Confidential

Coffee residues utilization

Literature survey

In commission of Agentschap NL and KNVKT

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Colophon

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Samenvatting

In opdracht van de KNVKT en Agentschap NL werd door Wageningen UR, Food and Biobased Research een onderzoek uitgevoerd naar de mogelijkheden om bijproducten die vrijkomen in de koffieindustrie op een betere manier te benutten. Hiervoor werd een uitgebreide deskstudie uitgevoerd (hoofdstuk 2 en 3), waarbij een gedetailleerd (engelstalig) verslag van patent en literatuuronderzoek het uitgangspunt is geweest voor dit rapport. Aanvullend werd informatie verzameld van relevante internet sites en werden interviews afgenomen bij verschillende koffiebranderijen om inzicht te krijgen in de restproducten die vrijkomen bij de koffieproduktie en een inschatting te kunnen maken van de hoeveelheden. Hierbij werden vrijkomende emballage en productieverliezen niet meegenomen.

Koffie bijprodukten vrijkomend in de Nederlandse Koffie industrie (data CBS /VNKT)

	Volume /jr	
Groene bonen	160.000 ton	Branden 15 wt% verlies (-24.000 ton)
Gebrande bonen	136.000 ton	Koffie zetten 30 wt% verlies (-41.000 ton)
Totaal residu	95.000 ton	

Residu	**Volume /jr**	**Huidige waarde**
Koffiedik[a]	80.000 ton	nil
Koffiedik[b] (incl. vlies)	15.000 ton dry weight (400 ton)	€2.000.000 (133 €/t)
Perswater	100.000 m^3	-/- €400.000
zilvervlies[a]	1.500 t	-/- €120.000
zilvervlies[b]	65 t	-/- €6500 (100 €/t)

a komt verspreid vrij
b komt geconcentreerd vrij bij geïdentificeerde koffie verwerkende industrie

Jaarlijks wordt in Nederland 160 duizend ton groene koffiebonen geïmporteerd en door de koffiebranderijen verwerkt voor de locale consumptie en export. Bij het roosteren van de groene koffieboon gaat ca 15% aan gewicht verloren. Het kaf of zilvervlies dat vrijkomt bij branden van de koffie wordt afgevangen en meestal per container afgevoerd tegen kosten van ca 100 € / ton. Het grootste aandeel biomassa dat vrijkomt bij de bereiding van koffie is het koffiedik, het gemalen donkerbruin gekleurde (natte) residu dat overblijft na filteren van de koffie. Het grootste deel hiervan (ca 80.000 ton / jaar) komt verspreid vrij, deels in de horeca en cateringsector (30%), maar grootdeels in de individuele huishoudens (70%). Opties voor gescheiden inzameling hiervan lijken vooralsnog niet realistisch tenzij een hoge toegevoegde waarde kan worden gecreëerd. Bij de industriële productie van instantkoffie en automaatkoffie komen wel substantiële hoeveelheden koffiedik in geconcentreerde vorm vrij (ca 15.000 ton droge stof/ jaar). Deze wordt nu gedeeltelijk ter plekke benut als brandstof in de stoomboilers en gedeeltelijk afgevoerd als biomassa voor bijstoken in een energiecentrale. Een schatting van de economisch waarde (133 €/ton) werd gemaakt op basis van de verbrandingswaarde.

Op basis van de gemiddelde samenstelling van de belangrijke residufracties koffiedik (SCG) en zilvervlies (chaff) werden de mogelijkheden voor alternatieve toepassing hiervan geëvalueerd. In koffiedik blijft een aanzienlijke fractie lipiden achter. Door extractie van deze lipide fractie neemt de energiewaarde van koffiedik af, maar daar staat tegenover de waarde die dit vertegenwoordigd als grondstof voor biodiesel produktie en/of farmaceutische producten.

Een grove inschatting van de vrijkomende hoeveelheden en de economische waarde van alternatieve toepassingen staan in onderstaande tabellen weergegeven.

Mogelijke verwaarding van koffieresiduen: lipids, terpenes and sterols

	Volume	Value
Extraction lipid fraction of 15.000 ton SCG	2250 ton	-/-500.000 €
Lipids food grade	2250 ton	1.250.000 €
Diterpenes for pharma	150 ton	1.500.000 €
Phytosterols for food	100 ton	1.300.000 €
Biodiesel from triglycerides	1900 ton	950.000 €
Conversion of triglycerides to FAME	190 ton	6650 €
remaining biodiesel product	1700 ton	1.360.000 €

Voor toepassing van deze fractie als voedselkwaliteit olie is scheiding van vetten, sterolen en terpenen wenselijk. Deze hebben meerwaarde als farmaceutisch product of voedingssupplement. Afhankelijk van de verkregen oliekwaliteit kan een keuze voor biodiesel omzetting worden overwogen.

