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KIRK-OTHMER

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**CHLOROCARBONS AND CHLOROHYDROCARBONS—C₂
TO
COMBUSTION TECHNOLOGY**



A Wiley-Interscience Publication

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CP Chemicals, Inc.

COCAINE. See ALKALOIDS; ANESTHETICS; PSYCHOPHARMACOLOGICAL AGENTS.

COCHINEAL. See COLORANTS FOR FOODS, DRUGS, AND COSMETICS; DYES, NATURAL.

COCOA. See CHOCOLATE AND COCOA.

COCONUT OIL. See FATS AND FATTY OILS; VEGETABLE OILS.

COFFEE

Coffee was originally consumed as a food in ancient Abyssinia and was presumably first cultivated by the Arabians in about 575 AD (1). By the sixteenth century it had become a popular drink in Egypt, Syria, and Turkey. The name coffee is derived from the Turkish pronunciation, kahveh, of the Arabian word *gahweh*, signifying an infusion of the bean. Coffee was introduced as a beverage in Europe early in the seventeenth century and its use spread quickly. In 1725, the first coffee plant in the western hemisphere was planted on Martinique, West Indies. Its cultivation expanded rapidly and its consumption soon gained wide acceptance.

Commercial coffees are grown in tropical and subtropical climates at altitudes up to ca 1800 meters; the best grades are grown at high elevations. Most individual coffees from different producing areas possess characteristic flavors. Commercial roasters obtain preferred flavors by blending or mixing the varieties

before or after roasting. Colombian and washed Central American coffees are generally characterized as mild, winey-acid, and aromatic; Brazilian coffees as heavy body, moderately acid, and aromatic; and African robusta coffees as heavy body, neutral, slightly acid, and slightly aromatic. Premium coffee blends contain higher percentages of Colombian and Central American coffees.

Green Coffee Processing

The coffee plant is a relatively small tree or shrub belonging to the family Rubiaceae. It is often controlled to a height of 3 to 5 meters. *Coffea arabica* (milds) accounts for 69% of world production; *Coffea canephora* (robustas), 30%; and *Coffea liberica* and others, 1%. Each of these species includes several varieties. After the spring rains the plant produces white flowers. About six months later the flowers are replaced by fruit approximately the size of a small cherry, hence they are called cherry. The fruit on a tree can include underripe, ripe (red, yellow, and purple color), and overripe cherries. It can be selectively picked (ripe only) or strip picked (predominantly ripe plus some underripe and overripe).

Green coffee processing is effected by either the dry or wet method. The dry method produces so-called natural coffees. The wet method usually produces the more uniform and higher quality washed coffees.

The dry method is used in most of Brazil and in other countries where water is scarce in the harvesting season. The cherries from strip picking are spread on open drying ground and turned frequently to permit thorough drying by the sun and wind. Sun-drying usually takes two to three weeks depending on weather conditions. Some producing areas use hot air, indirect steam, and other machine-drying devices. When the coffee cherries are thoroughly dry, they are transferred to hulling machines which remove the skin, pulp, parchment shell, and silver skin in a single operation.

In the wet method, as practiced in Colombia, freshly picked ripe coffee cherries are fed into a tank for initial washing. Stones and other foreign material are removed. The cherries are then transferred to depulping machines which remove the outer skin and most of the pulp. However, some pulp mucilage clings to the parchment shells that encase the coffee beans. Fermentation tanks, usually containing water, remove the last portions of the pulp. Fermentation may last from twelve hours to several days. Because prolonged fermentation may cause development of undesirable flavors and odors in the beans, some operators use enzymes to accelerate the process.

The beans are subsequently dried either in the sun or in mechanical dryers. Machine-drying continues to gain popularity in spite of higher costs because it is faster and independent of weather conditions. When the coffee is thoroughly dried, the parchment is broken by rollers and removed by winnowing. Further rubbing and winnowing removes the silver skin to produce ordinary green unroasted coffee, containing about 10-12% moisture.

Coffee prepared by either the wet or dry method is machine-graded by sieves, oscillating tables, and airveyors into large, medium, and small beans. Damaged beans and foreign matter are removed by handpicking, machine separators, electronic sorters, or a combination of these techniques. Commercial coffee is graded

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according to the number of imperfections present, such as black beans, damaged beans, stones, pieces of hull, or other foreign matter. Processors also grade coffee by color, roasting characteristics, and cup quality of the beverage. After all processing, coffee will maintain acceptable quality for approximately one year.

Coffee Chemistry

Chemical Composition of Green Coffee. The chemical composition of green coffee can affect roasted flavor quality. The chemistry can vary according to species, variety, growing environment, post-harvest handling including wet or dry processing, and storage time, temperature, and humidity. The composition data in Table 1 are given as a range compiled from literature (2-4).

Robustas generally have lower amounts of lipid, trigonelline [535-83-1], and sucrose [57-50-1], and higher levels of caffeine [58-08-2] and chlorogenic acid (3-caffeoquinic acid) [327-97-9] when compared to arabicas. While the protein level is considered similar between robustas and arabicas, protein structure and function, including enzymatic activities, is under genetic control and can vary. Some literature indicates slightly higher levels of free amino acids (nonprotein) in green robustas compared to arabicas, eg, 0.8 vs 0.5%, respectively (5). Wet processed beans tend to have slightly lower mineral content compared to dry processed beans.

