The changes in chemical properties of coffee during roasting: A review

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Abstract. Due to its chemical compounds, coffee has a good taste, pleasant aroma, stimulant effect, and health benefits. Roasting is a critical process to develop a good flavor and cup quality of the coffee brew. This article reviews the coffee chemical reaction proceeds during roasting, evaluates the roasted degree by physic and chemical approach and biochemical changes. The articles were compiled from ScienceDirect, SpringerLink, ResearchGate, and Google Scholar. Out of all of the collected papers, 40 articles were covered in this paper. The initial process of roasting is water content evaporating and continuously is followed by roasting phase including pyrolysis, Maillard reaction and caramelization. The roasted coffee degree is determined by visual, weight loss, acidity, and pop beans sound. The bioactive compounds of coffee such as chlorogenic acids, caffeine, and trigonelline affect brewed coffee's cup quality. Chlorogenic acid and trigonelline significantly decrease during the roasting process. However, caffeine is quite stable during roasting. The roasted coffee performs a function in the consumers’ health since in vitro and in vivo analysis present that bronze roasted espresso has the most powerful activity as anti-inflammatory and antioxidant.

1. Introduction
Coffee is a popular non-alcoholic beverage that has been consumed over centuries [1,2]. It is the most traded commodity in the food sector, or just below petroleum in the global commodity sector [3,4]. The popularity of coffee has increased due to the fresh and pleasant flavor, the stimulant effect, and its benefits to humans’ health [2]. Over a hundred coffee species had been found, however, Arabica (Coffea Arabica L) and Robusta (Coffea canephora) are the most cultivated coffee species in the world with a share of 70% and 26%, respectively [5,6]. To get the best experience of drinking a cup of coffee, the quality of it can be affected by numerous factors such as climate, soil, altitude, processing method, roasting level and process, and brewing technique in which the roasting process became the critical point [7].

A complex reaction occurs during roasting i.e. the Maillard reactions, sugar decompositions, lipid oxidations, and pyrolysis [8]. The interaction between the release of amino acids and reducing sugars, called the Maillard reaction, induced the formation of aroma precursors [9]. The caramelization stage creates the color of coffee, while pyrolysis reactions produce volatile and non-volatile compounds and contribute to the signature aroma and taste of a cup of coffee [10–12]. The temperature and roasting
time are critical factors to provide a decent sensory profile of a cup of coffee [13]. Several levels of temperatures and roasting time had been studied depending on the roasting machine. Mehaya [14] uses a drying oven to roast a coffee at 160-220°C for 10 to 40 minutes, while [15] use Probat B to roast coffee beans at 200°C for 18 to 22 minutes. The temperature and roasting time themselves are determined by coffee roasting degree which is the visual classification of the color to determine the actual degree of roast of a bean. It could be divided into the green bean, early yellow, brown, 1st crack done, very light, light, medium, and dark [10].

Different roasting degrees result in a unique flavor and the bioactive compounds of a cup of coffee. The bioactive compounds such as phenolic, alkaloids, Maillard reaction products (MRPs), and terpenoids can provide a health-beneficial effect [16,17]. It has a high antioxidant activity which prevents our body from degenerative diseases such as type 2 diabetes mellitus [18], Parkinson's, Alzheimer's, and several types of cancer [10]. However, some of the bioactive compounds, namely total phenolic compounds (TPC) and chlorogenic acids (CGA), tend to be gradually degraded during the roasting processes where it is affected by the level of the temperature and the intensity of the roasting process [10]. Therefore, the objective of this review is to compile the information related to chemical reaction proceed and biochemical changes during roasted, and evaluation of the degree of roasted coffee by physic and chemical approach.

2. Method
During performing this review, it was explored from some databases such as ScienceDirect, SpringerLink, ResearchGate, and Google Scholar to identify and to download the abstracts, reports, journal articles and review articles. The articles were published in English from January 2000 to 2021. The manual search term was used “roasted coffee” with additional keywords such as reaction, analysis, bioactive, physicochemical, and benefits to human health. About 40 articles were used in this article, and it divided into chemical reaction during roasting, analysis of roasted degree, physicochemical changes during roasting, and benefits of roasted coffee to human health.