Naast lipiden bevat koffiedik een groot aandeel aan koolhydraten. Met name het polysaccharide mannaan is interessant als grondstof voor verwerking tot dietary fibre of voor de productie van bioplastics. Een derde mogelijkheid is de productie van mannitol, dat als laagcalorische zoetstof wordt gebruikt. Nader onderzoek naar de meest haalbare opties (technisch en economisch) voor koffiedik valorisatie is noodzakelijk.

Mogelijke verwaarding van koffieresiduen: koolhydraten

	Volume	Value
Lipid-extracted SCG (85% of 15.000 ton)	12.750 ton	1.500.000 €
Extracted Mannan (40% of 12.750 ton)	5000 ton	-/- 550.000 €
Mannan to bioplastics		3.570.000 €
Mannan to dietary fibre		7.140.000 €
Mannan to mannitol		3.570.000 €
Melanoidins	7650 ton	-/- 950.000 €

Gescheiden inzameling van vrijkomend koffiedik uit de catering en horeca sector behoort tot de mogelijkheden indien de waarde als grondstof de moeite van transport en opslag rechtvaardigt. Onderzoek naar vrijkomende hoeveelheden en logistieke mogelijkheden voor gescheiden inzameling is hiervoor van belang.

Onderzoek naar de inzet van de isoleerbare koolhydraatfractie en de mogelijke omzetting tot functionele voedingsvezel en/of laagcalorische zoetstof (mannitol) is wellicht de meest winstgevende optie. Productie van biologisch afbreekbaar bioplastic uit koffiedik is nieuw en behoort technisch tot de mogelijkheden en zou bijvoorbeeld ingezet als disposable koffiebeker zeker een goede marketing zijn voor de koffie sector (Cradle to cradle). Gebruik van bioplastic uit koffiedik als CO_2-neutrale verpakkinsfolie is een andere mogelijke applicatie, die nader onderzocht kan worden.

De zilvervliezen of kaf kan worden ingezameld bij de verschillende koffiebranderijen. Een grove schatting levert een totaal van ca 2000 t kaf per jaar die vrijkomt in de Nederlandse koffieindustrie. Momenteel wordt deze geperst en afgevoerd als afval (negatieve waarde van ca 100 €/ton) of gecomposteerd. Er is geen onderzoek naar opwaardering van dit materiaal bekend. Naast de aanwezigheid van wat vezelmateriaal en bioactive componenten (lipiden, anti-oxidanten) is de waslaag van interesse. Met name van belang is het gehalte aan (400-500 μg/g) gealkyleerde 5-hydroxytryptamiden, die om te zetten zijn in serotonine, wat een bekende neurotransmitter is in de hersenen en wordt toegepast als anti-depressivum. Gezuiverd serotonin HCl wordt vermarkt voor 55 €/g. Bij een 50% conversie efficientie ofwel 0.2 kg/ton serotonine opbrengst zou dit een zeer winstgevende waardetoevoeging kunnen betekenen van ca 10.000 € per ton.

	SCG				
	↓				
solvent	extraction	→	lipids	separation	
	↓			purification	→
	defatted SCG			esterification	→ biodiesel
	↓				
solvent	extraction	→	mannan	purification	
	↓			derivatisation	→ bioplastic
	residue				
	melanoidin	→	phenolics		
	protein	→	amino acids		

Product	volume	energy value	market value
SCG	15.000 t	2.000.000 €	
Lipids extraction	2250 t	500.000 €	4.166.000 €
Mannan extraction	5100 t	550.000 €	3.570.000 €
Melanoidin/protein	7650 t	950.000 €	1.530.000 €
total			9.266.000 €

Aanbevelingen

Nader onderzoek naar de commerciële haalbaarheid van het gebruik van de geïdentificeerde koffierestproducten zilvervlies en koffiedik is van belang. Hierbij is (**A**) een nauwkeuriger inventarisatie van hoeveelheden vrijkomend afval die potentiëel inzetbaar is als grondstof voor verdere waardetoevoeging een eerste vereiste. Een gedetailleerde analyse van de kosten en baten van eventuele inzameling van verspreid vrijkomende afvallen en de logistieke organisatie (**B**) van een dergelijke operatie zou moeten worden uitgevoerd. Van belang is hiervan het break-even punt vast te stellen waarop de inzamelingskosten worden gecompenseerd door de toegevoegde waarde van de grondstof.

