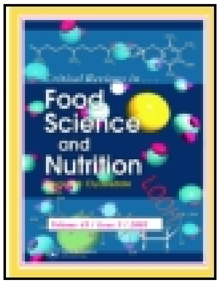

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K. Ramalakshmi [a] & B. Raghavan [a]
[a] Department of Plantation Products, Spices, and Flavour Technology, Central Food Technological Research Institute, Mysore 570 013, India
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Caffeine in Coffee: Its Removal. Why and How?

*K. Ramalakshmi and B. Raghavan**

Department of Plantation Products, Spices, and Flavour Technology, Central Food Technological Research Institute, Mysore 570 013, India

Referee: Dr. Donald N. Schenholt, Gillies Coffee Co., P.O. Box 320206, Brooklyn, NY 11232

* Author to whom correspondence should be addressed.

ABSTRACT: The popularity of coffee as a beverage is ever increasing despite the fact that there are reports antagonized to its consumption. Of the several factors cited, the alkaloid caffeine present in coffee can cause addiction and stimulate the central nervous system. It has an effect on the cardiovascular system with a slight increase in blood pressure and heart output. It undergoes biotransformation in the human body to form methylated derivatives of uric acid. In recent times, much effort has gone into the research on the removal of caffeine in coffee, resulting in a specialty product called decaffeinated coffee. Decaffeination methods mainly employ organic solvents or water or supercritical carbon dioxide. These methods with their attendant advantages and disadvantages are reviewed in this article.

KEY WORDS: caffeine metabolism, physiological effects, solvent decaffeination, water decaffeination, supercritical carbon dioxide, decaffeination of coffee.

I. INTRODUCTION

Coffee is one of the most popular beverages consumed throughout the world. The earliest documentation of coffee dates back to the tenth century. However, coffee may have been cultivated in Ethiopia, where it is indigenous, as early as 575 AD.[1] The cultivation of coffee spread to Yemen around 1400 AD. The coffee plant was introduced to the West Indies by the French in 1725 AD, from where the cultivation of coffee spread to South America. Around the same time the Dutch introduced the plant to Java, Surinam, and Sri Lanka. Later the cultivation of coffee spread to Africa and India.

Coffee plants belong to the family Rubiaceae. They are green shrubs with funnel-shaped flowers that develop into a pulpy fruit known as ‘cherry’, which contains two seeds otherwise called coffee beans. Coffee grows wild in Africa and Madagascar, and the genus includes a large number of species. Only three of them, namely, *C. arabica*, *C. canephora* (Robusta), and *C. liberica*, have been used successfully in commercial cultivation.[2] *Coffea liberica*, however, was devastated during the 1940s by epidemics of tracheomycosis, due to infection by *Fusarium xylaroides*, and commercial growth of this species has effectively ceased. Both *C. arabica* and *C. canephora* are available in a large number of varieties and cultivars. The former yields green coffee seeds bigger (longer) in size, better in aroma and generally fetches a higher price.[3] The latter is smaller, round, and yields a thicker brew. Two basic methods of processing, namely, dry (natural) and wet (washing), are used together with ancillary processes, including grading, cleaning, and polishing. In the dry method, the berries are sun dried and the coverings are removed by hulling. The beans are later cured in curing works. The product obtained is known in the trade as cherry coffee. In the wet method, the coverings are removed while the berries are still wet in a series of steps consisting of pulping, fermenting, washing, and drying. The product obtained is parchment coffee. The processing of green coffee is summarized in Figure 1.

The initial step in the preparation of any consumable product from coffee is roasting. The popularity of coffee as a beverage is due to many factors, such as aroma, taste, therapeutic effect, etc., that develop after roasting. Roasting is an operation of exposing the bean to a warming process so that bound moisture and the dry bean is heated to more than 200°C. Roasting alters the color, size, and shape of the bean. Many types of chemical reactions take place during roasting, viz., pyrolysis, oxidation, reduction, hydrolysis, polymerization, and decarboxylation.[4] After developing the coffee flavor by roasting, it is desirable to efficiently extract the roasted coffee solubles and volatiles that contribute the to coffee flavor. Roasted beans cannot be ground directly after roasting, because they are too soft. So the beans should be cooled and ground.[5]

II. EFFECTS OF CAFFEINE ON HUMAN BODY

A. Composition of Coffee

The chemical composition of green coffee mainly depends on the variety of the coffee, although slight variations are possible due to agroclimatic conditions, agricultural practices, and processing and storage. The average approximate composition of coffee is given in Table 1.

B. Caffeine in Coffee

Caffeine is of major importance with respect to the physiological properties of coffee and also in determining the bitter character. Caffeine is one of the most widely used psychoactive substances in the world, its estimated global consumption being 120 000 tonnes per year.[6] This

