DECAFFEINATED TEA – FOR CAFFEINE SENSITIVE TEA LOVERS

After caffeine was discovered and isolated by the German analytical chemist Friedlieb Ferdinand Runge in the late nineteenth century, the first commercially successful decaffeination process was invented by the German merchant Ludwig Roselius in 1903 [1].

The process of reducing the natural caffeine content in *Camellia sinensis* tea leaves to the specified maximum level is called **decaffeination**, and the resulting tea is called **decaffeinated tea**.

There is no harmonised legislation in place for the maximum level caffeine content remaining in the decaffeinated products including tea however; there is a maximum threshold of 4 mg/g in Germany, Austria and Slovakia and in some countries such as Belgium, France, Türkiye, Italy and Switzerland it is as low as 1 mg/g [2].

The US Food and Drug Administration (FDA) relies on the expertise of the Tea Association Technical Committee (TATC) on this issue and, in line with its recommendations, agrees that the maximum caffeine level of decaffeinated tea should be 0.4% [3].

Caffeine : Bioactive Compound of *Camellia sinensis*

Caffeine (1,3,7-trimethylxanthine) is a plant alkaloid with a chemical structure of $C_8H_{10}N_4O_2$ and a molecular weight of 194.19. In pure form, it is a bitter white powder(Figure 1).

The tea plant, one of the most important natural caffeine sources, contains between 2 and 5% caffeine. In addition to tea (*Camellia sinensis*), coffee (*Coffea spp*.), cocoa (*Theobroma cacao*), maté (*Ilex paraguariensis*), cola nuts (*Cola vera*) and guarana (*Paullinia cupana*) are the other well known natural sources of caffeine and also it is mostly ingested by the consumption of tea, coffee, chocolate candy, soft drinks and commercial drugs [4,5].

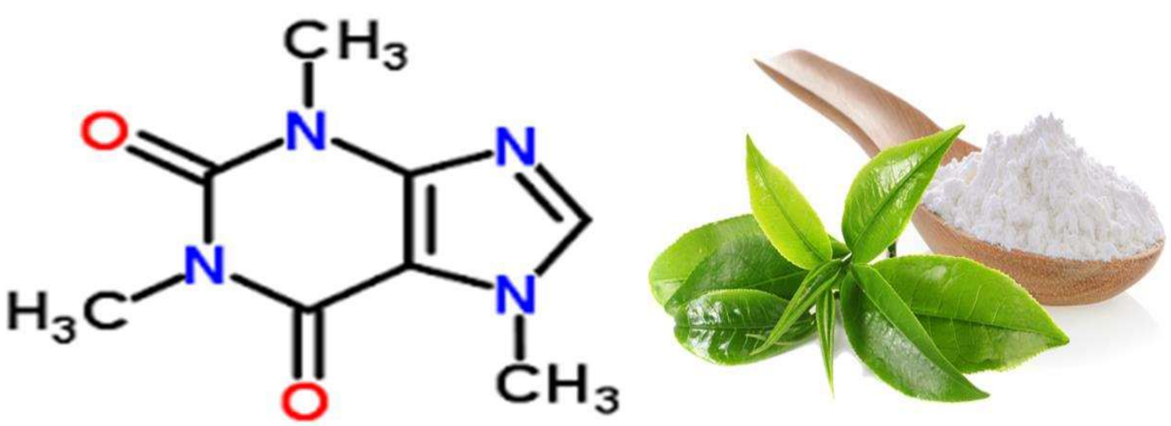

Figure 1. Chemical Structure of Caffeine (1,3,7-trimethylxanthine) and Pure caffeine

Caffeine (1,3,7-trimethylxanthine), an alkaloid is a psychoactive substance and acts as a central nervous system stimulator. Low to moderate doses (50-300 mg/day) elevates alertness, decreases fatigue, promotes mood, reduces depressive symptoms, and decreases the risk of suicide [6,7]. There is a considerable amount of evidence which suggests that moderate consumption of tea may protect against several forms of cancer, cardiovascular diseases, the formation of kidney stones, bacterial infections, and dental cavities [8]. Caffeine is an important input widely used in pharmacology.

However, higher levels of intake considerably trigger negative effects such as anxiety, restlessness, insomnia and tachychardia; these are observed primarily in caffeine-sensitive individuals. Additionally, higher dosages of caffeine show a toxic effect on women taking an oral contraceptive, pregnant women, young children, and those with liver disease. The maximum daily caffeine consumption of pregnant women should not exceed 200mg: the fetus can not metabolise the purine alkoloid and accumulated high levels of caffeine endangers the developing fetus [6, 7, 9].

Due to these negative effects safety upper limits have been set for caffeine consumption for certain groups of society.

Based on available data, the European Food Safety Authority (EFSA) has determined the safety limits for caffeine consumption as follows:

- For healthy adults in the general population, daily caffeine consumption of up to 400 mg (approximately 5.7 mg/kg body weight per day) does not pose a safety concern. Single doses of 100mg (about 1.4mg/kg bw) of caffeine may affect sleep duration and patterns in some adults, particularly when consumed close to bedtime.
- For pregnant/lactating women, intakes of up to 200 mg of caffeine per day do not raise safety concerns for the fetus and infant.
- A safety level of 3mg/kg bw per day is also proposed for habitual caffeine consumption by children and adolescents [10].