Vaststelling van de commerciële toepasbaarheid van de verschillende inhoudsstoffen en de economische waarde vereist (**C**) een technologisch onderzoek naar extracties en zuivering van componenten uit de koffierestproducten. Trapsgewijze bioraffinageprocessen om de maximale hoeveelheid waardevolle fracties te isoleren kunnen op laboratoriumschaal worden gesimuleerd. Door analyse van het fractioneringsproces en opstellen van een massa/ energiebalans is een inschatting te maken van de technische haalbaarheid. Door vervolgens voor de diverse componenten applicatieonderzoek (**D**) uit te voeren (bijvoorkeur in samenwerking met potentiële industriële gebruikers) kunnen reële inschattingen worden gemaakt van de commerciële potentie. De uitvoering van een gedetailleerde LCA (Levenscyclus analyse) (**E**) wordt aanbevolen om de milieueffecten en de duurzaamheid van het totale proces onomstotelijk vast te stellen.

Op basis van de verkregen data is een uitgebreid business plan op te stellen (**F**), waarbij commerciële partners kunnen besluiten te investeren in de voorgestelde reststroomverwaarding.

De verschillende onderdelen (**A-F**) kunnen parallel worden opgestart en verschillende scenario's verder uitgewerkt op basis van de uitkomsten van de onderzoeken.

A – inventarisatie hoeveelheden reststromen

B – logistieke organisatie

C – scheidingstechnologie en bioraffinage

Koffiedik - olie
- diterpenen
- phytosterolen
- mannaan
- melanoidine

Kaf
- lipiden
- vezels
- hydroxytryptamide

D – applicatie onderzoek

Functional foods (olie, phytosterolen, voedingsvezels, zoetstof, anti-oxidantia, etc)
Pharmaceutische en cosmetische producten (diterpenen, phytosterolen, serotonine, etc)
Biofuels (lipiden, FAME)
Bioplastics (mannaan)

E – Milieueffect en levenscyclus analyse

F – Business plan

Content

Terminology and abbreviations

See http://www.coffeereview.com/glossary.cfm?alpha=P

	Explanation	Translation
BOD	Biological Oxygen Demand	
CGA	Chlorogenic acid	
Chaff	= Silver skin	Kaf
Coffee drag	= SCG	Koffiedik
SCG	Spent Coffee Grounds	Koffiedik
Coffee meal	= SCG	
Coffee pulp	Residue from dehulling process	
Hulls	“ “	Schil
Husk	“ “	Schil
Mucilage	“ “	Slijm
MOS	Manno-oligosaccharides	
Percolation		Filteren
Silver skin	= chaff	Zilvervlies
Soot		Roet
Tar		Teer

1 Introduction

In the daily morning wake up ritual of millions of consumers world wide just a few milligrams are needed of coffee aroma and taste. Due to the caffeine content of the popular beverage it has a mild stimulating and energizing effect. Coffee is one of the most important agricultural commodities and is traded world wide. For the preparation of the beverage the extracted coffee beans are largely discarded as well as the other 95% of underutilized biomass from the shrubs or small trees that provide the bright red cherries.

An investigation into the possibilities for value addition for coffee residues was performed by Wageningen Universtity and Research (WUR) in commission of the Royal Dutch Association for Coffee and Tea (KNVKT) and AgentschapNL. This report is the outcome extended literature and patent research (chapter 2 and 3) combined with data obtained in interviews of different experts in the field.

Coffee is commercially a very significant commodity crop. Many citations found in literature state that coffee – as legal commodity – is second largest crop, only crude oil is larger [Loyd & Fadel, 2001]. This strong statement has been much argued and doubted. According to FAO/ICO coffee is ranking 4th as most valuable agricultural traded commodity. Due to the larger volumes of grains (e.g. rice, wheat and corn) and sugar these commodities represent larger trade volumes and values. After a number of years with low green bean prices the current ICO indicator prices are relatively high (January 2010: composite price 126.85 US cents/lb or ca 2.05 €/kg, with substantial higher prices for Arabicas). Trade of raw products, e.g. green beans, represents a volume of 8 million tons per annum and correspondingly a traded value of ca 16 billion € world wide. The trade value of the coffee beverages in retail and catering represents still a much larger amount.