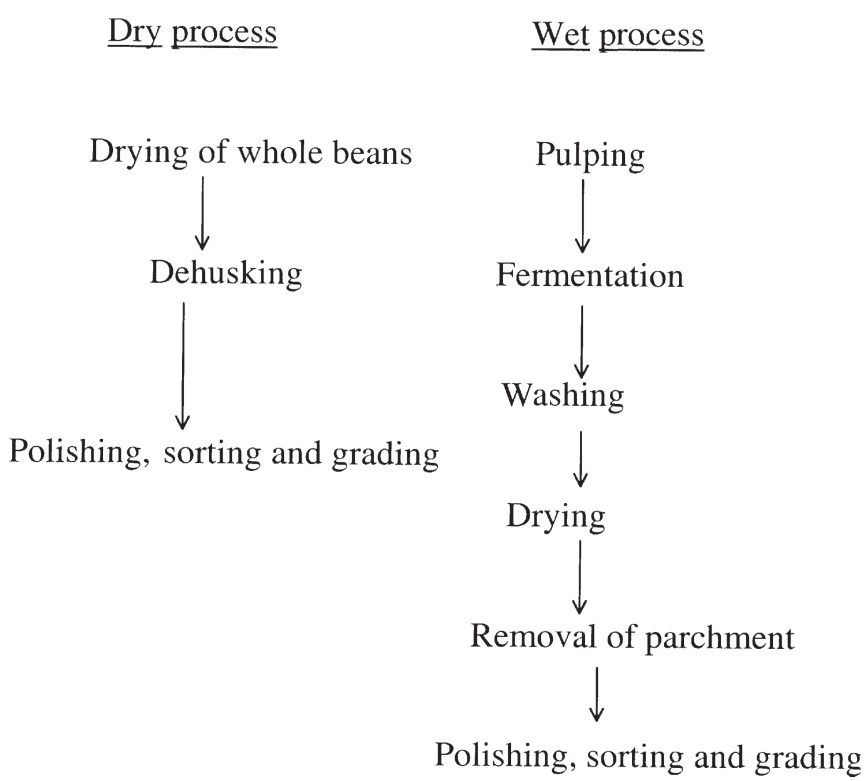

FIGURE 1. Processing of coffee. (Source: Varnam et al. 1994 (Ref. 2). Reproduced with permission.)

TABLE 1
Chemical Composition of Coffee

Component	Composition (%)
Reducing sugars	1.0
Sucrose	7.0
Pectin	3.0
Starch	10.0
Pentosan	5.0
Hemicellulose	15.0
Holocellulose (fiber)	18.0
Lignin	2.0
Oils	13.0
Protein	13.0
Ash	4.0
Chlorogenic acid	7.0
Other acids	1.0
Trignolleine	1.0
Caffeine	1.0

Source: Guide on Food Products, 1992 (Ref. 5).

has resulted in a great deal of interest in the effects of caffeine on the body and the mind.

Coffee is consumed because of its desirable bitter taste and for its "medicinal" benefits. The effect of coffee on human physiology varies from person to person and also on the quality and quantity of coffee consumed. The caffeine content of green coffee bean varies according to the species; canephora (robusta) coffee contains about 2.2%, arabica about 1.20%, and the hybrid 'arabusta' 1.72%. Environmental and agricultural factors appear to have a minimal effect on caffeine content. During roasting there is no significant loss in terms of caffeine. A typical cup of regular coffee contains 70 to 140 mg of caffeine, depending on preparation, blend, and cup size.[7]

C. Caffeine Metabolism

Chemically, caffeine is a purine derivative xanthine with methyl substituents attached at positions 1, 3, and 7. Reports on the biosynthesis and degradation of caffeine in coffee are limited. Both processes occur more rapidly in immature than mature fruit. The main biosynthesis route utilizes the purine nucleotide for the formation of caffeine, as shown in Figure 2.

In coffee plants caffeine is synthesized from xanthosine via 7-methyl xanthosine, 7-methyl xanthine, and theobromine. *S*-adenosyl methionine (SAM) is the actual source of the methyl groups. The caffeine is degraded relatively slowly and involves demethylation steps to yield theobromine and theophylline. Theophylline is catabolized to xanthine via 3-methyl xanthine. However, it is unclear whether 3-methyl xanthine and/or 7-methyl xanthine are intermediates in the conversion of theobromine to xanthine.[8] Xanthine is metabolized to urea, as shown in Figure 3.

Caffeine is moderately soluble in water, yet it is also hydrophobic enough to easily pass through biological membranes, probably for the most part by passive diffusion. Thus, caffeine is rapidly and completely absorbed from the gastrointestinal tract. More than 99% of caffeine is absorbed following its oral consumption, and peak plasma levels are generally attained within 15 to 45 min.[9] Furthermore, following absorption of caffeine, it is widely distributed in the body. In humans, 70% of a dose of caffeine is initially converted to 1,7 dimethyl xanthine and a further 25% similarly demethylated to form theophylline and theobromine. Less than 5% is metabolized by two reactions that do not involve demethyl-ation.[10,11] The rate of caffeine elimination can also vary markedly within a species, including man as a function of age, endocrine status, disease, or the presence of other drugs (Table 2).

A useful index of the rate of caffeine metabolism and excretion is its half-life in plasma, that is, the time required for plasma caffeine levels to be diminished by 50% as a result of biotransformation and excretion. The plasma half-life of caffeine varies considerably among the animal species (Table 3).

D. Physiological Effects of Caffeine

For the average consumer the physiological effects of caffeine are very closely associated with drinking coffee. There have been several reports on the phsychological effects of caffeine consumption[12–17] and its effects in conjunction with the consumption of alcohol and smoking[18–22] and drugs.[23–24] During the last decade, much at-

