Evaluation of the effect of roasting process on the energy transition and the crystalline structures of Arabica, Robusta, and Liberica coffee from Jambi Indonesia

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Abstract. The effect of the roasting process has been evaluated to determine of the energy transition and the crystalline structure of three types of coffee, Arabica, Robusta, and Liberica coffee both green and roasted coffee with the roasted temperature at 200°C and 230°C. The crystalline structure of the coffee was evaluated with X-ray powder diffraction (XRD). The result exposes that the three types of green coffee showed that an amorphous structure whereas the roasted coffee denotes a crystal structure of sucrose. The varied temperature in the roasting process leads to changes in the crystal structure shown by the peak shift of 2θ for all types of coffee. The added cations, such as Fe^{2+}, Ca^{2+}, and Mg^{2+} ions on Liberica coffee induced of changes in the crystal structures, which are assigned by the peak shift, that imply of metal ions of the sucrose complexes happened in the solution, except for the addition of Mg^{2+} ion.

1. Introduction
Roasting coffee is a complex process of heat transfer in closed conditions, where coffee beans will experience weight loss, volume increase and the decrease in density during roasting. It is well known that roasting process causes the chemical and physicochemical characteristics of green coffee beans. The coffee beans will experience changes such as colour, pH level, taste and aroma associated with the Millard reaction [1][2]. Thermal reaction in the roasted coffee beans is decarboxylation, dehydration, fractionation, isomerisation, polymerization, and sugar complexes [3][4]. Besides, the roasting process causes improve profile thermal and crystal behaviour of the coffee [5]. Although a few recent studies about thermal behaviour and identification of a chemical change of Arabica and Robusta coffee in the roasting process have established [6][7][8] but there is very limited information for Liberica coffee beans. Meanwhile, the extracts of C. liberica have higher antioxidant capacity compared to those of C. Arabica and C. Robusta [9].

The thermal and crystal behaviour of coffee can be evaluated by using thermal analytical techniques, among which differential scanning calorimetry (DSC) and by X-ray diffraction. Variation of temperature on the roasting process can be applied to study the phase transition through the change of structure of the coffee using XRD analysis. While the change of thermal properties will be monitor by DSC [1], [10]. The experiment of green coffee using DSC shows a high and fast decomposition after 200 °C until 289 °C [11]. The XRD spectra of spent coffee grounds (SCG) coffee silverskin (CS) show a similar trend, indicating the crystal regions of both coffee residues [12].
We focused on the comparative study of thermal behaviour and crystal structure formed during roasting of arabica, robusta, and liberica coffee. We have recently described the thermal behaviour and characterization of liberica coffee beans using DSC, spectroscopic methods and XRD. The XRD analysis shows that there is a formation of polysaccharide crystal, but the structure is not confirmed yet. There have limited investigations of crystal structure formed of roasted coffee, although the knowledge of its thermal changes and chemical characterizations of coffee beans may be of importance to compare the characteristic of a varied coffee bean.

2. Materials and methodology
All experiments were performed using a Fike 500i drum roaster, 2016 made in Indonesia and heating gas propane. For all trials 1 kg batches green beans were roasted. Green coffee beans of liberica, arabica, and robusta samples from Jambi Province, Indonesia with a moisture content of around 12% were roasted at temperature 200 °C and 230 °C, roasting time up 21 minutes were selected from trials using as criteria the visual colour (light, medium and dark) of the roasting process coffee beans. Green bean and roasted coffee beans than they were ground to be powder.

To study the transformations experimented by the coffee beans after roasting, three techniques were utilized to analyse powder samples of green and roasted material. Differential scanning calorimetry (DSC) was carried out with DSC Perkin Elmer DSC 4000. To study the transformations experimented by the coffee beans after roasting, two techniques were utilized to analyse powder samples of green and roasted material. To determine the crystal structure were used an X-ray diffractions (XRD) PAnalytical Xpert3 powder goniometer PW 3050/60 type of Bragg-Brentano. Data diffraction of XRD was collected using a target atom Cu (1.54 Å) at 40 kV and 30 mA at range 2θ 15º - 70o, step 0.040 and measurement time of 0.5 s per step. The calculation of the diffraction pattern using a database Crystallography Open Database (COD) on HighScorePlus (HSP) analysis software. Rietveld method was used for phase identification that analyses and separate peaks overlapping diffraction patterns and complex. The principle Rietveld analysis method is to match the peak profile calculation of the peak profile observations.