Environmental management has become more and more important for companies and there is competition between companies for increasing the sustainability and 'green' image of their products. The environmental impact of coffee production is complex as there are many factors accumulating along the coffee production and supply chain [Salomone, 2003]. Factors that affect the impact are the use of fertilizers and crop protection chemicals, mechanization of harvest and transportation, energy used for drying and the resources used for packaging. The residues and emissions that are liberated along the production chain representing in total an estimated 150 million tons of biomass (roughly calculated from 8 Mt green beans = 5%). In the context of the expanding biobased economy it is of interest that these wasted biomass residues can be minimized and used for production of CO_2 neutral energy or other value added products. This study is to identify the best options for enhanced use of these residues from the coffee production.

How many tons of unused biomass are still wasted in the coffee production chain? Is it profitable to for example to extract the residues for coffee oil as possible biodiesel feedstock, or extract carbohydrates for the production of 'green chemicals', aroma's and fuel? The options for use of coffee residues as raw materials for production of biobased materials are evaluated here. The possibilities are reviewed for implementation of biotechnology / biorefineries that now are being developed in other agro-industrial sectors. This study focuses on the residues that are liberated in the process from green beans to manufacturing of coffee beverage.

The Netherlands are a major importer of raw and roasted coffees (2008: ca 160 kton raw and ca 32 kton roasted) [VNKT jaarverslag / CBS]. The Royal Association of the Dutch Coffee and Tea industries (KNVKT) has initiated this study to find novel ways of increased sustainable development in the coffee industries. Besides energy saving and more environmentally friendly packaging the better use of biomass residues is of interest. Options for new ways of use of koffie residues are explored here in this study.

2 Composition of coffee residues; spent coffee grounds (SCG)

2.1 Introduction

Spent coffee grounds (SCG), the major residue in coffee beverage manufacturing, has been studied for alternative use and value addition. Currently the most spent grounds are dispersedly disposed off by consumers and catering or burned where accumulated quantities are sufficiently available in industries to recover the embedded energy. Some low value added uses have been identified and reported in patents and open literature, such as mixed composts, soil improvements, fertilizers, recipes for feeding animals or fermentation feedstock and substrates for mushroom production.

The gross composition of roasted coffee is given in Table 1 [Spiller 1998]. From this the insoluble residues in SCG can be derived, which still contain substantial amounts of protein (7.5%) and lipids (9.5%), but mostly insoluble polysaccharides and browning compounds including phenolics. Depending on the processing conditions of coffee extraction (temperature/ pressure) different weight percentage of dissolved coffee can be achieved.
The composition of the water insoluble fraction corresponds to SCG.

Table 1 Composition of roasted arabica coffee (% wt) (modified after [Spiller 1998])

Component		**Total**	**Water soluble**	**Water insoluble**
Protein		9	1.5	7.5
Lipids		9.5	9.5	
	Terpenes	2	trace	2
Carbohydrates				
	Polysaccharides	30	6	24
	Sugars	0.3	0.3	-
Organic acids		0.7	0.7	
	Chlorogenic acids	3.8	3.8	
Alkaloids		1.6	1.6	
Browning compounds		35.0	7.5	27.5
Ash		4.0	3.5	
Water		2.5	2.5	
Total		**100**	**27.5**	**72.5**

2.2 Proteins

The fresh dried coffee bean (endosperm) roughly contains 11-16 % proteins and free amino acids. The content of protein in roasted beans was reported to be 9%, of which 1.5% is soluble in water and the remaining 7.5 % part insoluble [Spiller, 1998] (see Table 1).
In roasted beans incorporation of proteins or amino acids in melanoidins have been demonstrated [E. K. Bekedam et al. 2008a]. The suitability of the proteins in SCG as industrial protein and functional ingredient in food and feed production (emulsifier, gelling properties, nutritional value) is considered poor due to its thermal history and contents of phenolics and melanoidins.

2.3 Lipids and oils (Appendix D)

Coffee seeds contain 7-16% of lipids and oil, which is largely lost in the coffee grounds. The coffee seed oil is not used as food oil because of undesirable high content of other lipids than triglycerides. The extraction of oils from SCG has been considered uneconomical, because the grounds need to be dried before effective extraction can take place.

2.4 Carbohydrates (Appendix E)

Coffee beans contain a substantial amount of carbohydrates, and a substantial part of these polysaccharides are water-insoluble (i.e. arabinogalactan, mannan and cellulose). The polysaccharide composition of different coffee beans are very similar.

In the roasting process the carbohydrate composition is affected. The polysaccharides present in green beans are partially degraded by roasting. Extractable and unextractable polysaccharide fractions were shown to be affected by the degree of roasting. The arabinose is more susceptible to degradation at elevated temperatures and especially the arabinogalactan content declines with more severe roasting.