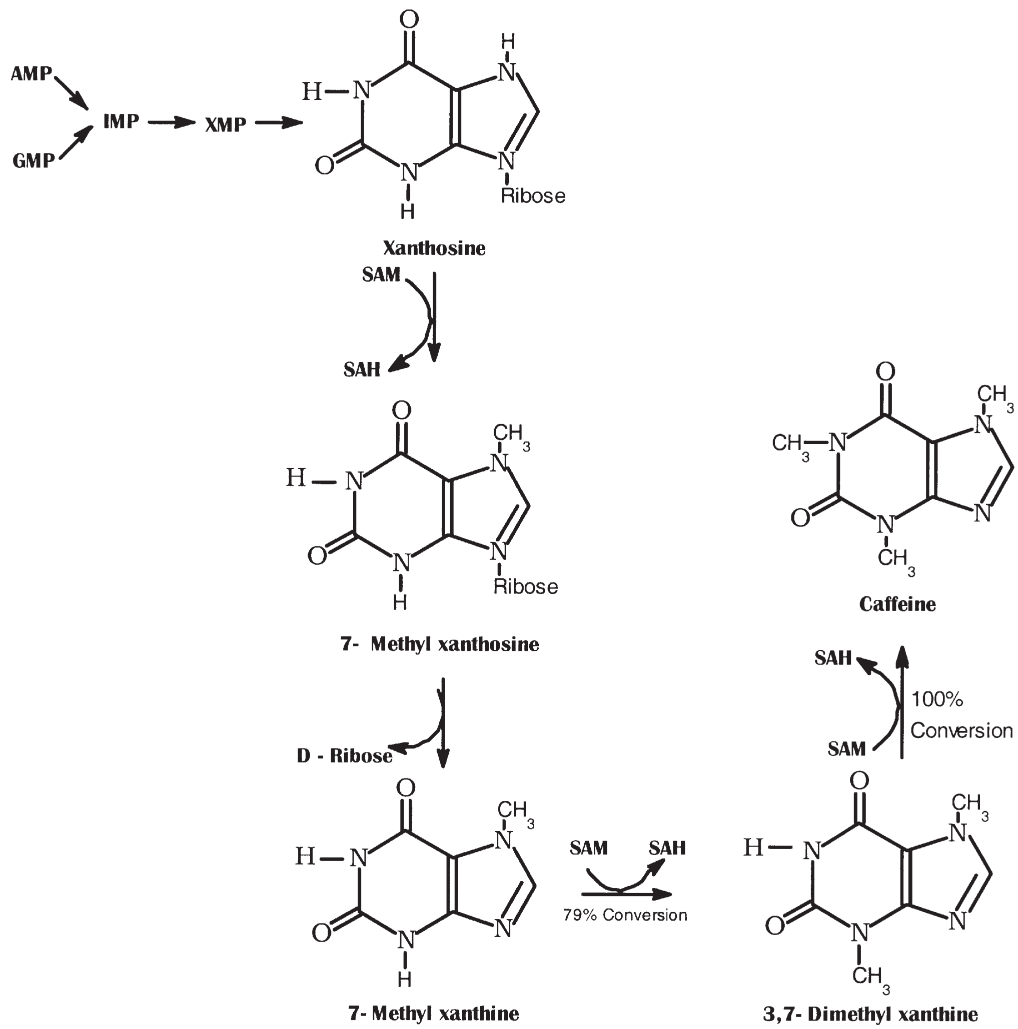

FIGURE 2. Formation of caffeine in *Coffea arabica* fruits.

tention has centered on the development of coronary heart diseases. A number of studies have been focussed to determine the effect of coffee/caffeine on heart diseases.[25–27] Rosemarin[28] observed conflicting results from epidemiological studies on coffee and coronary diseases. He suggested that coffee may induce cardiac arrhythmias, including potentially lethal ventricular ectopy in certain individuals. A decrease in the relative risk of coronary deaths with coffee consumption was found in the Norwegian study,[29] wherein coffee consumption was correlated with serum cholesterol levels and blood pressure. The effects of coffee on blood pressure and heart rate, using 107 normal adults (18 to 33 years old) were reported by Bak and Grobbee.[30] After a large-scale study in Norway comprising about 38,000 men and women in the 35- to 54-year-old age group, Tverdal[31] examined the association between the number of cups of coffee consumed per day and deaths from and coronary heart disease when taking other major coronary risk factors into account. Mean cholesterol concentrations increased from the lowest to highest coffee-consuming group. The relative risk for men who consumed less than one cup and those who consumed nine or more cups of coffee per day was estimated to be 2.2. For women, the corresponding relative risk was 5.1. Epidemiological studies have shown that the consumption of coffee at an acute level