The Food and Drug Administration (FDA) considers caffeine to be both a drug and a food additive and recommends a maximum caffeine intake of 400 mg per day for healthy adults [11].

Health-conscious consumers who do not want to ingest caffeine, especially people who are sensitive to caffeine, pregnant and lactating women, children and those with liver disease, are driving the expansion of the new market for decaffeinated products, especially tea and coffee [12, 13].

Decaffeinated Tea Production Methods

Although decaffeination can be applied to all types of tea (black, green, white, oolong, etc.), it is usually done on black tea, making it extremely sensitive to change in flavour. The aim of the decaffeination process is to preserve the initial valuable components of decaffeinated tea, excluding caffeine, at the maximum level and to ensure food safety [14].

For this purpose, studies continue to develop new solvents and/or extraction methodologies that will enable the production of decaffeinated tea with higher quality and efficiency.

The methods used to extract bioactive components, including caffeine, from plants such as tea and coffee are divided into two groups: conventional extraction methods and green extraction methods (non-conventional extraction methods).

Historically many solvents that are now banned were used for decaffeination; these included chloroform and methylene chloride (also known as paint stripper). Current commercially available methods for decaffeinating tea are the conventional extraction method based on organic solvents and one of the green extraction methods called Supercritical Fluid Extraction with Carbon Dioxide (SFE-CO_2).

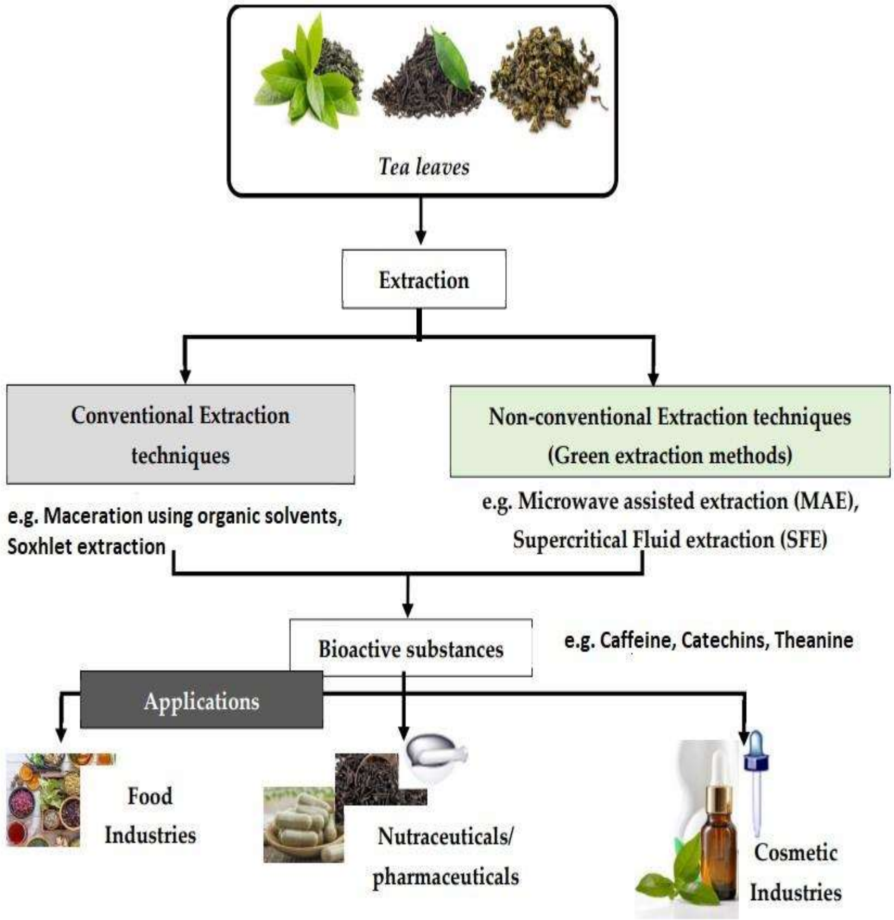

Figure 2. Schematic diagram regarding extraction of bioactive compounds from tea leaves and their applications

1. Conventional Extraction Methods

Soxhlet extraction, hydro-distillation, heat-reflux method, decoction and maceration are the main conventional extraction methods used to extract bioactive components from plant materials [15]. Conventional extraction methods are very time consuming and require relatively large quantities of solvents to remove caffeine from tea or other caffeine-containing products. During extraction, not only caffeine, but also great amount of other valuable tea components like polyphenols are removed with solvents. In addition to these disadvantages, conventional methods generally cause thermal degredation of valuable substances due to the long extraction time and high application temperature [15, 22, 23].