The Liquid Chromatography-Mass Spectrometer (LC-MS) analysis was using LC-MS Waters Quarto Micro Triple quadrupole with a retention time of 45 minutes and an analysis of a mass range of 500 to 1200 g/mol. The column temperature and sample were constant at 40 °C and 20 °C. The mobile phase used consisted of 90% water and 10% methanol with a flow rate of 0.2 ml/ min and a maximum pressure of 300 bar. The preparation of samples for LC-MS analysis were as follows: 500 grams of green coffee powder and roasted coffee were macerated with 150 ml of 96% ethanol solvent for 24 hours, and then it separated. The coffee bleach was then squeezed four times over four days. The obtained filtrate was evaporated using a rotary evaporator at a temperature of 70 °C until a coffee extract was obtained.

To study the effect of metal ions to coffee, three types of metal ions were added to roasted liberica coffee at 200 °C. The metal ions obtained from CaCl2, MgCl2 and FeSO4.7H2O (Merck). Each metal (0.8 grams) dissolved in 4 ml of distilled water and then mixed into a coffee of liberica (2 grams). Mixture is heated at 75 °C and oven until dry coffee powder at 100 °C. Samples were characterized using XRD.

3. Results and discussion

3.1 Roasting process
Roasting coffee is influenced temperature and time. The roasting profiles of arabica, robusta, and liberica coffee beans with the varied temperature 200 °C and 230 °C is presented in Figure 1. The roasting profiles of arabica, robusta, and liberica coffee beans show that there is no significant difference for all type of coffee during the roasting process. It means that the three types of coffees have same characteristic. In the beginning of the roasting process, the decrease in temperature indicates the occurrence of dehydration process in coffee. This dehydration process is the process of...
evaporation of water content in coffee. During the roasting process, the colour of the coffee will gradually change, from grey, greenish to brown, dark brown, and black. After the dehydration process, the roasting temperature rises steadily up to a temperature of 210 °C. The rise in temperature explains the occurrence of chemical and physical changes during roasting.

![Roasting profile of Arabica, Robusta, and Liberica coffee](image)

**Figure 1.** Roasting profile of Arabica, Robusta, and Liberica coffee.

The first stage was called the first crack that occurs in the 16th minute, temperatures around 190°C where the colour changes from yellow to brown, the beans sizes were doubled, and lose weight around 5%. The first cracking occurs at 6 minutes at 207 °C and the second cracking at 10 minutes with a temperature of 219 °C [8]. The first crack occurs due to the amount of gas that is formed that causes cracks in the cell wall of cellulose [13]. The occurrence of first crack signifies 75-80% of the total roasting time. The final stage in the roasting process was the second crack characterized by the colour change to dark brown and oily in coffee beans due to the breakdown of cellulose in the cell walls of coffee beans. The second crack occurs in the 21st minute, at temperatures around 200 °C. The roasting process causes the build-up of pressure inside the coffee bean due to the formation of the vapour and other gases, the second crack occurs when the pressure accumulation exceeds the strength of the cellulose wall [13]. The second crack occurs when the CO₂ pressure formed in the Stracke degradation exceeds the strength of the cellulose wall in the seed [2]. Loss of CO₂ indicates that excess sugar molecules begin to oxidize (caramelized reactions), producing non-cyclic aldehydes, ketones, and acids. As temperatures continue to rise, the organic molecules undergo thermal degradation that result in a chemical changes of coffee. The existence of the second crack was often used as a reference to the end of the roasting process in coffee beans.

### 3.2 DSC analysis

DSC was used to analyse thermal behaviour of green coffee beans and roasted changes under optimum and best auto hydrolysis condition. DSC can be used to determine the heat capacity and enthalpy of the materials. Figures 2 and Table 1 show a comparison of the DSC curve of three types of coffees. In general, all three types of coffee have similar DSC curves, except green liberica coffee. The green liberica coffee has two endothermic peaks, will be explained later. From the figure, the transition glass
(Tg) for all coffees did not have much difference, between -5.77 to -4.15 °C. In this condition, the amorphous portion of the crystalline polymer switches from the brittle/rigid to the soft/plastic state. This condition occurs due to the change of amorphous solid temperature in the form of heat capacity, but no phase change. The low value of Tg on the amorphous glucose due to the presence of fragmentation products with small molecular weight [14].