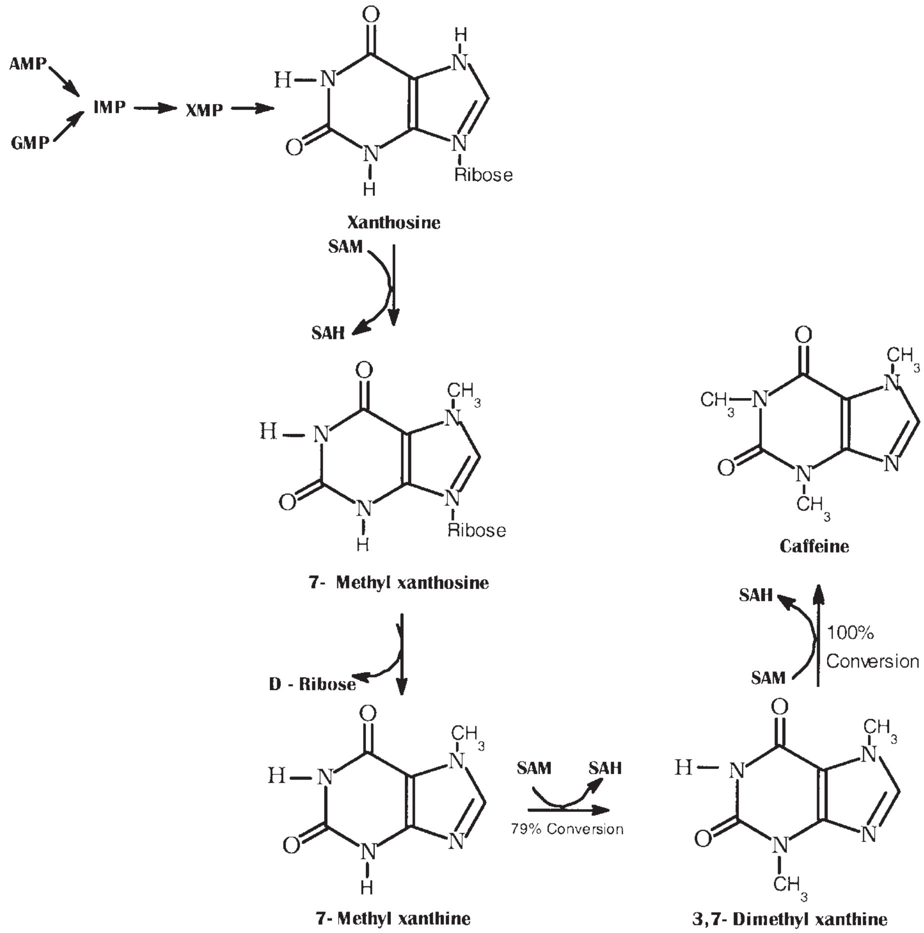

FIGURE 3

TABLE 2
Factors Modifying Caffeine Elimination in Man

Factor	Half life in plasma
None	5–6 h
Pregnancy	18 h
Oral conceptives	10.7 h
Cigarette smoking	3–4 h
Liver failure	Several days

Source: Von Borstel, 1983 (Ref. 9). Reproduced with permission.

produces a number of short-term responses, including an increase in blood pressure, plasma renin activity, urine production, and gastric acid secretion. The effect of coffee consumption on blood lipids, cholesterol, and blood pressure was investigated by Stensvold et al.[29] Bak and his co-

TABLE 3
Caffeine Biotransformation in Some Species

Species	Half life in plasma (h)	Major initial metabolites
Man	5–6	Paraxanthine (1,7–DMX)
Macaca monkey	6	Theophylline (1,3–DMX)
Beagle	4	Theophylline (1,3-DMX)
Rat	1.5–2	Theobromine (3,7–DMX)
Mouse	1.5	Theobromine (3,7–DMX)
Rabbit	1	Paraxanthine (1,7–DMX)

Note: DMX: Dimethyl xanthine

Source: Von Borstel, 1983 (Ref. 9). Reproduced with permission.

workers[32] reported on the effect of coffee on serum cholesterol, and Van Dusseldorp et al.[33] investigated the effect of decaffeinated vs. regular coffee on serum lipoproteins. Coffee consumption has been linked to cancers in many organs, but currently there appears to be little or no supportive evidence for these contentions.

There are many reports of caffeine linking with cancer of the bladder,[34–36] the pancreas,[37–39] and breast disease.[40] The risk of cancer of the colon and the rectum in relation to coffee consumption was investigated by Rosenburg et al.,[41] who suggested that coffee consumption was not related to an increased risk of large bowel cancer and that heavy consumption of coffee might reduce the risk of colon cancer. The way coffee interferes with sleep differs considerably from person to person. There are people who will have "sleepless night" even after a cup of decaffeinated coffee and others who sleep peacefully after a double espresso. Thus, caffeine is a behavioral stimulant that produces dose-dependent subjective effects in humans. The effect of caffeine on alertness was investigated by Zwyghuizen et al.,[42] who observed that caffeine increases daytime alertness and vigilance. An opposite effect of caffeine was reported by Rogestein,[43] describing the cases of six patients who had severe sleepiness apparently induced by caffeine.

Several authors have contributed reports attempting to determine whether women who consume caffeine-containing beverages take longer to become pregnant than those who abstain from such drinks. Wilcox[44] reported that consumption of more than one cup of coffee per day was associated with a 50% reduction in conception rate. In another study[45] an association was found between coffee consumption and delayed conception.

III. DECAFFEINATION

In man, a fatal dose of caffeine is estimated as 10 g or about 50 to 100 cups of average coffee (depending on strength and volume). It can cause excessive influence on the central nervous and respiratory systems, characterized by restlessness, excitement, insomnia, and possibly mild delirium. People do suffer from sleepiness, nervousness, intestinal discomfort, heart stimulation, and other effects after drinking "excessive" amounts of coffee. "Excessive" can be one cup for some, two cups for others, and three cups for people in general. Those who habitually drink coffee require a large dose for stimulation. This is because they develop a tolerance to the drink, whereas a non-coffee drinker will get "stimulating action" from even a single cup of coffee. Individual tolerances to dosages vary with age, sex, physical condition, environment, and other factors. Young people usually react negatively to drinking coffee. Middle-aged people find it stimulating and relaxing. Older people find it a useful stimulant, but avoid it due to negative body reactions.

A. History of Decaffeination

Runge first discovered and isolated caffeine in the late nineteenth century, and Roselius developed the first decaffeinating process for coffee in Germany in 1900.[46] In 1912 Roselius founded Kaffee Hag, the original commercial decaffeinated coffee. Similar operations were started in the U.S. by Kaffee Hag before World War I, but they were exported by the U.S. General Foods later bought out the "Sanka" trademark in 1932, and the process for exclusive use in the U.S. Since World War II, there has been a very significant rise in the use of decaffeinated coffee. One reason is that with the increased use of robustas possessing double the caffeine content, consumers pass over the margin of being comfortable after drinking coffee to being uncomfortable. Interestingly enough, decaffeination removes robusta's harshness (as well as flavor) and irritation leaving a bland coffee beverage with little flavor, whether consumed as R&G coffee or instant coffee. Newyork is a Swiss water town for specialty coffees. Swiss water was introduced to the American market in Newyork in 1979, and French water decaffeinated coffee was introduced in 1992. The use of solvent super critical CO_2 for decaffeination of coffee, commercialized by HAG-GF in Germany, is based on the 1970 patent of Kurt Zosel, a scientist at Max Planck Institute, Germany.