The effect of roasting on the coffee bean composition involves the darkening of the colour and the liberation of aroma compounds. The dark coloured compounds are formed due to a reaction between proteins and sugars, also called Maillard reactions.

The molecular weight of the polysaccharide fractions in the coffee affects the foam properties. Crosslinks with proteins (Maillard reactions) and lignins make it difficult to isolate polysaccharides from roasted coffee without additional treatment.

2.5 Organic acids (Appendix F)

Chlorogenic acid (CGA) occurs in relative high quantities in coffee tissues and is considered to be a promising source of biofunctional dietary supplement. In green beans the presence of non-volatile organic acids that are water soluble has been found up to 8.2 % on dry weight basis. Chlorogenic acid is with ca 7.0 % the main component of this fraction. The remaining 1.2 % includes oxalic acid, malic acid, citric acid, and tartaric acid [Sivetz & Desrosier 1979]. After roasting the amount of soluble chlorogenic acid has decreased to 4.5% while caffeic acid and quinic acid are liberated.

The presence of other phenolics such as tannins and lignins in coffee is poorly documented. In many cases the melanoidins formed during roasting (by sugars and amino acids) are classified as such.

2.6 Alkaloids (Appendix G)

Alkaloids (chemical compounds containing nitrogen) are among the most prominent biologically active substances.

The purine alkaloids present in coffee and tea are the most valued. Besides the predominant presence of caffeine in coffee beverages other related alkaloids are present in minute amounts. These are of similar purine alkaloid structure and are metabolites of caffeine (theobromine, theophilline, paraxanthine, theacrine, libertine, methylliberine [Viani, 1988]). The alkaloids are

extracted in the production of the coffee beverage. Remaining residues of caffeine in SCG are low and not considered economically worth while to extract. In the decaffeinated coffee production the highest value (more than the decaf coffee) is obtained from the extracted caffeine that is used in energy drinks industry.
Also the pyridine alkaloids trigonelline, niacin and quinolinic acid are present in coffee.

2.7 Mineral and metal content (Appendix H)

Coffee is known for its high potassium (K) content. Discriminative differences in mineral content have been shown between different varieties [Martin et al., 1998] and brews [Haswell & Walmsley 1998]. Phosphorus (P) and copper (Cu) are higher in robusta while arabica contains more manganese (Mn) (Table 2).

Table 2 Mineral content in different coffee types [Martin et al., 1998]

Mineral	Arabica (wt%)	Robusta (wt%)
K	1.5	1.7
P	0.152	0.20
Ca	0.107	0.130
Cu	$1.6.10^{-3}$	$2.2.10^{-3}$
Mn	$3.1.10^{-3}$	$1.6.10^{-3}$

Brewed coffee is rich in potassium (up to 200 mg/cup), magnesium (up to 20 mg/cup) and relatively high amounts of manganese (0.2 mg /cup) [Clarke &Macrae 1989].

3 Uses of coffee residues, spent grounds, pulp, chaff; literature & patent search

3.1 Introduction

The use of wasted biomass including coffee grounds has been reviewed in the context of increasing renewable energy demands [Nonhebel, 2005]. In the process of coffee beverage brewing solid residues are liberated known as spent coffee grounds (SCG) or coffee drag. Much of this biomass is generated at the site of consumption. It is considered economically impossible to recollect the dispersedly available waste from homes or catering. On the other hand, in the industrial brewing for soluble coffee production substantial amounts of these SCG residues are liberated and concentrated at the production site. The composition of SCG is given in Table 3.

Table 3 Composition SCG (% weight)

Component	Campbel et al 1976	Rolz 1975	Oi et al, 1981
Protein	11.8	4-12	8
Fat	23.1	1-2	
Total sugar			38
Fibre	42.5		40-50
Cellulose	12-20		
Pectin		6	
Ash	0.7		1.5
Dry matter	91.1		

So far disposal of this waste is economically and environmentally inefficient. Due to its composition (organic acids) and inefficient burning behaviour with resulting emissions and effects on air quality of the environment, landfill is often practiced. To find alternative ways of disposal of SCG much research has been done in the past [Ruiz, 1974; Pandey, 2004] in the area of animal feed, composting and fermentation. Especially the use of coffee residues in the primary production has been studied intensively for coffee pulp and husk [EU INCO project]. Conversion to biogas, animal feed, organic fertilizer, vermi-composting, and detoxification has been elaborated.

An extensive patent search was performed on coffee residues and a number of specific coffee constituents. Patents dealing with machines and methods of manufacturing of the beverage were omitted. Some patents dealing with coffee residues and extractions other than SCG were incorporated when considered relevant for this survey.