For crystallization temperature (Tc), there was a considerable difference of green compared to roast coffee for all types of coffees. The green coffee has higher Tc compared to roasted coffee, which were 120.05 °C, 111.38 °C, and 120.25 °C for arabica, robusta, and liberica, respectively. The value of Tc explains about the transition process of the material from amorphous to crystal phase, known as an exothermic process. The high exothermic peak values possessed by green coffee compared due to lots of dirt and water (hydrophilic groups) contains in the coffee. The moisture content of arabica coffee was higher than robusta coffee, which is 69.7% and 60.0%, respectively [10]. The exothermic peak of roasted coffee have associated the loss of mass about 20% due to the depolymerisation reaction [4], breaking bonds, a release of some volatile compounds, and evaporation of water contains in the coffee [12].

**Figure 2.** The DSC Curve of Arabica, Robusta, and Liberica Coffee.

| Samples            | Tg (°C) | Tc (°C) | Tm (°C) | \( \Delta H_m \) (Jg\(^{-1}\)) |
|--------------------|---------|---------|---------|-------------------|
| Green Arabica      | -4.15   | 120.05  | 388     | 1071.265          |
| Roasted Arabica 200°C | -5.74   | 113.93  | 342     | 612.205           |
| Roasted Arabica 230°C | -5.72   | 111.38  | 344     | 750.229           |
| Green Robusta      | -5.71   | 111.82  | 320     | 875.140           |
| Roasted Robusta 200°C | -5.73   | 111.95  | 340     | 810.780           |
| Roasted Robusta 230°C | -5.74   | 88.080  | 344     | 445.540           |
| Green Liberica     | -5.68   | 120.25  | 325     | 886.216           |
| Roasted Liberica 200°C | -5.77   | 123.63  | 344     | 850.129           |
| Roasted Liberica 230°C | -5.68   | 122.01  | 343     | 818.378           |
As for the value of $T_m$, the temperature of the melted crystals is called the endothermic transition. The $T_m$ values of the three types of coffees have no much difference, except for green arabica and liberica. Green arabica coffee has the highest $T_m$ value of 388 °C with the enthalpy of melting of 1071.265 Jg-1. The high $T_m$ value means the high content of impurities and water in the arabica coffee. The lowest enthalpy of melting possessed by roasted robusta 230 °C is 445.540 Jg-1. The results obtained relate to the thermal decomposition of the sample due to the presence of impurities and water (hydrophilic groups) in the sample and the crystalline nature of the materials [15][9]. The endothermic transition shows the decomposition of compounds containing carbon, hydrogen and oxygen. The different phenomenon occurs on green liberica coffee, as two endothermic peaks appear. The first endothermic peak was at 63 °C, which explains that there was evaporation of water in green coffee [12]. The second endothermic peak was at 325 °C and an associated to melting process with an enthalpy change of 886.21 Jg-1. While both types of roasted coffee, the DSC curve was relatively similar. The emergence of endothermic peaks in coffee was associated with impurities and the evaporation of water in the sample (indicating the presence of hydrophilic groups) [12]. The melting temperature indicates the melting of some constituents of coffee such as amino acids, lipids and sugars such as sucrose, glucose, fructose, arabinose, galactose, maltose and polysaccharides [4].

3.3 XRD analysis

The results of x-ray spectra of green and roasted coffee for the three types of coffee (arabica, robusta, and liberica) can be seen in Figure 3. The XRD spectra for all types green coffees and roasted coffee have the same trend, it means arabica, robusta, and liberica coffee has the same characteristic. It appears that green coffee for all types of coffee does not have a peak (Figure 3.a) as in coffee that has been roasted (Figure 3.b). The green coffee diffraction patterns show an amorphous pattern. While coffee beans undergo thermal treatment (roasting), the XRD spectra of roasted coffee for the three types of coffees showed a peak. The coffee that exposed to thermal treatment has the change in the distribution of the crystalline phases [11]. The thermal treatment on the coffee beans causes the change at least a part of the crystallinity observed in SCG structure due to an elimination of some water molecules incorporated into the crystal fraction, transforming some α-polymorph to β-crystal phase structures [11], [12]. The amorphous phase changes to semi-crystal in XRD results in accordance with DSC where the DSC results show a large $T_m$ point and energy change for the melting process ($\Delta H_m$) in green coffee associated with the water elimination process (Table 1). The value of $\Delta H_m$ of green coffee for the Arabica, robusta, and liberica are higher than roasted coffee.
In arabica coffee, the peak was identified at $\theta = 18.664^\circ$ with d-spacing 4.7542 Å and intensity of 100% and $hkl = (111)$. In addition, there were two more peaks at $\theta = 11.5821^\circ$ and $24.8565^\circ$. For robusta coffee, at $\theta = 24.0227^\circ$ with d-spacing 4.1708 Å and its intensity is 38.09% and $hkl = (211)$. In the XRD results for liberica coffee, the peak appeared at $\theta = 18.737^\circ$ with d-spacing 4.7319 Å and the intensity of 90.9% and $hkl = (111)$, and the other two peaks at $\theta = 11.6648^\circ$ and $24.8401^\circ$. The peaks that appear for all roasting condition of the three types of coffees corresponds to the peaks possessed by the crystalline sucrose, which are $\theta = 11.4426^\circ$, $18.842^\circ$, and $24.773^\circ$ (ICDD 00-024-1977). According to ICDD 00-024-1977, the crystal structure of sucrose is crystal sucrose with the monoclinic crystal system.