Secrecy has been a policy of almost all coffee bean decaffeinators, so little process data have been published. Patents have been the major source of public information. However, process " know-how" has become progressively available as the industry has spread out and more and more companies and people have become involved. There have been numerous process developments in decaffeination technology, the most important being solvent extraction of caffeine from prewetted beans with, for example, dichloromethane or ethyl acetate decaffeination using carbon dioxide and aqueous extraction using a solution of green coffee extract or water process.

B. Solvent Decaffeination

Until the mid-1970s, all the decaffeinaton methods used the solvent method only. Over the years mankind has utilized alkalis, acids, and even tried charging coffee with electricity in an effort to decaffeinate it. More often than not, the resulting beverage tasted decapitated as well as decaffeinated. Benzene, chloroform, ether, alcohol, trichloroethylene, carbon tetrachloride, acetone, ammonium hydroxide, and sulfuric acid have also been used during this century to decaffeinate the beans. The solubility of caffeine in various organic solvents is given in Table 4.

Ethyl acetate decaffeination is a process where the solvent owes its origin to natural sources.[46]

There are two basic methods for producing decaffeinated coffee using solvent, direct solvent extraction of the beans and water extraction of the beans followed by solvent extraction of the caffeine from the water extract. In green coffee, caffeine is fixed to the chlorogenic acid. In order to separate the caffeine from the chlorogenic acid and to allow the solvent to get access to the caffeine and to enable the latter to escape at the surface of coffee, the green coffee's moisture should be increased. This can be done by treating the beans either with super-heated steam or soaking followed by steaming.[47] In the direct solvent extraction process, green coffee beans are first

TABLE 4
Solubility of Caffeine in Organic Solvents

Solvent	Solubility%(W/V)	Temperature °C
Trichloro ethylene	1.5	29
Dichloro methane	9.0	33
Chloroform	15.0	25
Dichlro ethylene	1.8	25
Acetone	2.0	25
Ethyl alcohol	1.5	25
Ethanol	4.0	77
Ethyl ether	0.2	20

steamed to increase their moisture content, then they are treated with solvent to remove most of the caffeine. The beans are next heated to remove the residual solvent and excess moisture. In the indirect method, green beans are steeped in hot water to dissolve caffeine. Next the water is separated from the beans and treated with the solvent to remove caffeine. Then the flavor ingredients in the water are returned to the beans, which are then rinsed to wash off trace amount of the chemical. Decaffeinated coffee made by the indirect method does not pose the problem of residual solvent in the beans.

1. Methylene Chloride

Until the mid-1970s, methylene chloride was considered to be the best solvent for extraction of caffeine with satisfactory results. Methylene chloride is a colorless liquid with a pleasant sweetish odor, boiling at 104°F. Its vapor is not flammable, and when mixed with air is not explosive.[48]

Animal tests by the National Toxicology Program indicated that methyelene chloride was a safe solvent at low concentrations. At high levels of 4000 ppm, laboratory mice exhibited cancer symptoms, whereas rats did not. The Occupational Safety and Health Administration, USA, has estabilished current permissible exposure levels in the work place at 500 ppm. No cases of human cancer have been attributed to this solvent.[49]

The FDA has promulgated regulations that require methylene chloride levels below 10 ppm in decaffeinated coffee. After the extraction of coffee, the wet beans are dried at 212°F, which boils off most of the residual solvent. Roasting the coffee beans further removes residual solvent. Accordingly, the industry operates well below the 10 ppm level, with detectable amounts of 2 or 3 ppm. However, during recent years, doubts have araisen about its risk to humans.[50]

It is ironic to note that the reason for the ban on the methylene chloride was not because of possible ill health effects. Rather, methylene chloride has been identified as leading suspect in the alleged depletion of ozone layer. Any process using it, therefore given the inevitability of a certain amount escaping into the atmosphere during the solvent manufacture, transport, and use, presents a risk and this includes decaffeination of coffee.

2. Ethyl Acetate

Although there is no demonstrated hazards to human health by way of traces of methylene chloride residue in decaffeinated coffee, exaggeration of its suspected carcinogenicity has led to a search for a solvent free from toxicity criticism. The solvent of choice has become ethyl acetate, a natural component detected in coffee aroma and found to occur naturally in many fruits such as bananas, apples, and pears. It may be synthetically produced from petroleum sources. Ethyl acetate is an ester and is a clear, volatile, flammable liquid, with a characterisic fruity odor and a pleasant taste when diluted. Because it is completely digestible and consumed daily in a wide range of foods, from salad dressings to fruit desserts, its toxicity has never been questioned by the Food and Drug Administration or others. Ethyl acetate has been approved for decaffeination of coffee by the US FDA since 1982. Unlike the guidelines for methylene chloride, there is no set limit to the residual amount of ethyl acetate that may remain in the beans. Morrison et al.[51] described a continuous method for the accelerated decaffeination of green coffee beans involving wetting of the beans followed by countercurrent extraction using ethyl acetate for 3 to 5 h. The residual solvent is removed by steam stripping. In another patent,[52] the same authors described the method for removal of residual solvent preferably ethyl acetate by flash evaporation using an alternating cycle of pressure variation. Cafiver in Orizaba, Veracruz, Mexico, markets ethyl acetate-decaffeinated Mexican coffee in the U.S. and Canada, as do several other European and Southern Hemisphere American decaffeinators. Decaffeination of robusta coffee beans was carried out in this laboratory (unpublished data) using ethyl acetate.[53] The method consists of increasing the moisture content in green coffee beans followed by extraction. The condition of extraction and the quality of decaffeinated coffee are presented in Table 5.