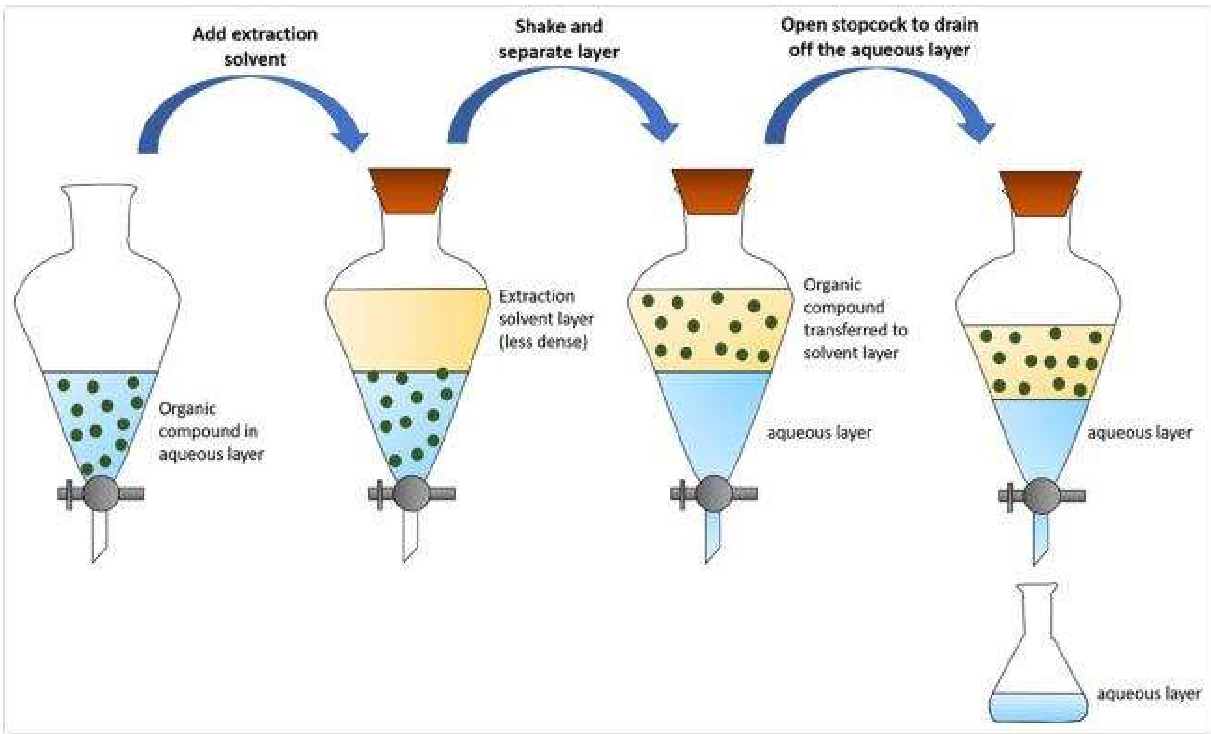

Figure 3. Process steps of lab scale solvent extraction

Maceration using organic solvents is one of the oldest extraction methods and is still widely used on an industrial scale in the decaffeination of tea.

1 a. Maceration Using Organic Solvents

The process of removing caffeine from tea using organic solvents is the oldest method of decaffeination. Until the mid-1970s, all decaffeination processes were carried out using organic solvents such as benzene, chloroform, petroleum ether, methylene chloride, trichloroethylene, carbon tetrachloride, acetone, methanol and ethanol. Although more than 30 solvents have been tested in decaffeination processes over the past 50 years, of these, methylene chloride and ethyl acetate now represent approximately 98% of all solvent extractions [16].

Decaffeination using organic solvents is usually done by first softening the tea leaves in water and then mixing them with the chosen organic solvent. Caffeine is approximately 9 times more soluble in organic solvents than in water at room temperature. Thus, most of the caffeine is extracted from the leaves into the organic phase, while the other main components of green tea, catechins and theanine, mostly remain in the leaves. It is then dried to obtain decaffeinated green tea [17].

Until the mid-1970s, the most popular organic solvent widely used for decaffeination was Methylene chloride. However, its use has been significantly limited as it has been determined that the use of this solvent contributes to the depletion of the ozone layer and also leaves toxic residues in decaffeinated products. Similarly, the use of other organic solvents such as chloroform, benzene, trichlorethylene, carbon tetrachloride, and acetone in the decaffeination process is severely restricted by food safety authorities around the world, especially EFSA and FDA, due to their inherent toxicity [13,15].

Ethyl acetate is an organic solvent still commonly used in the decaffeination of tea. Ethyl acetate is an ester and is a clear, volatile and flammable liquid with a fruity taste and a pleasant taste when diluted. It has been approved for use in decaffeination by the FDA since 1982. Among all other organic solvents, ethyl acetate is now the most preferred solvent in terms of food safety [15].

Like all other conventional extraction methods maceration extraction using organic solvents is characterized by longer extraction time, heavy solvent requirement, risking bioactivity, and less extraction yield [18].

2. Green Extraction Methods (Non-Conventional Extraction Methods)

In recent years, as consumer awareness about food safety and environmental protection increases, the tendency towards the use of green extraction methods in the food industry is rapidly increasing. In this context, the use of green extraction methods has become a new trend, especially in the isolation of bioactive components of the tea plant, as they promote greater environmental sustainability [19].