Table 1. Typical Analyses of Green Coffee, %^a

| Constituent ^c | Type ^b | |
|--------------------------|-------------------|--------------|
| | Robusta | Arabica |
| moisture | 11(10-13) | 12.5(10-13) |
| lipids | 10(7-11) | 15(14-17) |
| ash | 4.2(3.9-4.5) | 4.0(3.5-4.5) |
| caffeine | 2.0(1.5-2.6) | 1.3(1.1-1.4) |
| chlorogenic acid | 9(7-10) | 7(5-8) |
| carboxylic acids | 2(1-3) | 2.5(1.5-3.5) |
| trigonelline | 0.7(0.3-0.9) | 1.1(0.9-1.2) |
| protein | 11(9-13) | 11(9-13) |
| free amino acids | 0.8 | 0.5 |
| sucrose | 4(3-6) | 8(5-9) |
| reducing sugars | 0.5(0.4-0.6) | 0.1(0.1-0.2) |
| others ^d | 8.8(5-10) | 5.5(3-8) |
| polymeric carbohydrate | | |
| mannan | 22 | 22 |
| arabinogalactan | 17(16-18) | 15(14-16) |
| cellulose | 8(7-9) | 7(7-8) |

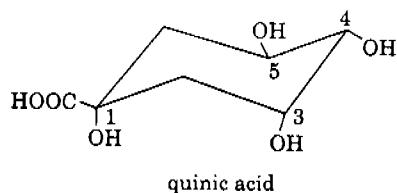
^aRefs. 2-4.

^bTypical value and (range).

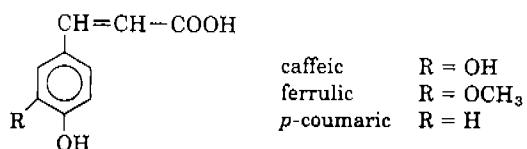
^cDry basis (db) (ex moisture; as is basis).

^dOthers by difference.

Numerous organic acids in coffee include acids of metabolic origin, eg, acetic, lactic, citric, malic, and oxalic; free quinic acid [77-95-2]; and various chlorogenic acid (CGA) isomers that appear to be species specific.



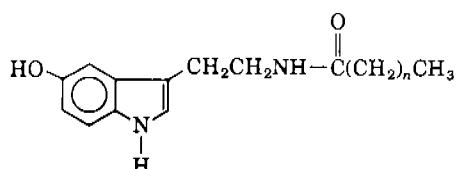
Of these, the CGA isomers are the principal acids and result from the esterification of the 3, 4, and 5 position hydroxyls of quinic acid with the carboxyls of several phenolic acids, including caffeic acid (C) [331-39-5], ferrulic acid (F) [1135-24-6], and *p*-coumaric acid (Cm) [501-98-4].



The principal CGA isomers identified in green coffee include three caffeoylquinic acid isomers, 3-CQA [327-97-9], 4-CQA [905-99-7], and 5-CQA [906-33-2]; three dicaffeoylquinic acid isomers, 3,4-diCQA [14534-61-3], 3,5-diCQA [2450-53-5], and 4,5-diCQA [57378-72-0]; and three feruloylquinic acid isomers, 3-FQA [1899-29-2], 4-FQA, and 5-FQA [40242-06-6]. The total CGA level is somewhat higher in robustas compared to arabicas. The 5-CQA is the predominant isomer both in arabicas, ie, 4-5% dry basis (db), and in robustas, 5-6% db, and is known to form *in vitro* and possibly *in vivo* complexes with caffeine [58-08-2]. Greater compositional differences between robustas and arabicas are found in the minor CGA isomers, eg, 3,4-diCQA, 5-FQA, CmQA, etc, which appear correlated to genetic origin (6). The greater level of certain CGA isomers in robustas, compared to arabicas, may explain its greater production of spicy, medicinal, phenolic flavors upon roasting. Analysis has demonstrated greater levels of compounds of phenolic origin in roasted robustas, eg, guaiacol derivatives (7). There are indications that the undesirable brown and black pigments in green coffee are formed by polyphenol oxidase [9002-10-2] polymerization of CQA isomers.

The cell wall complex of both robustas and arabicas contain a mannan [9052-06-6], an arabinogalactan [9036-66-2], and cellulose [9004-34-6]. The mannan is a low molecular-weight linear polymer of about 20-40 mannose sugars with β -1,4-linkages. It functions as a reserve polysaccharide providing energy to the sprouting coffee seed. The arabinogalactan is a high molecular-weight and highly branched polymer consisting of a β -1,3-linked galactose [59-23-4] polymer backbone with frequent side chains containing arabinose [147-81-9] and mannose [3458-28-4]. The cellulose appears similar to other plant celluloses (4).

The surface of the green coffee contains a cuticular wax layer (0.2–0.3% db) for both varieties. The wax contains insoluble hydroxytryptamides derived from 5-hydroxytryptamine [61-47-2] and saturated C18–C22 fatty acids.



About 75% of the interior oil consists of triglycerides containing about 35–41% palmitic (C16, *n*-14), 37–46% linoleic (C18:2), 8–12% oleic (C18:1), and 7–11% stearic (C18, *n*-16) [57-11-4] as the principal fatty acids on an oil basis. The remaining 20% of the lipid is distinctive and consists of fatty acid esters of the diterpene alcohols, cafestol [469-83-0] and kahweol [6894-43-5] (8). Free cafestol (0.3–0.7% db coffee) and kahweol (0.1–0.2% db coffee) are found in the oil of arabicas. Smaller amounts of cafestol (0.2–0.4% db coffee), trace levels of kahweol, and a new diterpene, 16-*O*-methylcafestol [108214-28-4] (0.06–0.1% db coffee), are found in the oil fraction of robustas; the latter is proposed as an indicator for the presence of robusta in a blend (9).