TABLE 5
Decaffeination of Coffee Using Ethyl Acetate

Material: solvent	Time of extraction (h)	Treatment	Caffeine removed (%)	Total soluble solids removed (%)
1:5	8	27°C	37–39	9–10
1:5	14	27°C	42–44	14–15
1:5	8	Hot water circulation	62–64	34–36
1:5	16	Hot water circulation	78–80	40–42

Source: Ramalakshmi et al., unpublished data (Ref. 53).

C. Decaffeination with Carbon Dioxide

The most selective process for removing just caffeine and not the other flavor precursors from coffee is carbon dioxide. Carbon dioxide is usually not thought of as a solvent, because it is a gas at normal atmospheric pressure and temperature. However, when it is compressed to a pressure greater than 50 times atmospheric, it becomes a dense liquid-like fluid. In this state it has other liquid-like properties, such as the ability to dissolve other materials when it is in a heavy glass or steel container under pressure.[54] It has a density about 80% that of water, but its viscosity is only 7%. These properties make it very penetrating and easy to recirculate using pumps, pipes, and valves. The solubility of caffeine in dry carbon dioxide is low, but if the carbon dioxide is saturated with water the solubility is tripled. Carbon dioxide does not affect the carbohydrates (sugars, starch) and peptides (proteins) that during roasting are converted into the various compounds responsible for the flavor and aroma of brewed coffee.

Carbon dioxide is a colorless, odorless, and tasteless gas that gives no solvent residue or has any deleterious effects when used as a solvent. It is also noninflammable and noncorrosive and can be liquified at a temperature below 88°F by applying a pressure above 73 atms.[55] The gas becomes supercritical at a pressure of approximately 72 bars and a temperature of approximately 90°F.

The carbon dioxide decaffeination process was discovered and developed by Kurt Zosel. The process was patented in the early 1970s and licensed to Cafe HAG and General Foods. Because the start up costs of a carbon dioxide decaffeination plant are quite high, this chemical-free method has been used primarily to decaffeinate large quantities of commercialgrade coffee. Carbon dioxide is a natural component of roasted coffee itself. Freshly roasted coffee beans contain a fairly high level of carbon dioxide, which escapes as a gas over several days.

There are several patents available on carbon dioxide decaffeination of coffee. Caffeine can be extracted from green beans using supercritical fluids, for example, carbon dioxide, nitrogen, nitrous oxide, methane, ethylene, propane as the extractants.[56] Efficiency of carbon dioxide can be improved by treating it with dimethyl sulfoxide before decaffeination of either wet or dry green coffee seeds.[57] Caffeine can also be extracted from roasted coffee using liquid carbon dioxide.[58] In general, the process of decaffeination using carbon dioxide can be described as follows. It begins with mixing green coffee beans with water to bring the moisture content to about 50%. The beans swell, pores open and caffeine is converted into a mobile form that can diffuse out of the bean. The moisturizing step is essential for decaffeination irrespective of the solvent used. The swollen beans are loaded into a thick-walled stainless steel extractor that is then sealed. Liquid carbon dioxide is pumped in at the operating pressure of about 300 atms and is heated to about 150°F. After the system is filled, carbon dioxide is recirculated between the extractor and scrubber. Carbon dioxide flowing through the extractor dissolves caffeine. In the scrubber, caffeine is removed from carbon dioxide using water. Manipulating the carbon dioxide to water ratio is key to this operation. In the extractor there is a high ratio of carbon dioxide to water. In the scrubber the ratio is not so high because extra water is added there. The scrubber water preferentially carries away the caffeine. The recirculation is continued for 8 to 12 h, depending on the initial caffeine content of the green beans. The target caffeine content for the decaffeinated beans is usually 0.08%. If the beans are arabica with only about 1% caffeine to begin with then the recirculation time is nearer to 8 h. At the end of recirculation, carbon dioxide is pumped from the system to a strong tank and is recycled to the next batch. The beans are unloaded from the extractor for drying. At this point they still contain moisture and a trace of carbon dioxide. The subsequent drying step reduces the moisture to its original level and vaporizes the carbon dioxide.[59]

The advantages of this process are that (1) there is no harmful residue because carbon dioxide is a safe, nontoxic material that is completely and easily removed from the decaffeinated coffee as well as from the aqueous solution of byproduct caffeine, (2) the product is of a superior quality with flavor and appearance very close to that of undecaffeinated coffee and superior to the products obtained from other decaffeination methods, and (3) losses of coffee solubles (other than caffeine) are quite low, less than other decaffeination methods, resulting in greater product yield. There are two major restrictions of carbon dioxide decaffeination. In developing this process, one needs to optimize the precise processing parameters.[60] There has to be a great deal of knowledge in the operation of high-pressure facilities in general, and there has to be a very good technical infrastructure for maintenance of the plant. Decaffeination plant using carbon dioxide being capital intensive is commercially feasible only at an annual capacity of atleast 3000 tons per year.

D. Water Decaffeination

The "water process" using water for decaffeination was developed by the Coffex Company in 1938 in Switzerland. However, commercialization of the process was slow; only in the late 1970s, was coffex able to realize the commercial production, with an initial capacity of 4000 tons per year. Caffeine has a specific solubility in water that varies widely with temperature. At room temperature, caffeine dissolves in water at a maximum solubility of 2%, whereas it can dissolve in boiling water to make a 70% solution. An additional factor in the aqueous extraction is that the caffeine is combined with organic acids within the green bean cells. This must be hydrolyzed by heat to liberate the free caffeine.