3.2 Animal feed

3.2.1 Poultry and ruminants

According to older patents SCG was incorporated in animal feed (for horses, cattle, pigs, poultry etc) by mixing it with other ingredients such as wheat bran or rye bran [J.H. Speyerer, GB18991118/ GB 1898 24631]. The references in literature for feeding of coffee grounds to

poultry [Hammond, 1944; Carew et al 1967] and cattle [Campbel et al 1976; Mather and Apgar, 1956] are reporting to give deleterious effects.
For cattle the effects of addition of different amounts of coffee grounds to feed was studied. The coffee grounds depressed feed intake and increased urinary output with increased water uptake. It caused diuresis and renal, urethral and bladder irritation. In rats the undesirable factors were diminished by water extraction while ether extraction for lipid removal eliminated most of them [Campbel et al 1976].
Without further treatments for detoxification coffee residues are unsuitable as animal feed. By hydrolysing (saponification) of coffee grounds an animal feed product could be prepared [Nestlé, DE2943021, 19800508]

Dried coffee pulp has been considered as animal feed after extraction of caffeine or fermentation, but the low digestibility allows only for partial addition in diets [Gaime- Perraud et al., 2000]. Solid state fermentation was studied to find strains capable of degradation of caffeine [Gaime-Perraud, 1995]. Ensilage of coffee pulp using natural anaerobic fermentation of lactic bacteria that ferment the water soluble carbohydrate fraction yields organic acid (mainly lactic acid) and preserves the forage. A good quality of silage usually is difficult to obtain in tropical conditions. Mixing with other crop residues is therefore proposed. The high alkaloid and tannin content remains to have negative effects on the digestibility.

3.2.2 Aquaculture
Feeding of coffee pulp to fish has been explored [Garcia & Baynes 1974; Christensen 1981] and found to have no negative effects (up to addition of 30%) on growth rate and yields of fish.

3.3 Fermentation

3.3.1 Introduction
Microbial fermentation of the coffee residues as carbon source has been reported. Various approaches from anaerobic fermentation of waste waters, composting and solid-state fermentation have been published to produce a range of products ranging from biogas and edible fungi to specialty chemicals such as aromas and hormones. Most work was done on the coffee residues in the primary production phase (pulp, hulls).

3.3.2 Methane fermentation and biogas production
- Methane fermentation of coffee grounds could be enhanced by pretreatment with organic solvent extraction (dioxane) and cellulolytic enzyme treatment [Oi et al., 1981].
- Anaerobic digestion of waste water rich in coffee grounds was assessed [Dinsdale, et al., 1996]. The coffee waste had a high (26-33%) lipids content with lower carbohydrate levels (3.5 – 5.3 % hemicellulose; 11.1-13.8 α-cellulose) and 9-11% lignin, 1.7-1.1 % protein and ash (1.4-3.3%). In mesophilic digestion especially lipid degradation was observed. Anaerobic co-

digestion of coffee solid waste and sewage sludge was assessed in mesophilic batch assays. Methane production and solid weight reduction were in the normal range [Neves et al, 2006].

- The waste water from coffee beverage production after biological treatment still contains recalcitrant organic compounds such as tannins, and melanoidins that are difficult to remove [Benjankiwar, et al., 2003]. Also free fatty acids may for a substantial part of the organic fraction.

3.3.3 Solid state fermentation

Solid state fermentation processes of coffee residues have been studied for protein enrichment, biological detoxification, to produce enzymes, organic acids, food aroma compounds, biopesticides, mushrooms, pigments, xanthan gum, gibberelic acid (GA_3 plant hormones), etc.

- The production of fungal (detoxifying) enzymes (tannases / decaffeinase) by bioreactors and continuous solid state fermentation of coffee pulp [Hakil et al., 1998; Van de Langemaat et al., 1999] was shown most effective with *Penicellium frequentans* and *Aspergillus phoenicis* strains for tannase production.
- Coffee pulp was treated with *Streptomyces* strains to upgrade the nutritional value by solid state fermentation. The contents of polyphenols declined after growth of the bacteria. [Orozco et al., 2008]. Detoxification and improvement of the nutritional quality of coffee husks was performed by solid state fermentation using fungi [Brand et al., 2000ab, 2001, 2002]. The anti-physiological factors (caffeine and tannins) were found to be removed by solid state fermentation of coffee hulls with filamentous fungal strains (*Rhizophus*, *Phanerochaete* and *Aspergillus*).