The comparison XRD spectra of green and roasted coffee with different roasting temperature, namely: 200 °C and 230 °C for arabica, robusta, and liberica coffee is shown in Figure 4 and the XRD data of $\theta$ and the intensity of the peak are presented in Table 2.
Figure 4. XRD spectra of green and roasted coffee (a) Arabica (b) Robusta (c) Liberica.

The three spectra show the trends are similar for all types of coffees. The green coffee, without thermal treatment, was in the amorphous phase, while the roasted coffees have amorphous and crystalline region. The significant difference of spectra is evidence of the change in the distribution of the amorphous to crystalline phases when the coffee is exposed to thermal treatment [11]. The thermal heating induces the formation of a crystal in the roasted coffee. It is known that the change in hydrated caffeine by the heating process is due to a water molecule incorporated into its crystal structure [11]. The thermal heating with temperature variations of 200 ºC and 230 ºC cause slightly change of 2θ (Table 2). Caffeine in the form of a-polymorph transforms into a b-crystal phase at 141ºC and remains in this phase until melting process at 236 ºC [16]. The crystal structure of sucrose hydrates is seen in Figure 5.

### Table 2. The XRD data analysis of Arabica, Robusta, and Liberica roasted coffee at 200ºC and 230ºC

| Type of coffee | 200ºC     | 230ºC     |
|----------------|-----------|-----------|
|                | 2θ        | Intensity (%) | 2θ            | Intensity (%)  |
| Arabica        |           |            |               |               |
| 11.582         | 23.9      | 11.518     | 12.1          |               |
| 18.664         | 100       | 18.265     | 64.9          |               |
| 24.856         | 44.2      | 24.42      | 23.3          |               |
| Robusta        |           |            |               |               |
| 11.442         | 25        | 11.805     | 26.5          |               |
| 19.285         | 79.8      | 19.262     | 100           |               |
| 24.022         | 38.09     | 24.001     | 32.1          |               |
| Liberica       |           |            |               |               |
| 11.664         | 16.4      | 11.735     | 5.55          |               |
| 18.737         | 90.99     | 18.149     | 72.3          |               |
| 24.84          | 31.3      | 24.523     | 3.629         |               |
3.4 LC-MS analysis
The LC-MS spectrum of liberica coffee is shown in Figure 6 and the data m/z is tabulated in Table 3. Caffeine compounds were identified in all coffee samples, either green or roasted green coffee. Caffeine compounds appear on m/z between 194-195 g mol$^{-1}$. Caffeine appears either on or after roasting green coffee because caffeine is stable to heat. Caffeine does not significantly change during roasting, but may slightly decrease due to sublimation. For the other chemical compound, there is chemical change due to the thermal treatment of the coffee.

Figure 6. LC-MS spectra of liberica coffee (a) green (b) roasted at 200 °C.
Table 3. LC-MS data of Liberica Coffee

| Compound                  | Formula       | m/z       | Green | Roasted 200 °C |
|---------------------------|---------------|-----------|-------|----------------|
| Choline                   | C₅H₁₄NO      | 104.15    | -     | -              |
| Trigonelline              | C₇H₇NO₂      | 137.97    | 138.04|                |
| Caffeine                  | C₈H₁₀N₄O₂    | 194.82    | 194.75|                |
| Feruloylquinic acid       | C₁₇H₂₀O₉     | 407.17    | -     |                |
| Sucrose hydrates          | C₁₈H₂₀O₁₀    | -         | 435.13|                |
| Diferuloylquinic acid     | C₂₇H₂₈O₁₂    | 583.11    | -     |                |