1. Swiss Water Decaffeination

The idea of water decaffeination was originally thought of by Jean Maclang in 1934, who decided to remove caffeine from coffee without using a chemical solvent. Until the late 1970s, scientists and engineers at Coffex modified the process to prevent the removal of the coffee flavor with an activated carbon filter and then started a chemical decaffeination plant in Switzerland.[61] In the original Swiss water process, green coffee beans were soaked in hot water and caffeine and flavor from the green beans dissolved into the water.[62] The water was then circulated through an activated carbon filter that removed the caffeine. The beans were then removed and transferred to a drying tank and the water to an evaporator where it was concentrated. When the beans were half-dry, the flavor-charged water was sprayed back into the beans and the flavor was reabsorbed. In the mid 1980s, the procedure was refined at Coffex North America plant in Vancouver, wherein the flavor-charged caffeine-free water was used to remove caffeine from the subsequent batches of beans.[63] After a batch of beans has been processed and the carbon filter removed the caffeine, a new generation of Swiss water decaffeination uses this flavor-charged water to decaffeinate subsequent batches of beans. The caffeine-free water absorbs the caffeine from the new beans, but the flavor components cannot pass into the already flavor-saturated water. The key to Swiss water decaffeination is that the original flavor components never leave the bean. So the decaffeinated beans retain their original rich, full flavor and are 100% chemical free. The various types of Swiss water coffees available are Colombians, Mochal/Java blends, Kenya AA, Brazil santos, Strictly Hard bean Guatemalas, and Sumatra Arabica.[64] Although the Swiss water process was reported to yield a less tasteful brew than other methods of decaffeinated coffees,[65] this deficiency was overcome during the late 1980s.

2. French Water Decaffeination

Ed. Wakeham, a trader for Cofinco, introduced French water decaffeinated product for the first time using 'french water', with a pH factor of seven. French water decaffeination was introduced in Newyork by 1992. It is currently available for Colombian coffee and is decaffeinated using only the 'purest' ground water.[66] The process consists of soaking the coffee beans in hot boiling water for over 24 h when water leaches out caffeine as well as coffee solids from the beans. After this process is completed, the water is drawn off, the beans are dried, and the decaffeination process continued. As the beans are drying, the water charged with caffeine solids is purified through a natural filter that absorbs the caffeine without any chemical reactions with water. The caffeine-free water is then added to the beans that have been dried. The dry beans act as a sponge reabsorbing the coffee solids back into them. The beans are dried once again. This results in 99.9% caffeine-free beans. The advantage of drying beans twice is that they contain less residual water and absorbtion of coffee solids is more.

E. Various Absorbents

Caffeine is transferred from steamed green beans to an intermediate from that it is recovered by thermal desorption.[67] Some of the absorbents used are activated charcoal, molecular sieves, silica gels, bentonites, and organic ion-exchange resins.

1. Nitrous Oxide

The applicability of nitrous oxide as solvent for caffeine depends on the relatively high solvent power of nitrous oxide for this substance.[68] The solvent power of nitrous oxide for caffeine when compared with carbon dioxide is higher. The process of decaffeination using nitrous oxide as a gaseous solvent has to be carried out in the same way as any separation process employing a mass separation agent in a two-step process, the first of which is the decaffeination and the second is the separation of caffeine from the solvent. Decaffeination by this process is carried out using nitrous oxide at a pressure of 200 bar, with an extraction time of about 10 h corresponding to two extraction cycles per day.

F. Decaffeination of Coffee Extracts

There are a number of patents relating to decaffeination of coffee products, rather than green coffee involving the use of organic solvents and supercritical carbon dioxide. It would be necessary to remove first all the organic volatiles that are responsible for the aroma/flavor before decaffeination. Caffeine containing green coffee extract can be decaffeinated by contact with caffeic acid which forms an insoluble caffeine/caffeic acid, complex and can be separated easily.[69] The process of using caffeic acid for decaffeination is applied in roasted coffee extract also. The aroma of roasted coffee is not lost or impaired by this process.[70] There are also processes available for decaffeination of coffee extracts using carbon dioxide,[71,72] ethyl cellulose, activated carbon,[73] and dimethyl sulfoxide.[74]

G. Microbial Decaffeination

There are reports in the literature using microorganism for decaffeination of coffee. The microorganism is of *Acinetobacter* sp. and uses caffeine as its only source of C and N. The process involves an aqueous coffee extract that is incubated with the microorganism under aerobic conditions until a substantial part of the caffeine is metabolized, after which the cells of the microorganism are separated out. The advantage of the process is that the product obtained is free from the usual solvent residues remaining after conventional treatment.[75]

Aqueous caffeine-containing liquids, for example, coffee extracts are decaffeianted by either fermenting the liquid with *Pseudomonas* microorganisms, *Pseudomonas putida* NRRL B-8051, *P. fluorescens* NRRL B-8052, and *P. fluorescens* NRRL B.8053 or by contacting the liquid with a caffeine-mobilizing enzyme preparation isolated from the above.[76]

IV. MARKET AND PRICING

Decaffeinated coffee remains a strong and profitable segment of the specialty coffee industry. The number of decaffeinated coffee consumers has grown more than 4- to 5-fold in the last 4 decades.[77] Decaffeinated versions of specialty coffee drinks are becoming increasingly popular in the U.S., and numerous coffee shops and restaurants are adding more varieties of decaffeinated coffees to their menus. Therefore, 20% of the world's coffee produce can be decaffeinated, with the existing capacity of decaffeination plants to meet the requirements of decaffeinated coffee consumers.