Green extraction methods are environmentally friendly extraction methods that offer various advantages compared to traditional approaches, such as reducing the consumption of extraction solvents, using non-hazardous substances, shortening the extraction time and less energy consumption [20].

Supercritical Fluid Extraction (SFE), Ultrasound-Assisted Extraction (UAE), Enzyme-Assisted Extraction (EAE), Pressurized Liquid Extraction (PLE), Pulsed Electric Field Extraction (PEF) and High-Voltage Electrical Discharges (HVED) and High-Hydrostatic Pressure Extraction (HHPE) are the main green extraction methods proposed to date [15, 22].

Although laboratory-scale decaffeination experiments have been conducted using some of these green extraction methods, it does not seem possible to scale up those methods other than the SFE method to industrial scale at this time. SFE is the only green method yet that adequately meets conditions such as selectivity, low extraction temperature, short extraction time and suitability for mass production, which are necessary to produce quality and safe decaffeinated tea [15].

2 a. Decaffeination Using Supercritical Fluid Extraction (SFE)

Supercritical CO_2 ($SCCO_2$), used as a solvent in the decaffeination of tea using the SFE method due to its many superior properties, is one of the most functional green solvents. With its advantages like having a higher diffusion coefficient and lower viscosity, rapid penetration ability, high selectivity, recyclability and safety, $SCCO_2$ has taken the place of organic solvents and proven its usefulness in food industry including decaffeination of tea. It is also relatively inert, inexpensive, non-toxic, non-flammable, readily available in high purity and leaves no residues in decaffeinated tea. In addition, it should be emphasized that the use of CO_2 does not produce any additional effect on the earth's ozone layer or aggravate the `greenhouse effect', because commercial CO_2 is obtained as a by-product from fermentation processes rather than by the combustion of fossil fuels [21].

Supercritical fluids have characteristics of both gases and liquids. Supercritical state is achieved when the temperature and the pressure of fluid is raised over its critical value. The critical state of liquid CO_2 is at a temperature of only 31.1 ^{o}C and pressure of 7.38 MPa and the corresponding critical density is 0.466 g/mL. Furthermore, use of CO_2 protects product quality and it is ideal for heat-sensitive molecules as many tea bioactive components are. At the end of the process, carbon dioxide and the extract are easily separated by pressure reduction of the extractor [21,23,24].