The characteristic note of green beans is attributed to methoxypyrazines which have very low threshold values (10). The characteristic musty earthy note of robustas was recently identified as 2-methylisoborneol [2371-42-8] (11).

Green bean storage for extended periods, or under abusive conditions of elevated temperature and humidity, causes fading of color, and changes in roast flavor. The loss of reducing sugars and free amino acids upon storage at 60°C have been noted and suggest the Maillard reaction. Enzymatic or oxidative mechanisms in the development of off flavors are also possible (12).

Effects of Roasting on Components. Green coffee has no desirable taste or aroma; these are developed upon roasting. Many complex physical and chemical changes occur during roasting including the obvious change in color from green to brown. In the first stage of roasting, loss of free water (typically 11% of the bean) occurs. In the second stage, chemical dehydration, fragmentation, recombination, and polymerization reactions occur. Many of these are associated with the Maillard reaction and lead to the formation of lower molecular-weight compounds such as carbon dioxide, free water, and those associated with flavor and aroma; and higher molecular-weight colored materials, both soluble and insoluble in water. Some of the reactions are exothermic and produce a rapid rise in temperature, usually accompanied by a sudden expansion or puffing of the beans, with a volume increase of 50–100% depending on variety and roasting parameters. The loss of carbon dioxide and other volatile substances, as well as the water loss produced by chemical dehydration during the latter stage, accounts for most of the 2–5% dry weight roasting loss. Most of the lipid, caffeine, inorganic salts, and polymeric carbohydrate survive the roasting process (13).

Table 2 indicates some of the chemical changes that occur in green coffee as a result of roasting. The data are presented as a range and typical value (when appropriate) compiled from the literature and other sources and reflect the fact

Table 2. Approximate Analyses of Roasted, Brewed, and Instant Coffee, %^a

| Constituent ^b | Roasted | Brewed ^c | Instant |
|------------------------------|---------------|---------------------|-----------|
| moisture | 4 (1-5) | | 3.5 (2-5) |
| oil | 17 (16-20) | 0.8 (0.2-1.0) | (0.1-0.6) |
| ash | 4.5 (4-5) | 14 | 9 (7-11) |
| caffeine | 1.2 (1.0-1.6) | 4.8 | 3.5 (2-5) |
| chlorogenic acid | 1.5 (1-3.5) | 14.8 | (3-9) |
| carboxylic acids | 3 (2-4) | 3.0 | 5.5 (4-8) |
| trigonelline | 0.5-1.0 | 1.6 | (0.5-2) |
| protein | 8-10 | 6 | (1-6) |
| reducing sugar | 0.2 | 0.4 | (1-5) |
| sucrose | 0.2 (0-0.5) | 0.8 | (0.6-0) |
| aroma compounds | ~0.1 | ~0.1-2 | ~0.05 |
| browning products and others | (22-11) | 29.4 | (20-35) |
| polymeric carbohydrate | 38 | 24 | (30-50) |
| mannan | 20 | | |
| arabinogalactan | 12 | | |
| cellulose | 6 | | |

^aTypical value and (range).^bDry basis (ex moisture; as is basis).^cRef. 14.

that the chemistry is highly dependent on degree of roast and starting material. The principal water-soluble constituents, about 25% of the green coffee, are involved. These include some of the protein, the free amino acids, trigonelline, reducing sugars, sucrose, chlorogenic acids, organic acids, and inorganic salts. Most sucrose disappears early in the roast. The reducing sugars that form react rapidly with the free amino acids via the Maillard reaction to form aromatic compounds and color.

Roasting denatures and insolubilizes much of the protein. Some of the constituent amino acids in the protein are destroyed during the latter stages of roasting and thus contribute to aroma and flavor development. Analysis of the protein amino acids in green and corresponding roasted coffee show marked decreases in arginine, cysteine, lysine, serine, and threonine in both arabica and robusta types after roasting. Alanine, glycine, leucine, glutamic acid, and phenylalanine increase upon roasting and are relatively stable (15). Cysteine [52-90-4] and methionine [63-68-3] are the probable sources of the many potent sulfur compounds found in coffee aroma, e.g., mercaptans, organic sulfides, thiazoles, etc. Other amino acids are capable of generating aromatic compounds such as pyrazines, pyrroles, etc.

About 50-80% of the trigonelline is decomposed during roasting. Trigonelline is a probable source for niacin [59-67-6] but also a source of some of the aromatic nitrogen compounds such as pyridines, pyrroles, and bicyclic compounds found in coffee aroma (16). Certain acids, such as acetic, formic, propionic, quinic, and glycolic, are formed or increase upon roasting, while other acids present initially in the green coffee, such as chlorogenic acid isomers, citric, and malic, disappear with increasing degree of roast. The composite of acids in brew of a lightly

| | |
|-----------|--|
| Instant | |
| 3.5 (2-5) | |
| (0.1-0.6) | |
| 9 (7-11) | |
| 3.5 (2-5) | |
| (3-9) | |
| 5.5 (4-8) | |
| (0.5-2) | |
| (1-6) | |
| (1-5) | |
| (0.6-0) | |
| ~0.05 | |
| (20-35) | |
| (30-50) | |

roasted coffee contribute to the taste quality termed "fine acidity." Brews of darkly roasted coffees are less acid. Slight cleavage of the triglycerides and the diterpene and sterol esters occurs during roasting. It is likely that some oxidation of lipid components is initiated during the roasting stage. However, some of the Maillard products generated upon roasting may act as antioxidants (qv), slowing down the deterioration of the lipids upon storage. The aromatic, oil-soluble aroma compounds slowly partition into the oil phase after the roasted bean is allowed to cool and equilibrate.