Choline, trigonelline, and caffeine are components of nitrogen compounds in addition to proteins and amino acids that are non-volatile compounds so they are not lost during roasting [2]. Choline (C₅H₁₄NO) was identified only in green liberica coffee at m/z 104.15. Trigonelline is a pyridine derivative that contributes to the aroma and bitter taste of coffee drinks. Trigonelin (C₆H₅NO₂) with a molecular weight of 123.111 g mol⁻¹ was identified both in green and roasted liberica coffee at 137.97 and 138.04, respectively. Trigonelline will be identified on m/z 138 as [M + H]⁺ [17]. Caffeine is one of the most important compounds in the coffee that determines the quality of coffee. In theory, caffeine has a molecular weight of 195.19 m/z. The results of this study indicate the presence of alleged caffeine with a near-theoretical molecular weight, where molecular weight in green liberica coffee and after roasting 200 °C is 194.82 m/z and 194.75 m/z. Caffeine is detected at molecular weight of 195.08 m/z [18].

Chlorogenic acid (C₁₆H₁₈NO₉) is an ester group formed from a combination of quinic acid and some trans cinnamic acids, generally caffeic, p-coumaric and ferulic acid [19]. Chlorogenic acid can protect coffee plants from microorganisms, insects and UV radiation. While the benefits of chlorogenic acid for human health as an antioxidant, antiviral, hepatoprotective, and act as anti-spasmodic [5]. Chlorogenic acid in coffee can be found in the form of caffeoylquinic (CQA), pcoumaroylquinic (pCoQA), feruloylquinic acid (FQA), dicafeoylquinic (dCQA) and caffeoylferuloylquinic acid (CFQA) [20]. In this study, chlorogenic acid is present in feruloylquinic form acid and diferuloylquinic acid in Robusta coffee extract [18], where the highest intensities are 406.73 m/z and 583.11 m/z respectively.

Sucrose hydrates identified only in roasted coffee with m/z 435.13. The fructose/glucose reacts with amino acids during the roasting process to form volatile compounds and melanoidin complexes [13].

3.5. Addition of metal
It well is known that coffee as natural antioxidant sources [11], [12]. As preliminary study pharmacological effects of coffee, three types of metals have been added to the liberica-roasted coffee, which is Fe²⁺, Mg²⁺, and Ca²⁺. Iron sucrose complex (ISC) is effective in increasing haemoglobin, serum ferritin, and other haematological parameters on therapy for moderate anaemia in pregnancy [21]. Figure 7 and Table 4 shows the XRD spectra of addition metals on roasted liberica coffee. For the addition of three metals, the peak only appears in addition of Fe²⁺ with the activity of 2θ = 18.272°, d-spacing = 4.8553 A, and Intensity of 62%. The preliminary study can be predicted as an iron sucrose complex (ICD). While for Mg²⁺, and Ca²⁺, no sucrose peaks formed. It can be suggested for LCMS to make sure that ICD was observed.
Counts

![Image](82x489 to 520x716)

**Figure 7.** XRD Spectra of metal addition to roasted liberica coffee at 200°C (a) Ca\(^{2+}\) (b) Mg\(^{2+}\) (c) Fe\(^{2+}\)

**Table 4.** Comparison of XRD data of metal addition to roasted liberica coffee at 200 °C

| Without metal ion added | Fe\(^{2+}\) ion | Ca\(^{2+}\) ion |
|-------------------------|----------------|----------------|
| 6.228                   | 6.221          | 6.387          |
| 11.664                  | 9.566          | 9.259          |
| 18.737                  | 18.272         | 44.680         |
| 24.84                   | 20.873         | 50.123         |
| 72.692                  | 23.759         |                |
| 88.316                  | 27.551         | 41.912         |

4. Conclusion
Thermal behaviour of arabica, robusta, and liberica green coffee associated with a glass transition around -5.77 to -4.15 °C for green and roasted coffee. The high exothermic peak of (Tc) appears for all type green coffee indicates that the high water and volatile compound content in the coffee for the occurrence of thermal decomposition processes in coffee. The green Arabica coffee has the highest exothermic peaks at 120.05 °C. The green liberica coffee has two endothermic peaks associated to the evaporation of water and the melting of some constituents of coffee such as amino acids, lipids and sugars such as sucrose, glucose, fructose, arabinose, galactose, maltose and polysaccharides. The green Arabica has the highest melting temperature at 388°C with energy change for melting process 1071.265 Jg⁻¹. We have established experimentally by XRD that there is an increase of a crystalline phase of the sucrose with activity in 2θ = 18° with monoclinic crystal system for all types of roasted coffee. Addition of iron ion to the roasted liberica coffee forms iron sucrose complex that identified at 2θ = 18.272°. While the addition of Mg\(^{2+}\) and Ca\(^{2+}\) are not identified any peaks of sucrose.

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