3.3.4 Mushrooms

The production of fungi and mushrooms on spent coffee residues was studied. Coffee pulp, husk, leaves and spent ground were tested for their suitability [Leifa et al., 2000abc, 2001; Fan et al., 2001] as substrate in solid state production of different fungi strains. Edible fungi could successfully be grown on coffee pulp [Martinez-Carrera et al. 1989, 2000] while the residue is more suitable as animal feed or fertilizer. Edible mushrooms (*Pleurotis*, *Lentinula* and *Auricularia*) were produced on commercial scale utilizing (partially) coffee pulp as substrate. The seasonal availability and the spontaneous fermentation of coffee pulp was considered a drawback. Also transportation costs and substrate handling restrict its larger scale use.

3.3.5 Aroma production

Coffee husk was used as substrate to grow fungi (*Cerastocystis frimbriata*) for production of aroma components [Soares et al., 2000; Pedroni Medeiros, et al., 2003]. The water extracted coffee husks showed a good adaptation of the fungus and production of 13 (identified) natural aroma compounds (alcohols, esters, aldehydes, ketones).

3.3.6 Hormones
Production of gibberillic acid (GA_3), a plant hormone widely used in the agro-industry, by solid state fermentation of coffee husks was published [Machado et al., 2000, 2002] and patented [Soccol, et al., 2000]. Some special fungi strains (*Gibberella* sp / *Fusarium* sp) are capable of production of moderate quantities of GA_3 on coffee husk as carbon substrate source.
Weak estrogenic response was observed in mice by coffee ether extracts [Kitts 1987].

3.3.7 Enzyme production
- The mucilage has a high pectin content and could be used as a substrate for pectinases [EC3.2.1.15] and cellulase [EC3.2.1.4] induction [Boccas et al., 1994].
- Tannase (or tannin acyl hydrolase [EC 3.1.1.20]) finds application in chemical, pharmaceutical and food industries. Production of tannase by fungal strains grown on coffee residues was studied [Van de Lagemaat et al., 2000]. *Penicillium frequentans* was found to produce substantial amounts of extracellular tannase. *Aspergillu nigers* strains were studied for their suitability to produce extracellular tannase [Aguilar et al., 2000] by SSC.

3.4 Compost, soil conditioner

3.4.1 Introduction
Coffee spent grounds have been considered suitable for mulching and as (organic) fertilizer. It is reported to be rich in N, P and K, and slightly acidic. Home disposal of coffee grounds is recommended to blend into compost or garden mulching in beds and borders or spread on lawns. Also the chaff can be mixed into compost at low dose. Starbucks in North America makes its SCG available to its customers for free, packed in reused coffee bags. Caffeine has been reported to be effective against slugs and snails.

3.4.2 Organic fertilizer
The use of coffee residues as organic fertilizer was considered. Because the high contents of N, P, and K in coffee pulps the use as soil conditioner was suggested. The effort for returning the wet and fast degrading waste to the coffee plantations is considered not cost effective. Composting of the pulp is necessary to prevent rapid exothermic fermentation.

- Controlled composting of industrial solid waste was shown to be possible for coffee grounds using the aeration piles method [Nogueira et al., 1999].
- Mulching with coffee inhibits growth of weeds and coffee extraction residue has been claimed in a patent as soil conditioner and garden mold [G. Goldmann – US Pat 3640696, 19691009].
- Horticultural soil or soil protecting agents based on coffee residues [G. Goldmann, DE1803103, 19700416] fermented and mixed with other ingredients (silicic acid, charcoal) with excellent sorption properties.

- Blending of organic wastes including coffee grounds for the production of fertilizer, by continuous fermentation systems [T. Suzuki, JP4198079, 19920717]
- Mixed organic wastes including coffee grounds were fermented, compressed, tabulated and dried, which is to be applied as fertilizer pellets.[Y.S. Sim, KR20000000218, 20000115]
- Aerobic fermentation of coffee residue with addition of ammonium sulphate was patented [Nippon steel Corp, JP5294772, 19931109]

3.4.3 Manure and soil amendment agent

- Activated carbon produced from coffee grounds mixed with egg shells [M. Morita, JP2008285572, 20081127] as litter for absorbing excrements and use as soil amendment agent.
- Addition of fumigatory pyrethroid insecticide to coffee grounds and water absorbent resin for treatment and disposal of animal excrements [Daiki KK, JP8298889, 19961119]

3.4.4 Vermi-composting

- Cultivation of earthworms (*Eisenia foetida*) on coffee pulp has been studied [Davila and Arango 1991]. It helps to fasten the decomposition of the biomass and the worms can be applied as fish or chicken feed [Salazar and Mestre, 1991]. Vermi-culture on coffee pulp was reviewed [Aranda and Barois, 2000] and concluded a suitable tool for solving the environmental impact of coffee pulp disposal.
- Coffee drag is suitable for vermin-cultural production [Munroe 2010] and considered suitable in organic farming. Especially in the US and Canada coffee drags are used and marketed to produce vermin-compost.