Aroma. The chemistry for the formation of aroma compounds during roasting is complex (17,18). A significant portion of these compounds is derived from lipids, organic acids, eg, chlorogenic acids, carbohydrates, eg, sugars, and proteinaceous material, eg, amino acids, either by degradation to reactive products, which include saturated and unsaturated aldehydes, ketones, dicarbonyls, amines, and hydrogen sulfide, or by interaction via the Maillard nonenzymatic browning reaction. The latter stages of the Maillard reaction result in the formation of structurally more complicated heterocyclic compounds, many containing sulfur, oxygen, and nitrogen. The number of volatile flavor compounds identified in coffee has increased to about 800 (19) and may ultimately exceed 1000 as a result of a combination of advanced analytical techniques including gas chromatography (gc), mass spectrometry (ms), fourier transform infrared spectrometry (ftir), and nuclear magnetic resonance spectrometry (nmr). Although present in minute quantities as low as ppb or ppt, volatile flavor compounds are extremely important to the aroma of freshly roasted and ground coffee and to the flavor balance in a cup of coffee. Table 3 summarizes the volatile components by chemical class of roasted coffee (19,20).

A relatively new methodology called aroma dilution analysis (ada), which combines aroma dilution and gas chromatography-olfactometry to gain a better understanding of the relative importance of aroma compounds, was recently done for coffee. In a roasted Colombian coffee brew, 41 impact compounds were found with flavor dilution threshold factors (FD) greater than 25, and 26 compounds had FD factors of 100 or above. While the technique permits assessment of the impact of individual compounds, it does not evaluate synergistic effects among compounds (13).

Chemistry of Brewed Coffee. The chemistry of brewed coffee is dependent on the extraction of water-soluble and hydrophobic aromatic components from the coffee cells and lipid phase, respectively. Factors that affect extraction and flavor quality of brewed coffee are degree of roast; blend composition; grinding technique; particle size and density; water quality; water to coffee ratio; and brewing technique or device, such as drip filter, percolator, or espresso, which defines the water temperature, steam pressure, brewing time, water recycle, etc. Extraction yields upon home brewing range from about 9 to 28% and typically about 23% dry basis roasted and ground (R&G) (21). The trend in the United States with some notable exceptions has been toward weaker brew strengths, with typical recipes of about 5 g of R&G coffee per 6 oz cup (brew solids concentration about 0.7%), compared to about 10 g a generation ago (brew solids about 1.2%). As a comparison, espresso typically uses about 8 to 12 g of coffee per 2 oz of beverage (brew solids ranging from about 3 to 5%). Espresso being brewed rapidly under steam pressure (brew time ranging from about 15 to 35 s) contains a relatively large

Table 3. Aromatic Components of Roasted Coffee^a

| Chemical class | Number of compounds |
|-------------------------------------|---------------------|
| hydrocarbons | 74 |
| alcohols | 20 |
| aldehydes | 30 |
| ketones | 73 |
| acids | 25 |
| esters | 81 |
| lactones | 3 |
| phenols (and ethers) | 48 |
| furans | 127 |
| thiophenes | 26 |
| pyrroles | 71 |
| oxazoles | 35 |
| thiazoles | 27 |
| pyridines | 19 |
| pyrazines | 86 |
| amines and misc. nitrogen compounds | 32 |
| sulfur compounds | 47 |
| miscellaneous | 17 |
| <i>Total</i> | <i>791</i> |

^aRef. 19,20.

amount of oil droplets (about 0.1–0.2% basis brew) and suspended colloidal solids (about 0.3% basis brew) which contribute to the greater turbidity and mouthfeel of this beverage compared to filter brewed coffee (22).

Instant Coffee. The chemistry of instant or soluble coffee is dependent on the R&G blend and processing conditions. This is indicated in Table 2 by the wide range of constituents. In addition to the atmospherically extractable solids found in brewed coffee, commercial percolation generates water-soluble carbohydrate by hydrolysis which contributes to the yield. This additional carbohydrate includes the sugars, arabinose, mannose, and galactose; oligosaccharides derived from mannan and arabinogalactan; and the partially hydrolyzed polysaccharides, mannan and arabinogalactan. It improves the drying properties and retention of volatiles by the extract, and reduces hygroscopicity. These water-soluble carbohydrates formed the basis for the first 100% pure instant coffee developed by General Foods Corp. in the late 1940s.

Roasted and Ground Coffee Processing and Packaging

The main processing steps in the manufacture of roast and ground coffee products are blending, roasting, grinding, and packaging. Green coffee is shipped in burlap bags (60–70 kg) or in bulk containers (16,500–18,000 kg). Prior to processing, the green coffee is cleaned to remove string, lint, dust, husk, and other foreign matter. Coffee of different varieties or from different sources may be blended before or after roasting at the option of the manufacturer.

