been conducted. Chocolate condensate is containing pyrazines, valuable components that provide chocolate flavor. The results showed that pyrazine compounds could be extracted using a non-polar solvent because the pyrazine compounds contained in the chocolate condensate are non-polar. The most suitable cocoa powder production is by using spray drying method with the temperature of the production from chocolate condensates is at 90°C.

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