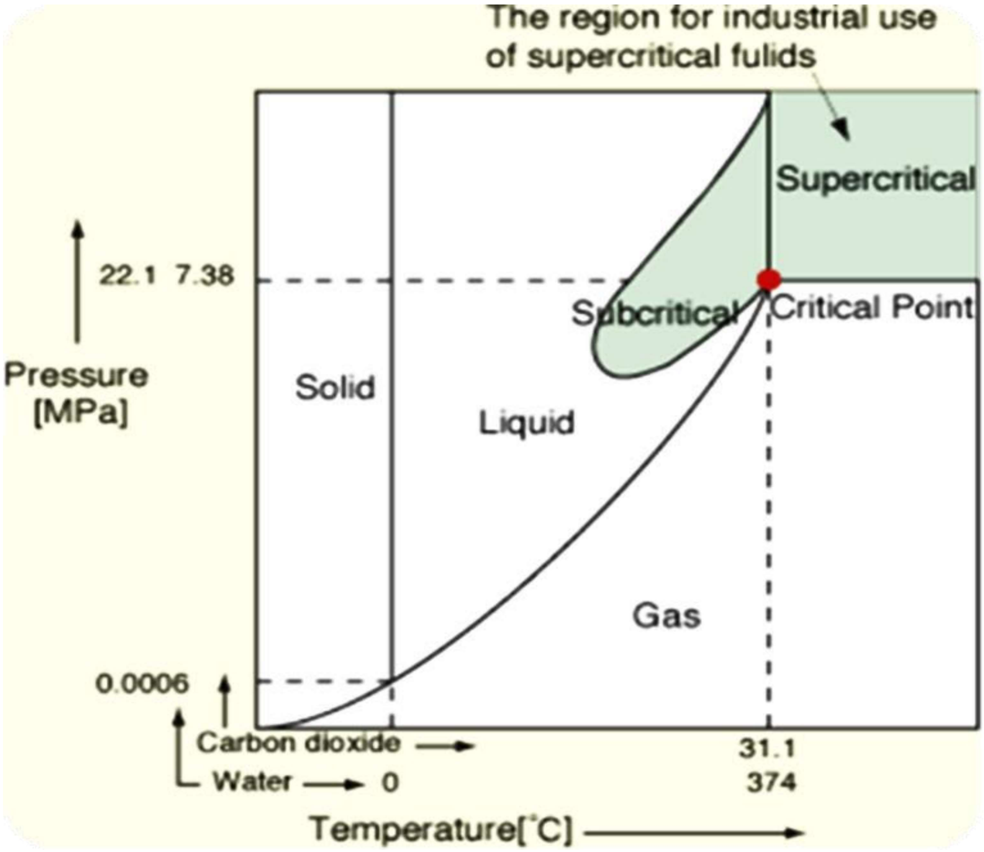

Figure 4. Supercritical state of CO_2 at Tc = 31.1 °C and Pc = 7.38 MPa

The only obstacle to the use of $SCCO_2$ in decaffeination is that $SCCO_2$ is a nonpolar or low polarity solvent. $SCCO_2$ is often used very efficiently in the extraction of solutes that have little or no polarity. Thus, due to the high polarity of caffeine, it is desirable to add a polar solvent to $SCCO_2$ as a modifier to increase the polarity of $SCCO_2$, so that $SCCO_2$ can be used to remove caffeine from green and black tea. As a polar solvent, ethanol is a well-known modifier in the food industry. It is also easily removed from the final product by evaporation at room temperature. The solubility of caffeine increases markedly with the quantity of ethanol added to the supercritical solvent, thus reducing extraction costs and increasing extraction yield [9, 25, 26].

Decaffeination of tea (green, oolong, black) using SFE-CO_2 usually begins by first standardizing the particle size of the tea leaves (<1 mm diameter). The moistened tea is loaded into the extractor vessel. As shown in Figure 5, liquid CO_2 from the dip tube (1) fills into the storage tank (3) that is cooled by the recirculating cooling bath (2) and then liquid CO_2 passes through a cooler (4) at 0–4 ^oC to the high-pressure pump (5) and vessel (8) respectively. Thus, the pressure among the storage tank, the high-pressure pump and the vessel is balanced. Liquid CO_2 is heated to desired supercritical conditions using CO_2 heater (6), then it is compressed to the desired working pressure using a high-pressure pump (5). The pressurized and heated CO_2 bypassing the separator-1, passes through the micrometering valve (10), to the separator-2 (11). A small fraction of the liquid CO_2 is intermittently discharged using the separator-2 collector (12) and the separator-2 drain (13). The remainder of the liquid CO_2 is condensed using the CO_2 condenser (14), introduced into the system and provided with circulation. In order to increase the caffeine extraction yield, food grade ethanol (mol% EtOH) is added to the system using the modifier pump (7).

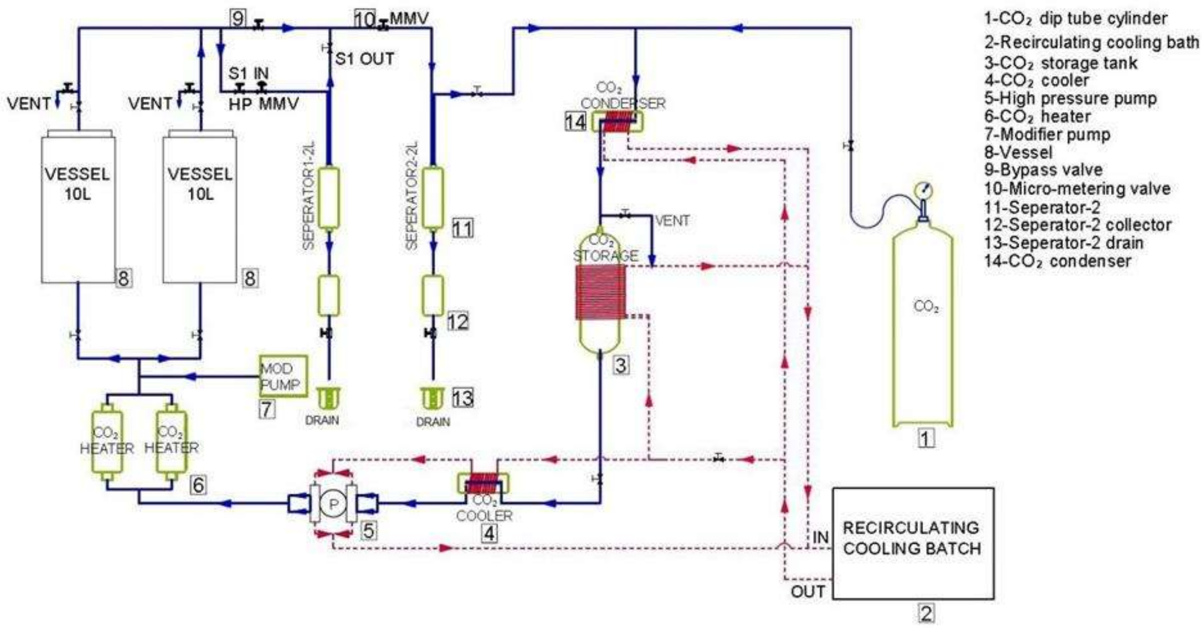

Figure 5. Schematic flow diagram of SFE-CO_2 extraction system

Figure 6. Process parameters entered and controlled via computer

In general, process parameters are entered and controlled via software of a device integrated computer, thus dynamic extraction is performed during extraction time. After extraction the decaffeinated tea is discharged from the extractor's vessel and dried in the oven until the final moisture content reached 4.0% [27].