Roasting Technology. Roasting is usually by hot combustion gases in rotating cylinders or fluidized-bed systems; infrared and microwave roasted coffees have recently come to market in Japan. Roasting times in batch cylinders were traditionally 8–15 minutes, whereas much of the coffee produced today is roasted in continuous fluidized beds in only 0.5–4 minutes (23–25). In either case, the initial step of roasting is a moisture elimination and uniform heating step. When the bean temperature exceeds about 165°C, the reactions have switched from endothermic to exothermic and the roast has begun to develop. This stage is generally accompanied by a noticeable crackling sound like that of corn popping and the beans swell to as much as twice their unroasted volume. The final bean temperature of 185–250°C is determined by the flavor development desired for the finished goods, whether a blend or individual varieties are roasted. A water or air quench terminates the roasting reaction. Most, but not all, of any water added is evaporated from the heat of the beans. Theoretically, about 700 kJ is needed to roast one kg of coffee beans. A roaster efficiency of 75% or more (933 kJ/kg) is possible with recirculation of the roaster gas, whereas older, nonrecirculating units operate with an efficiency as low as 25% (2800 kJ/kg). The acceptability of the roast is judged by either a photometric reflectance measurement on the roasted bean or a ground sample of the bean, and adjustments of the temperature controls which initiate the quenching end point. The faster fluidized-bed roasting processes (batch or continuous) are the basis of high yield coffee products. These units are generally operated at lower air temperature, *i.e.*, 185–400°C vs 425–490°C, resulting in a more uniform roast throughout the bean, an increase in extractable soluble solids of 20% or more, and higher aroma retention. The higher circulation rate of roaster gas required for fluidization increases heat transfer to allow a faster roast at lower temperature. Exhausted roaster gas often must be incinerated for environmental pollution purposes. The use of infrared heat (gas-fired ceramics) or microwave energy to speed up the roasting process while providing a more even roast has also been patented (26,27).

The roasted and quenched beans are air cooled and conveyed to storage bins for moisture and temperature equilibration before grinding. Residual foreign matter (mostly stones), which may have passed through the initial green cleaning step, is removed in transit to the storage bins by means of a high velocity air lift which leaves the heavier debris behind. The roasted beans may flow by gravity or be airveyed to the grinders.

Grinding. Grinding of the roasted coffee beans is tailored to the intended method of beverage preparation. Average particle size distributions range from very fine (500 μm or less) to very coarse (1100 μm). A finer grind will allow greater solids extraction, but may slow the brewing process because of increased flow resistance and reduced wettability. Most coffee is ground in multistep steel roll mills in order to produce the most desirable particle size distribution. After passing through cracking rolls, the broken beans are fed between two more rolls, one of which is cut or scored longitudinally; the other, circumferentially. The paired rolls operate at speeds designed to cut rather than crush the cracked particles. For finer grinds, a second pair of more finely scored rolls running at higher speed is positioned below the first set. Some coffee is flaked, to increase extractability without slowing brewing speed, by passing through closely spaced smooth rolls after grinding (28). This is a crushing step which disrupts the cellular structure.

A normalizer mixing section after grinding provides a uniform distribution and may be used to adjust density before packaging.

Packaging. Most roasted and ground coffee sold directly to consumers in the United States is vacuum-packed in 0.37, 0.74, or 1.1 kg metal cans. After roasting and grinding, the coffee is conveyed, usually by gravity, to weighing-and-filling machines that achieve the proper fill by tapping or vibrating. A loosely set cover is partially crimped. The can then passes into the vacuum chamber maintained at 3.3 kPa (25 mm Hg) absolute pressure or less. The cover is clinched to the can cylinder wall and the can moves through an exit valve or chamber. This process removes 95% or more of the oxygen from the can. Polyethylene snap caps for reclosure are placed on the cans before they are stacked in cardboard cartons for shipping. A case usually contains 8.8 kg of coffee, and a production packing line usually operates at a rate of 250–350 0.37 kg cans per minute.

Vacuum-packed coffee retains a high quality rating for at least one year. The slight loss in fresh roasted character that occurs is because of chemical reactions with the residual oxygen in the can and previous exposure to oxygen prior to packing (29).

Coffee vacuum-packed in flexible, bag-in-box packages has gained wide acceptance in Europe. The inner liner, usually a plastic-laminated foil, is formed into a hard brick shape during the vacuum process (30). In the United States, a printed multilaminated flexible structure is used to form the brick pack which is sold as is at retail. These types of packages provide a barrier to moisture and oxygen similar to that of a metal can.

Inert gas flush packing in plastic-laminated pouches, although less effective than vacuum packing, can remove or displace 80–90% of the oxygen in the package. These packages offer satisfactory shelf life and are sold primarily to institutions.

Some coffee in the United States, and an appreciable amount in Europe, is distributed as whole beans, which are ground in stores or by consumers in their homes. Whole-bean roasted coffee remains fresh longer than ground coffee. The specialty gourmet shop trade based on this system has grown significantly in the United States since the early 1980s. If the coffee is freshly roasted an excellent product is provided; if the roasted beans are allowed to sit in an unprotected bin or bag for more than a few days, oxidation reactions will cause the product to degrade.

Optimal packaging of roasted whole beans in foil laminate bags requires the use of a one-way valve which allows carbon dioxide gas released from the beans to escape and prevent air from entering the package. This permits packing the coffee soon after roasting. A specialty mail-order trade for roasted whole beans packaged in this form, as well as roasted and ground in vacuum-packed foil laminate pouches, has also grown since the early 1980s.

Instant Coffee Processing and Packaging

Instant coffee is the dried water-extract of ground, roasted coffee. Although used in Army rations as early as the U.S. Civil War, the popularity of instant coffee as a grocery product grew only after World War II, coincident with improvements in

manufacturing methods and consumer trends toward convenience. Extensive patent literature dates back to 1865. Instant coffee products represented 15% of the coffee consumed in the United States in 1991 (31).