3. The important chemical reactions during the roasting process
Some factors affect the roasting process of coffee, such as the variety of coffee, temperature, time, airflow, and roasting method [19]. From physicochemical changes, the roasting process of coffee can be affected by water activity (Aw) which is associated with Millard reaction (low Aw condition). The roasting process consists of two stages; the drying stage and the roasting stage. These stages can be distinguished by the temperature in which the drying stage is carried out below 160°C while the roasting stage uses the temperature between 160 and 260°C [20]. Several mechanisms could alter the bean during the roasting process such as the intense heat-absorbing which the structure will start to change at 50°C, protein denaturation, and water evaporation [13,21]. The dehydration process causes reductions in the moisture content of coffee (from 10-12% of green beans to 2.5% of roasted beans). In correlation to the water content of the beans, Aw is more describer the coffee roasted degree. The Aw of coffee was significantly decreased from early-stage roasted (early yellow, brown, and 1st crack) to light roast; however, its value did not significantly different at the further roasted stage. A particular amount of water describes water vapor regarding give a high pressure and exaggerate the volume of the bean. At the low roasted coffee, indicates that the Maillard reaction is in progress [10].

After the endothermic stage was completed, the process continued to the thermal decomposition and pyrolysis reaction which can turn the coffee into brown color [13,22,23]. It starts at 190°C in which is an important pyrolytic reaction that creates a pleasant aroma and taste of coffee. Some reactions such as lipid oxidation, Maillard reaction, and caramelization simultaneously occur during the process [8]. The high intensity of heat from the roaster machine will oxidize the double bond of fatty acid, hence the iodine of coffee oil will be reduced [24].

Most consumers consider the flavor, color, and texture of a coffee that can be affected by the Maillard reaction [25]. The reaction started with creating Schiff base (N-substituted Glycosmine) by the reaction between the release of amino acids and reducing sugars. These compounds, with the use of Amadori
rearrangement, produce low molecular of volatile and non-volatile compounds. Then, the Strecker degradation occurs by the interaction between amino acids and dicarbonyl compound which thereafter formulates a-reactive dicarbonyls compounds such as pyruvaldehyde and diacetyl. These reactive compounds will react with other compounds (ammonia and hydrogen sulfide) to develop flavor compounds such as pyrazine, pyridine, pyrrole, and furan [5]. In the coloring process, Ketsamine, one of Amadori rearrangement products, is polymerized to produce melanoidin which contributes to the yellow-brown color of coffee [10]. During the roasting process, the Maillard and pyrolysis reactions generate gases that are predominantly carbon dioxide (chemical formula CO\textsubscript{2}). Some parts of the gas are released during the process, while most of the gas remains stuck inside the coffee and they will slowly desorb. The release of gas during the roasting process increases the beans’ pressure by more than 10 bars and gradually expands the beans’ volume [26]. Finally, the roasted coffee beans immediately cooled to prevent an exaggerated roast that could alter the flavour [20].

4. Roasting coffee analysis
Roaster coffee has some variations based on the adopted technologies such as hot air, infrared, and microwave. The roaster manufacture developed it by considering energy efficiency and pollutant control [26]. Numerous roasters in the market encourage researchers to evaluate the roasting degree. Roasted coffee has several levels since coffee colors alter from gray-blue-yellow-orange-brown-dark-black during roasting. Several techniques are used to determine the degree of roasting of coffee, such as bean pop, pH, weight loss, bean temperature, aroma, flavor, chemical composition, gas composition and volume [20]. Popping beans is one of the simple techniques to determine the roasted degree i.e., the first sound, namely 1st crack. The roasted coffee degrees based on popping sound are categorized to light (initial of 1st crack beginning), medium (1st crack peak), medium-dark (initial of 2nd crack), dark roast (final of the second crack) [27]. Researchers and roaster manufacture had taken several approaches in evaluating the degree of roasted coffee, as shown in (Table 1).