The maximum caffeine level of decaffeinated tea obtained with SFE-CO_2 should be 0.4% or less. While removing caffeine from tea, production parameters (pressure, extraction time, extraction temperature, CO_2 flow rate and modifier concentration) must be optimized in order to preserve other bioactive components (catechins, theanine, etc.) in tea at the highest possible level [13, 23].

In a pilot-scale study in Türkiye on decaffeination of black tea using SFE-CO_2 extraction, 46 trials were conducted and maximum extraction yield (100%) was achieved under two different extraction conditions; one of which was at 375 bar pressure, 62.5^oC temperature, 300 min extraction time, 2L/min CO2 flow rate and 5 mol% modifier concentration and the other was at 375 bar pressure, 62.5 ^oC temperature, 300 min extraction time, 3 L/min CO_2 flow rate and 2.5 mol% modifier concentration[27].

Figure 7. Pilot scale Supercritical Fluid Extractor

Although the initial investment cost of SFE is higher than for conventional methods, SFE-CO_2 has essential advantages such as improved selectivity, good mass transfer performance, higher extraction yields, better fractionation capabilities, flexibility of operation conditions, adjustable range parameters, clean, safe and reliable process, non-flammable, non-toxic, easy post-treatment, and the opportunity to work at low temperature and environment-friendly conditions [16, 21, 27].

After the decaffeination process with the SFE-CO_2 method, two products with high added value are obtained: decaffeinated tea and raw caffeine. In a pilot-scale study, in addition to decaffeinated black and green tea, crude caffeine with the purity of 65-70% was obtained as the second value-added product. In the same study, crude caffeine was purified by sublimation. The caffeine obtained from SFE-CO_2 extraction was sublimated to two stage sublimation and achieved 99.9% purity. [28].

Figure 8. Value-added products after decaffeination

Eliminating the wastes released after conventional extraction methods and purifying the resulting decaffeinated tea and caffeine is time-consuming and costly, and the wastes cause environmental pollution. However, there is no residue in the tea after decaffeinization using the SFE-CO_2 method, and caffeine impurities can be easily removed by sublimation, which is an environmentally friendly method.

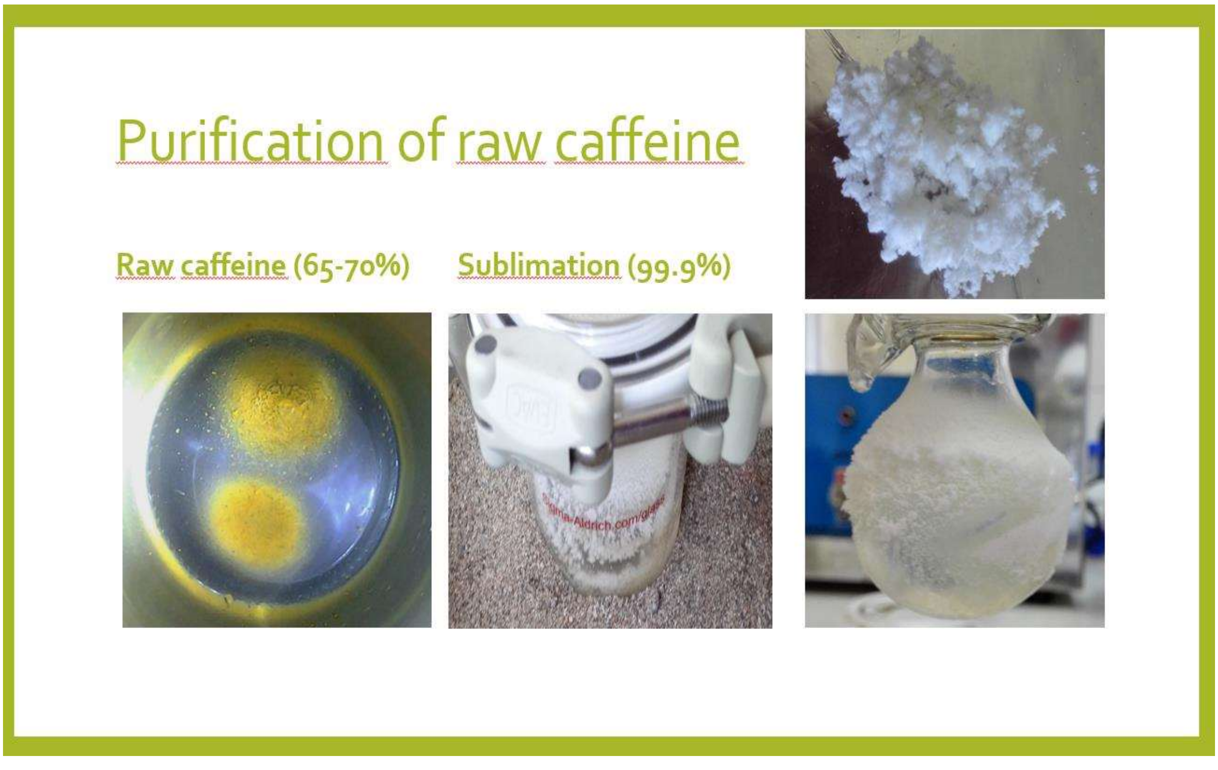

Figure 9. Sublimation of raw caffeine for purification

3. Other Developments

In the field of tea technology and breeding, studies on the removal of caffeine from the *Camellia sinensis* tea plant, and natural decaffeination through enzymatic and microbial degradation are ongoing in order to produce caffeine-free tea [36, 37].