Green beans for instant coffee are blended, roasted, and ground similarly to those for roasted and ground products. A concentrated coffee extract is normally produced by pumping hot water through the coffee in a series of cylindrical percolator columns. The extracts are further concentrated prior to a spray- or freeze-drying step, and the final powder is packaged in glass or other suitable material. Some soluble coffees, both spray- and freeze-dried, are manufactured in producing countries for export.

Blend/Roast/Grind. Blends of Brazilian, Central American, and Colombian milds as well as African, Asian, and Brazilian robustas are prepared to achieve desired flavor characteristics. The batch- or continuous-type roasters used for roasted and ground coffee also are used for instant coffee. Grinding of roasted beans for an instant coffee process is adjusted to suit the type of commercial percolation system to be used. The average particle size is generally larger than that used for domestic brewing to avoid excessive pressure drops across the percolator columns. Similarly, very fine particles are avoided.

Extraction. Commercial extraction equipment and conditions have been designed to obtain the maximum yield of soluble solids with the desired flavor character. Conceptually, most commercial systems can be represented by a series of countercurrent batch extractors. The freshwater feed, at pressures well above one atmosphere and temperatures high enough to hydrolyze the coffees' polysaccharides to oligosaccharides, contacts the most spent coffee grounds. During the final extraction stage, fresh ground coffee is contacted with an extract of these oligosaccharides at temperatures near the atmospheric boiling point.

Significant factors influencing extraction efficiency and product quality are grind size, feed water temperature and temperature profile through the system, percolation time, ratio of coffee to water, premoistening or wetting of the ground coffee, design of extraction equipment, and flow rate of extract through the percolation columns.

Percolation trains consisting of 5–10 columns are the norm. Height to diameter ratios usually range from 4:1 to 7:1. To improve extraction, the ground coffee may be steamed or wetted. Feed water temperatures ranging from 154 to 182°C are common and the final extract exits at 60–82°C. To minimize flavor and aroma loss prior to drying, the effluent extract may be cooled in a plate heat exchanger. The yield, a function of the properties of the particular blend and roast, the operating temperatures, and the percolation time, is generally controlled through adjustment of the soluble solids drawn off from the final stage. Extraction yield is calculated from both the weight of extract collected and the soluble solids concentration as measured by specific gravity or refractive index. Soluble yields of 24–48% or higher on a roasted coffee basis are possible. Robusta coffees give yields about 10% higher than arabica because of a higher level of available polysaccharides and caffeine. The latest technology in thermal extraction of spent grounds provides roasted yields in excess of 60% (32).

Extract is stored in insulated tanks prior to drying. Because high soluble solids concentration is desirable to reduce aroma loss and evaporative load in the driers, most processors concentrate the 15–30% extract to 35–55% prior to drying.

(33). This may be accomplished by vacuum evaporation or freeze concentration. Clarification of the extract, normally by centrifugation, may be used to assure the absence of insoluble fine particles.

The flavor of instant coffee can be enhanced by recovering and returning to the extract or finished dry product some of the natural aroma lost in processing. The aroma constituents from the grinders, percolation vents, and evaporators may be added directly or in concentrated or fractionated form to achieve the desirable product attributes.

Drying. The criteria for good instant coffee drying processes include minimization of loss or degradation of flavor and aroma, uniformity of size and shape in a free-flowing form, acceptability of the bulk density for packaging, product color acceptability, and moisture content below the level required to maintain shelf stability (less than 5%). Operating costs, product losses, and capital investment are also considerations in the selection of a drying process.

Spray Drying and Agglomeration. Most instant coffee products are spray-dried. Stainless steel towers with a concurrent flow of hot air and atomized extract droplets are utilized for this purpose. Atomization, through pressure nozzles, is controlled based on selection of the nozzles, properties of the extract, pressures used, bulk density, and capacity requirements. Low inlet air temperatures (200–280°C) are preferred for best flavor quality. The spray towers must be provided with adequate dust collection systems such as cyclones or bag filters. The dried particles are collected from the conical bottom of the spray drier through a rotary valve and conveyed to bulk storage bins or packaging lines. Processors may screen the dry product to assure a uniform particle size distribution.

Most spray-dried instant coffees have been marketed in a granular form, rather than the small spherical spray-dried form, since the mid-1960s. The granular appearance is achieved by steam fusing the spray-dried material in towers similar to the spray drier. Belt agglomerators are also common.

Freeze Drying. Commercial freeze drying of instant coffee has been a common practice in the United States since the mid-1960s. The freeze-drying process provides the opportunity to minimize flavor degradation due to heat (34).

Sublimation of ice crystals to water vapor under a very high vacuum, about 67 Pa (0.5 mm Hg) or lower, removes the majority of the moisture from the granulated frozen extract particles. Heat input is controlled to assure a maximum product end point temperature below 49°C. Freeze drying takes significantly longer than spray drying and requires a greater capital investment.

Packaging. In the United States, instant coffee for the consumer market is usually packaged in glass jars containing from 56 to 340 g of coffee. Larger units for institutional, hotel, restaurant, and vending machine use are packaged in bags and pouches of plastic or laminated foil. In Europe, instant coffee is packaged in glass jars or foil-laminated packages.

Protective packaging is primarily required to prevent moisture pickup. The flavor quality of regular instant coffee changes very little during storage. However, the powder is hygroscopic and moisture pickup can cause caking and flavor impairment. Moisture content should be kept below 5%.

Many instant coffee producers in the United States incorporate natural coffee aroma in coffee oil into the powder. These highly volatile and chemically un-

stable flavor components necessitate inert-gas packing to prevent aroma deterioration and staling from exposure to oxygen.