The prices of decaffeinted coffee are subjected to a wide variation and it is well known that Swiss water usually costs more compared with coffees decaffeinted using other processes. Findings indicate that Swiss water coffees generally sell at approximately $20 per kilogram, whereas dichloromethane decaffeinated coffees sell at approximately $17.50 per kilogram. Prices for a cup of regular vs. decaffeinated coffee were similiar, with 84% of retailers charging the same price for both types. A few charge more for decaffeinated coffees. Decaffeinated coffee cup sales, therefore, represent a promising and profitable opportunity for specialty coffee retailers.[78,79]

V. CHARACTERISTICS OF DECAFFEINATED COFFEE

A. Definition and Composition

The International Standards Organisation (ISO 3509-1989) has defined decaffeinated coffee as 'coffee from which caffeine has been extracted'.[80] There is considerable national legislation specifying the maximum residual amount of caffeine. In the U.K. and most other European countries, the maximum caffeine content for decaffeinated roasted coffees is set at 0.1% (dry basis), although in the U.S. there is no specific legislation, but manufacturers generally claim that more than 97% of the caffeine has been removed. For de-caffeinated instant coffee, in European community countries, the maximum caffeine content is set at 0.3% (dry basis). This figure is generally accepted elsewhere in the world except in the U.S. where a 97% elimination figure is usual.

B. Physical and Chemical Characteristics

Decaffeination is a process applied to green coffee after which the decaffeinated green coffee is roasted and ground or converted into instant coffee exactly as for the corresponding non-decaffeinated products. The composition of these decaffeinated coffees apart from caffeine content therefore will be almost corrospondingly identical. However, there are slight differences, and also of flavor, depending on the particular decaffeination process employed. Decaffeinated coffees have always been being rated inferior in taste and aroma properties as well as appeal, because beans are subjected to severe treatment such as steam stripping and the final stage of drying. The net result is that decaffeinated coffee beans change color and are often not as green as they were originally and vary in shades from dark brownish black, to dark green (at best), to reddish brown and are sometimes discolored. The color of the final decaffeinated beans is strongly influenced by the acidity of the green beans. If this is not controlled, during the process of decaffeination the final bean colors vary from orange to red brown. Most of the bean surface waxes are removed, giving the beans a dull appearance before and after roasting. If sugars have been allowed to remain on the surface, these burn during roasting, lending an appearance to the roasted beans. Taste changes resulting from decaffeinated coffees usually make robusta beans much milder in taste and aroma; it often upgrades the harsh arabica beans into a milder and more acceptable beverage.

Decaffeinated beans roast differently than natural green beans with less bean expansion, less "popping", etc., because the sucrose content has been altered. Udayasankar et al.[81] compared the appearance of the green beans decaffeinated by both supercritical carbon dioxide and dichloromethane, and observed that the appearance of the beans decaffeinated with the former was like normal beans except that they were puffed slightly, whereas in case of the latter the beans looked grey and shrivelled due to the long hours of steaming during solventization. The decrease in total soluble solids in decaffeinated beans was due to depletion of caffeine, but the higher loss of soluble solids found in dichloromethane decaffeinated coffee beans may be due to leaching during steaming to remove the solvent residue in the beans. The color and the appearance of the roasted decaffeinated coffees were observed to be similar irrespective of the method of decaffeination. From Table 6 it can be concluded that there is decrease in petroleum ether extract in the case of solvent-extracted beans, but it is very less in supercritical-extracted coffee beans.

VI. CONCLUSION

Caffeine, the alkaloid present in coffee, is not tolerated by some people. This necessitates the demand for decaffeinated coffee. Because the robusta variety of coffee is rated inferior in aroma quality and fetches less price to the producer, it could be used as the starting material for the purpose of decaffeination. Earlier methods made use of chlorinated solvents for the extraction of caffeine. However, the harmful effects of the solvent residues have made it imperative to look for alternate safer solvents. Ethyl acetate is one such safe solvent permitted in most countries.

There have been several reports regarding the use of carbon dioxide as a safe solvent in a supercritical extraction system for the decaffeination of coffee. The major advantages of this solvent are that the extraction can be carried out at near ambient temperatures, the solvent does not leave any residue, and it selectively extracts caffeine, leaving behind aroma precursors and water solubles such as carbohydrates and protein.

Roasting characteristics, namely, density, swelling ratio, and breaking strength, play an important role in determining the quality of decaffeinted coffee. While the swelling ratio of decaffeinated coffee was comparable to the caffeinted coffee, the breaking strength was more in decaffeinted coffee ranging from 17.70 to 9.95 lb/in, for light to dark roasts. The cup quality of decaffeinated coffee is very much dependent on the degree of roasting; the color of roasted beans has to be much darker compared with caffeinated coffee to get a brew of matching cup quality. Further, the quality of roasted and ground decaffeinated coffee required is also more, almost 1.5 times the caffeinated coffee. This is quite understandable considering the fact that the total soluble solids in the decaffeinated coffee are much lesser compared with caffeinated coffee.

From the foregoing facts encompassing physiological effects of coffee, it is not possible to flatly say that coffee consumption is healthy or unhealthy. However, with the increasing awareness and health consciousness, the market for

TABLE 6
Proximate Analysis of Decaffeinated Roasted and Ground Coffee

Type of coffee	Total ash (%)	Total N (%)	Crude protein[a] (%)	Caffeine (%)	Pet. ether extract (%)	Tannins (%)
Untreated	4.5	2.6	14.2	2.12	9.70	10.30
Dichloromethane extracted	4.3	2.2	14.5	0.05	4.50	10.10
Supercritical CO_2 extracted	4.4	2.3	14.8	0.06	6.00	11.00

[a] Noncaffeine N × 6.25

Source: Udayasankar et al., 1986 (Ref. 81). Reproduced with permission.

decaffeinated coffee may expand in the years to come.

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