On the other hand a new natural decaffeinated tea variety, called cocoa tea, has been domesticated from a wild caffeine free species (*Camellia ptilophylla*). Cocoa tea contains 3–5% theobromine and no caffeine, while in regular tea there is 2–5% caffeine and a little of theobromine (0.05–0.5%). However the increase in theobromine, another methylxanthine alkaloid, is open to discussion [38].

Health Benefits of Decaffeinated Tea

Since the early 20th century, many scientific studies have been conducted on the components and health benefits of tea. The results of these studies showed that tea has an antiviral, antimutogenic, antiobesity, antidiabetic, anti-aging, anticariogenic effects, bone health protection effect, cholesterol reducing effect and protective effect on cognitive health thanks to the crucial bioactive components of tea such as polyphenols, and especially catechins and theanine [29-33].

An ideal decaffeination method is the one that reduces the caffeine content to below 0.4% while preserving all bioactive components except caffeine. The most important bioactive components in question are theanine and polyphenols, especially catechins and oxidation products of catechins.

During decaffeination using conventional organic solvent extraction, while caffeine is removed from the matrix, some of the bioactive components like polyphenols that are desired to remain in the matrix are separated from the tea via the solvent. Although this value varies depending on the type of solvent and process parameters, the polyphenol loss in decaffeinated tea may reach up to 40%. SFE is more specific for the extraction of caffeine from tea. Thanks to its high selectivity, this method removes low molecular weight caffeine from the tea while ensuring that high molecular weight catechins and oxidation products (TF, TR) remain in the decaffeinated tea [34].

In the previously mentioned pilot-scale study the decaffeination of green tea was also tested using SFE-CO_2 extraction, 12 trials were carried out with 375 bar pressure, 62.5^oC temperature and 180 min extraction time were used as constant variables in these trials (Table 1). In two parallel experiments where 3 LPM CO_2 flow rate and 5 mol% modifier concentration parameters were applied, the remaining caffeine value in decaffeinated tea was reduced to 0.03%. This value is well below the specified maximum limit of 0.4%. During this decaffeination process, the caffeine content in green tea was removed by 98.7%, while the total polyphenol content decreased by 1.3% and the EGCG content decreased by 0.3% (Figure 10). These results are a clear indication of how successful the SFE-CO_2 method is as a decaffeination method [28].

There is less diminution of the bioactive components of the SFE decaffeinated tea, especially polyphenols and theanine, depending on the extraction method and solvent used in decaffeination, ensuring that decaffeinated teas, like caffeine-containing teas, contain bioactive components that are beneficial to human health.

Table 1. Caffeine, total polyphenol and EGCG content of decaffeinated green tea using SFE- CO2 method *(Constant variables: pressure 375 bar, temperature 62.5 ^{0}C, duration 3 hours)*

Experiment Code	Modifier conc. EtOH (mol %)	CO_2 Flow Rate (LPM)	Caffeine (%)	Total Polyphenol (%)	EGCG (%)
Replicate Sample	-	-	2,37	16,707	6,68
E 1	2,5	3	0,39	15,701	6,43
E 2	5	3	0,03	15,687	6,31
E 3	5	2	0,16	15,357	5,59
E 4	0	3	1,15	16,129	6,22
E 5	5	2	0,19	15,157	5,61
E 6	0	2	0,93	16,601	6,46
E 7	2,5	2	0,41	16,696	6,20
E 8	2,5	3	0,35	15,654	6,40
E 9	2,5	2	0,45	15,984	6,20
E10	5	3	0,03	15,257	6,30
E 11	0	2	1,18	16,409	6,40
E 12	0	3	0,86	15,829	6,25