Decaffeinated Coffee Processing

Decaffeinated coffee products represented 18% of the coffee consumed in 1991 in the United States (31). Decaffeinated coffee was first developed commercially in Europe about 1900. The process as described in a 1908 patent (35) consists of first, moisturizing green coffee to at least 20% to facilitate transport of caffeine through the cell wall, and then contacting the moistened beans with solvents.

Until the 1980s, synthetic organic solvents commonly were used in the United States to extract the caffeine, either by direct contact as above or by an indirect secondary water-based system (36). In each case, steaming or stripping was used to remove residual solvent from the beans and the beans were dried to their original moisture content (10–12%) prior to roasting.

In the 1980s, manufacturers' commercialized processes which utilized either naturally occurring solvents or solvents derived from natural substances to position their products as naturally decaffeinated. The three most common systems use carbon dioxide under supercritical conditions (37), oil extracted from roasted coffee (38), or ethyl acetate, an edible ester naturally present in coffee (39). Specificity for caffeine and caffeine solubility is key to selection and system design. Because caffeine can be selectively removed from water extracts of green beans by activated charcoal, several processes which utilize water or recycled green coffee extract have been described and are also considered natural decaffeination. If water is used, the green coffee extract produced is externally decaffeinated and the noncaffeine solids containing important flavor precursors are reabsorbed before drying and roasting. The use of recycled green extract obviates the need for a separate reabsorption step as the caffeine deficient green extract selectively leaches caffeine. Pre-absorbing sugar on activated charcoal to improve its specificity also has been commercialized (40). The degree of decaffeination, based on comparison to the starting material, is controlled using known time-temperature relationships for the particular process for each bean type.

In all the above mentioned processes of coffee decaffeination, changes occur that affect the roast flavor development. These changes are caused by the pre-wetting step, the effects of extended (four hours plus) exposure at elevated temperature as required to economically extract the caffeine from whole green beans, and the post-decaffeination drying step.

To make an instant decaffeinated coffee product, the decaffeinated roast and ground coffee is extracted in a manner similar to nondescaffinated coffee. Alternatively, the caffeine from the extract of untreated roasted coffee is removed by using the solvents described previously.

Economic Importance of Coffee

Coffee has been a significant factor in international trade since the early 1800s. It is among the leading agricultural products in international trade along with

wheat, corn, and soybeans. The total world production of green coffee in the 1989-1990 growing season was 97.1 million bags; exportable production was 73.4 million bags with an export value of \$6.7 billion (Table 4) (41).

In 1990, the United States import from producing countries totaled 21 million bags of green coffee equivalent (Table 5). This includes 19.6 million bags of green coffee, 0.2 million bags of roasted coffee, and 1.2 million bags of soluble coffee with a total value of \$1.9 billion (42). More than 79% of this import came from countries in the western hemisphere.

Historically, any factors that affect the balance of supply and demand, eg, political, climatic, etc, have contributed to the high volatility of green coffee prices. The International Coffee Organization (ICO), consisting of seventy-two producer and consumer nations, developed the International Coffee Agreement (ICA) in 1962 to achieve stable prices through export quotas adjusted by indicator price change. The breakdown of the ICA in 1989 led to the historically low prices of the early 1990s. In September 1990, an extension of the 1983 International Coffee Agreement was approved until the end of September 1992 (43) to provide more time for the seventy-two national council of the ICO to renegotiate a new accord.

Table 4. World Production of Green Coffee, 1989-1990^a

| Country | Exportable production ^b | % |
|------------------|------------------------------------|--------------|
| Brazil | 15,500 | 21.1 |
| Colombia | 11,538 | 15.7 |
| Indonesia | 5,575 | 7.6 |
| Ivory Coast | 4,700 | 6.4 |
| Mexico | 3,350 | 4.6 |
| Guatemala | 3,162 | 4.3 |
| Uganda | 3,045 | 4.1 |
| El Salvador | 2,607 | 3.6 |
| Costa Rica | 2,198 | 3.0 |
| Ecuador | 1,849 | 2.5 |
| Zaire | 1,780 | 2.4 |
| Honduras | 1,722 | 2.3 |
| Kenya | 1,665 | 2.3 |
| Cameroon | 1,393 | 1.9 |
| Peru | 1,219 | 1.7 |
| Ethiopia | 1,200 | 1.6 |
| Papua New Guinea | 1,081 | 1.5 |
| India | 1,000 | 1.4 |
| Vietnam | 950 | 1.3 |
| Madagascar | 870 | 1.2 |
| Tanzania | 844 | 1.1 |
| others | 6,137 | 8.4 |
| <i>Total</i> | <i>73,385</i> | <i>100.0</i> |

^aRef. 41.

^bThousands of 60-kg bags.

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Table 5. World Imports of Green Coffee in 1990^a

| Country | Imports ^b | % |
|------------------------|----------------------|--------------|
| United States | 21,009 | 27.5 |
| Germany | 13,012 | 17.0 |
| France | 6,301 | 8.2 |
| Japan | 5,506 | 7.2 |
| Italy | 5,242 | 6.9 |
| The Netherlands | 3,199 | 4.2 |
| Spain | 3,017 | 3.9 |
| United Kingdom | 2,898 | 3.8 |
| Canada | 2,253 | 3.0 |
| Belgium/Luxembourg | 2,149 | 2.8 |
| Eastern Europe | 1,604 | 2.1 |
| other Western Europe | 9,006 | 11.8 |
| other Asia and Oceania | 1,216 | 1.6 |
| <i>Total</i> | <i>76,412</i> | <i>100.0</i> |

^aRef. 42.^bThousands of 60-kg bags.