The alters of coffee color during roasting was the indicator to stop roasting process. Based on agtron value, the intensity of roasted coffee from very light to very dark was dramatically decreased, 90.8-32.3 [28]. Franca [29] used the oven as roaster coffee by the stable temperature at 200°C takes 30 min (light), 60 min (medium), 90 min (medium-dark), and 120 min (dark). Coffee roasted degree evaluated based on weight loss and luminosity intensity. Weight loss of light, medium and dark roasted coffee is 14, 15, and 19%, respectively. Roasting temperature significantly affected weight loss; wheather it is below 200°C reduces the weight loss faster due to water vapour [29,30]. The lightness intensity of roasted coffee decreased as roasted coffee degree increase as well. However, evaluating the degree of roasted coffee by luminosity intensity has a weakness since the value at a poor quality is lower than the good quality of coffee [29].

Roasted degree also evaluated based on the acidity of coffee using pH metric and titration. Light roast of coffee has the strongest acidity, while the darkest roast tend to lowest [31]. Herawati [20] categorized the degree of roasted coffee according to popping sound and associated to visual intensity (lightness) and water activity. Water activity has a significant effect on distinguishing the roasting degree of coffee from early yellow to 1st crack, while very light to dark roast tend to be stable [20]. Empirically, the degree of roasted coffee is determined by expertise specializing in roasting and quality control.
Table 1. Evaluation method the degree of roasted coffee.

| Roaster/Sample           | Methode                  | Result                                           | References |
|--------------------------|--------------------------|--------------------------------------------------|------------|
| Probat (TP 2)/Arabica    | Agtron Spectrophotometer | Very light-light: 90.8 Light-moderate light: 80.8 Moderate light-medium light: 71.8 Medium light-medium: 62.3 Medium-moderate dark: 48.5 Moderate dark-dark: 40.5 Dark-very dark: 32.3 | [32]       |
| Pacorini/Arabica and Robusta | Weight loss (%)       | Light (14%), Medium (15%), Dark (19%)           | [33]       |
| Oven/Arabica coffee      | Weight loss (%)         | Light (14%), Medium (15%), Dark (19%)           | [4]        |
| Oven/Arabica coffee      | Visible (Luminosity value) | Light (29-31) Medium (26-27) Dark (23-24)     | [29]       |
| IMEX (Cafe Rosto Pro 1)/ Robusta | Acidity (pH)         | Light (5.27) Medium (5.53) Dark (5.66)         | [26]       |
| IMEX (Cafe Rosto Pro 1)/ Robusta | Acidity (titration)   | Light (0.31%) Medium (0.24%) Dark (0.22%)      | [31]       |
| Probat (BRZ 2)/Robusta   | Bean pop associated with visually (lightness) | Roasting level: Lightness: Green bean: 46.35 Early yellow: 47.37 Brown: 39.61 1st crack: 32.02 Very light: 22.33 Ligh: 20.28 Medium: 18.49 Dark: 17.21 | [9]        |
| Probat (BRZ 2)/Robusta   | Bean pop associated and Aw | Roasting level: Aw: Green bean: 0.65 Early yellow: 0.56 Brown: 0.37 1st crack: 0.22 Very light: 0.15 Ligh: 0.17 Medium: 0.14 Dark: 0.15 | [9]        |

5. Physicochemical changes during roasting

Green bean to roasted coffee causes physical changes, such as water content, shape, density, structure, and color [7]. The changes in morphology characteristics of the beans during roasting were observed using SEM. The accumulation of carbon dioxide (chemical formula CO₂) from Maillard reaction inside the beans produced blow holes at 1st crack or first pop sounds. At the second pop hearing,
observed the oily above the surface inclined, the crack longer and in the middle of the bean the cell structure began to rapture [7]. Moisture content and lightness intensity were decreased along with the roaster degree increased [20]. Besides physical, the roasting process affects chemical changes since the complex chemical reaction took place i.e., caramelization, Maillard reaction, and pyrolysis produce pleasant flavor (Table 2). The pH range of coffee brewed from green beans is 5.41-5.91 which is higher than roasted (4.95-5.39). Nevertheless, the pH of brewed coffee at different degrees has a different term, which is at light roasted has a lower pH than dark [26]. Moon [14] support these result as well, french roast has a highest pH (6.09-6.18), compared to green (5.65-5.88) and light roasted bean (4.86-5.23). From a sensory perceivable, light roast acidity is lower compare to dark roast. The pH or acidity of roasted coffee a potentialy due to aliphatic acids formation during roasting [34]. Roasted coffee contains macro components such as carbohydrates, proteins, fats, and minerals; and bioactive compounds as well such as chlorogenic acid, trigonelline, caffeine, tocopherols, and diterpenes [22,34].