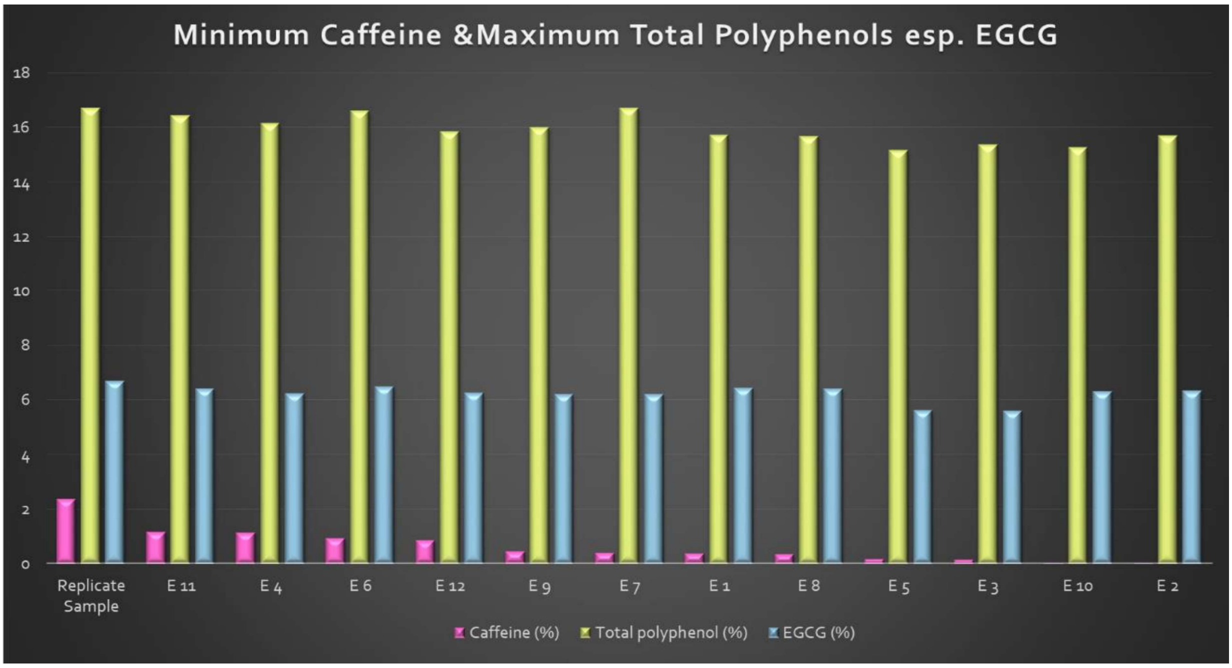

Figure 10. Caffeine, total polyphenol and EGCG content of decaffeinated green tea using SFE-CO2 method

Since excessive caffeine intake significantly triggers negative effects such as anxiety, restlessness, insomnia and tachycardia seen in caffeine sensitive individuals, tea lovers sensitive to caffeine are recommended to consume decaffeinated tea to eliminate those negative effects. In addition, women using oral contraceptives, pregnant women, young children and those with liver disease should definitely choose decaffeinated tea in order to get rid of the potentially toxic effects of caffeine and be able to drink tea as much as they desire.

In other words, if decaffeinated tea is produced with the environmentally friendly SCF-CO_2 method with high selectivity, it not only contains the health benefits of tea, but also protects people who are sensitive to caffeine from the negative effects of caffeine.

In scientific studies, it has been found that the extract values of black and green teas decaffeinated by the full-scale SFE-CO_2 method are even higher than the initial studies and this is due to the higher pressure applied.

Figure 11. Tasting decaffeinated green and black tea samples

Colour and taste scores of decaffeinated black tea samples with low residual caffeine value were higher than samples with high caffeine content. Although the dried tea appearance was lighter than desired in black tea samples with very low caffeine content, contrary to expectations, no significant negative effect was observed in the brew colour. It was stated that the bitterness in the samples decreased compared to the initial black tea sample, but the astringency remained almost the same [35]. In decaffeinated green tea samples, the colour and taste scores of samples with low residual caffeine value were higher than samples with high caffeine content. Compared to the initial green tea sample, the bitterness in decaffeinated green teas decreased and the taste was more acceptable [28].

Conclusion

Ideal decaffeinated tea (black, green tea, etc.) is tea produced from quality tea using environmental friendly extraction methods whose caffeine content is reduced to 0.4% and below, while the other bioactive components of the tea are preserved at the highest possible level. Decaffeinated teas produced to this standard enable caffeine sensitive tea lovers to drink tea with pleasure anytime and anywhere, and to benefit from the bioactive compounds in the tea.

The market share of decaffeinated tea is increasing as the number of health-conscious consumers who are sensitive to caffeine or choose to limit their caffeine consumption increases, including pregnant women, lactating woman, people with certain health conditions, and those who simply want to reduce their caffeine intake.

In today's world, consumers are also increasingly conscious of the environmental and social impact of their choices. At this point, it becomes crucial that the methods used in decaffeination of tea are environmentally friendly.

Of the two methods currently used in the production of decaffeinated tea on an industrial scale, SFE-CO_2 is an environmentally friendly method, also known as the green extraction method. The other one is organic solvent extraction, which should be urgently integrated with new technologies and use environmentally friendly solvents, also known as green solvents, instead of the organic solvents currently used.

In ongoing studies, in addition to decaffeination through enzymatic and microbial degradation, the environmentally friendly gene transcription method might also be used.

Similarly, among the Swiss and French water decaffeination techniques used in the decaffeination of coffee, the Swiss Water Extraction method, in which the flavour is preserved well, could be used for tea by integrating with new technologies and eliminating its deficiencies.

At last decaffeinated tea can match the quality of its caffeinated cousin. Decaffeinated tea, once considered a niche choice for those who couldn't tolerate caffeine, is now gaining popularity among a wider audience of tea drinkers.

Decaffeinated tea is tea that everyone can drink anytime and anywhere. Enjoy

Dr Saziye ILGAZ

European Speciality Tea Association

Board Member

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