Coffee Regulations and Standards

Various standards and regulations for green coffee are set either by legislation in the producing and consuming countries, eg, the United States, France, or the European Economic Community, or by voluntary standards set by various trade organizations and associations in the consuming countries, eg, National Coffee Association or London Terminal Market. These standards and regulations define what is being purchased by contract and protect consumers against fraud and potential health risks. They include defining designations as species, geographical origin, processing, and crop year; and quality grades/types including level and type of defects, bean size, extraneous matter, agricultural residues, flavor, color, bulk density, and percentage of maximum moisture. Legislation in the consuming countries also covers processed coffee for fraud or potential health risks. International organizations such as the International Coffee Organization (ICO) based in London, the International Organization for Standardization (ISO), the Codex Alimentarius Commission of the United Nations (FAO/WHO) based in Rome, and the National Coffee Association (NCA) based in New York help achieve standardization in international trade, support research, and provide information about methods of analysis, guide to storage and transport, publications, meetings, etc (44,45).

Decaffeination Regulations. For decaffeinated roasted coffee, EEC standards indicate the maximum content of caffeine as 0.1% db; for decaffeinated instant coffee it is 0.3% db. In the United States, decaffeination usually signifies that 97% of the caffeine has been removed. Permissible solvents for decaffeination processes are defined by national legislation, eg, FDA or EEC directive. The maximum residual solvent content after decaffeination, roasting, or instant coffee processing is to be kept within good manufacturing practice, ie, very low ppm levels or below at point of sale (46).

Caffeine and Health. Caffeine is listed in the U.S. Code of Federal Regulations as a multipurpose, generally recognized as safe (GRAS) substance and in *Food Chemicals Codex*, published by the U.S. National Academy of Sciences/National Research Council, as a flavoring agent and stimulant. Consumption of caffeine in coffee, tea, and soft drinks has been studied for health concerns with regard to every organ system. In the early 1990s, numerous publications continue to appear and much active research continues to be done, but a consensus has developed among knowledgeable scientists that consumption of caffeine in moderate amounts is not associated with any serious health consequences (47-53).

Caffeine is considered by pharmacologists to be a mild stimulant of the central nervous system. It has been shown to promote feelings of well being and increased ability to perform certain mental tasks efficiently. There are people who are oversensitive to the effects of caffeine; overindulgence by these individuals, eg, intake of more than 600 mg caffeine/d, can bring unwanted effects such as anxiety, restlessness, sleeping difficulties, headache, or palpitations of the heart (54).

Coffee Substitutes

Coffee substitutes, which include roasted chicory, chick peas, cereal, fruit, and vegetable products, have been used in all coffee consuming countries. Although consumers in some locations prefer the noncoffee beverages, they are generally used as lower cost beverage sources. Additionally, it is not unusual for consumers in some of the coffee producing countries to blend coffee with noncoffee materials.

Chicory is harvested as fleshy roots which are dried, cut to uniform size, and roasted. Chicory contains no caffeine, and on roasting develops an aroma compatible with that of coffee. It gives a high yield, about 70%, of water-soluble solids with boiling water and can also be extracted and dried in an instant form. Chicory extract has a darker color than does normal coffee brew (55).

New Technology

Coffee Biotechnology. A number of advanced biotechnology techniques are being investigated to improve and/or develop coffee varieties as well as to better utilize roasted coffee (56).

In South and Central America, breeding selection programs are in progress to improve coffee disease resistance, productivity, and cup quality. Micropagation methods based on multiplying cells in a bioreactor have also been reported (57) and will allow for the propagation of identically cloned plants, thus eliminating nonuniformity in coffee plant material. Coffee plant regeneration studies from protoplasts, ie, coffee cells without cell walls, have been reported (58) and may serve as a key part of the methodology involved in transforming coffee plants via recombinant DNA techniques. The first successful results in transforming coffee cells with marker genes have been described (59). The potential applications of recombinant DNA to coffee plants are immense.

Coffee bioconversions through enzymatic hydrolysis have been used to modify green coffee and improve the finished product (60). Similarly, enzymes have been reported which increase yield and improve flavor of instant coffee (61). Fermentation of green coffee extracts to produce diacetyl [431-03-8], a coffee flavor compound, has also been demonstrated (62).

Potential consumer benefits from biotechnology (56) are cost and quality. The use of biotech means to increase the level of various sulfur-containing amino acids in coffee proteins, and to enhance sucrose and oil levels, could have an impact on the flavor and aroma of the finished ground coffee product. Also, caffeine level modification/elimination through genetic manipulations of the coffee plant could yield low caffeine coffee without additional processing by the manufacturer.

Liquid Coffee Products. Liquid coffee concentrates in frozen form have been available for many years for the food service or catering businesses, but they have not made a significant impact in either this market segment or in the grocery market, mainly because of inconvenience. Liquid coffee products, generally pre-sweetened and ready to drink with milk added, represent a significant part of the Japanese and Korean coffee markets. Much of this product is sold in vending machines, hot and cold, for immediate consumption. The beverage is prepared by mixing the diluted coffee extract from a commercial percolator with the desired additives such as milk, sugar, and flavorants. It is then packaged in a container (generally a can) suitable for retort processing to provide a product that can be distributed without refrigeration. Recently the U.S. market has seen entry of several similarly processed products.

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COGENERATION. See ENERGY MANAGEMENT; POWER GENERATION.

COKE. See COAL; COAL CONVERSION PROCESSES, CARBONIZATION.