The main source of polyphenol compounds in coffee, chlorogenic acids (CGA), has potential as an antioxidant. CGA is an unstable compound that is easily changed during roasting through isomerization at the first step, continue to epimerization, lactonization, and degradation to formulate a low molecular weight. Chlorogenic acid is the main polyphenol substance in coffee, and it decreases during postharvest process, especially roasting process [19]. Roasted coffee contains CGA is vary, around 1.30-3.54 g/100 g. Alkaloids substances such as Trigonelline confirmed reduce as well; however, caffeine was stable during roasting process. Trigonelline and caffeine in roasted coffee are around 0.72-1.03 g/100 g and 0.88-1.53 g/100 g, respectively. Chlorogenic acids, trigonelline, and caffeine content in the green bean is varied, from 2.80-5.42 g/100 g; 0.80-1.08 g/100 g; and 0.85-1.03 g/100 g, respectively. Those three bioactive compounds, chlorogenic acids (CGA), caffeine, and trigonelline, affect the cup quality of brewed coffee [35].

| Physical/Chemical changes | Result | References |
|--------------------------|--------|------------|
| Physical                 | Roasting at 200-240 oC for 10-15 min causes microstructure of coffee changes. The Maillard reaction produces CO2 beside flavor component as well. Accumulation of CO2 increases the pressure inside and expand the volume bean. | [7]          |
| Physical                 | Moisture content of green coffee is 11.13 g/100 g, and it is decreased to 0.75 g/100 g at dark roasted. Lightness green coffee is 46.35, and it is decreased to 17.21 at dark roasted as well. | [20]         |
| Chemical                 | The pH of light roasted of brewed coffee lower compare to dark roast. | [15]         |
| Chemical                 | Macro component such as carbohydrate and protein decrease during roasting, however ash, fat is stable | [34]         |
| Chemical                 | Chlorogenic acids, total phenolic compounds, antioxidant activity were reduced during roasted. However caffeine was stable and melanoids increase during roasting. | [20]         |
| Chemical                 | Antioxidant activity, CGA and trigonelline were significantly reduce during roasting and caffeine was stable. From cupping evaluation, medium roasted coffee had higher score on profile aroma, flavor, aftertaste, acidity, balance, and overall compare to light and dark roasted coffee. | [35]         |
| Chemical                 | The highest total phenolic, total flavonoids, total phenolic acids, and caffeine were detected in light roast, and decrease along with the roasting degree increase | [36]         |
6. The benefits of roasted coffee to health

Coffee consumption is not only to get a psychoactive response nor get pleasant on it, but it is more valuable in social activity. Consumer coffee may take a cup or more in daily, depend on the people and occasion. Daily consumption of coffee has become a lifestyle today, and it has a positive effect on improving healthiness, such as liver functions, psychoactive response, neurological and metabolic disorders [37]. The health benefits of coffee consumption had been analyzed in vitro and in vivo. The in-vitro analysis found that green coffee extracts potently as a scavenger of ROO•,H2O2,H2O•,NO•, and ONOO− correlated to CGA concentration [38]. Furthermore, CGA reduction after gastrointestinal digestion was found through in-vitro analysis. However, the rest of CGA is still quite high to contribute antioxidant activity [6]. Brewed roasted coffee has the ability to inhibit \( \alpha \)-glucosidase so that it could serve as an anti-diabetic management [39]. Based on roasted degree through in vitro and in vivo analysis, bronze roasted coffee had higher activity as anti-inflammatory and antioxidant [6]. Epidemiology study shows that consume coffee less than 4 cups a day potent to reduce glucose impairment and reduced diabetic type 2 disease [40].

7. Conclusion

The physical, chemical and taste properties of coffee are affected by temperature and roasting time. A complex reaction is involved during the roasting process, consequently generating the color, aroma and flavour of coffee. Determining of roasted degree of coffee could be accomplished through various methods, however being attentive to the popping sound and visuals is the easiest. The bioactive compounds of coffee, polyphenols, is decompose at some stage in roasting process. Regarding the benefits to patron health, the medium roasting degree considers maintain bioactive compounds and the flavour is acceptable.

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