3.5 Pest control

The effects of caffeine and coffee grounds on the development of mosquito eggs and larvae (vector for spreading diseases such as dengue, yellow fever) was studied. With addition of coffee grounds the reduction of the number of adult mosquitoes produced was observed [Laranja et al., 2003].

3.6 Energy, biofuel and biodiesel

3.6.1 Introduction

Currently the husks are often burned at the sites for generation of processing heat (15 MJ/kg), but the corrosiveness of the emitted gasses deteriorate the equipment. Also the SCG fraction liberated at instant coffee manufacturing is currently used as boiler fuel (Chapter 8).

The instant coffee industries yield large amounts of biomass especially in the form of SCG. The current way of disposal is its use as fuel in the boilers, which is not always done on the most efficient way [Silva et al., 1998]. The high water content in the coffee grounds (50-60%) make it less efficient as fuel. Coffee grounds were determined to have a calorific heating value of 12.5-

15.0 MJ/kg on dry matter base (High heating value HHV / Milne) [Phyllis data base]. In wet form (60% water) this is reduced to 5-6 MJ/kg. Gasification with dual fluidized bed technology at 800 °C of dried coffee grounds (10% moisture) is easily converted to product gas (>70%) with a high heating value [Xu et al., 2006].

3.6.2 Biodiesel

- The extraction of oil from SCG and its conversion to biodiesel (transesterification) yields 10-15% oil depending on the coffee species (Robusta or Arabica) [Kondamudi et al., 2008]. The high content of unsaponifyable lipids may require additional purification of the coffee oil before biodiesel can be produced.
- Coffee oil extraction (long chain fatty acids LCA fraction is high in linoleic acid 46%; unsaponifyable: 5% sterols and terpenes, tocopherols; [Spiller 1998].
- Composition of fatty acid methylesters mixture extracted from coffee grounds: palmitic 7.2%, stearic 9.4%, oleic 9.7%, linoleic 10.4%, eicosapenteanoic (EPA) 11.4%, eicosanic acid 12.6% (see also Table 11).
- EPA is a long chain omega 3 fatty acid considered as one of the essential fatty acids that are used in food supplements. It is considered of interest to source ω3 EPA from biodiesel [Daniells, 2009].

3.6.3 Briquettes and pelletizing

- Compressed briquette (as fuel or fire logs) was prepared from coffee grounds in a combined composition with combustible wax and other additions (cellulose) [US5910454, 19990608].
- Patents for pelletizing coffee grounds for preparation of solid fuels have been claimed [R.K. Sprules US5910454, 19990608]. Coffee grounds have a net energy value per pound of 490-650 Btu (=6-8 MJ/kg) [Goluke & MacGauhey 1976].

3.7 Carbonization and activated carbon

3.7.1 Introduction

Coffee hulls were used to produce activated carbon by steam and CO_2 activation. Activated carbons are obtained with small external areas and microporous structure. The activated carbon would be suitable for gas and liquid phase absorption, as pollutant, odour removal, gas separation and catalysis [Nabeis et al., 2008a,b].

3.7.2 Activated carbon

Many patents were filed for the conversion of coffee grounds by carbonization in activated carbon. Some examples are given below:

- Formed charcoal from coffee grounds was prepared by carbonization with addition of binders (starch, CMC, PVA) [JP10060464, 19980303].

- Activated carbon from coffee waste was performed by stepwise parching (300-400 °C), charring (600-700 °C) and chemical activation by alkali [Kim Hak Hee, KR100259546, 20000615]
- A simplified production process for activated carbon production was described [Tokyo gas Co Ltd, JP2001287905, 200011016] using cellulose of coffee grounds in a packed pressurized cylinder.
- The production of activated carbon from lees of coffee was described using carbonates as activating agents (K_2CO_3, $CaCO_3$, $MgCO_3$) [King Car Food Ind Co Ltd, JP2005075686, 20050324; US2003196954, 20031023].
- Manufacturing method for activated carbon from coffee grounds [Invitro Plant Co Ltd, KR20060108345, 20061017] by alkaline extraction and stepwise roasting or calcining.

3.7.3 Biosorbent

Coffee residues have been used as filter for metal ion absorption or dye absorption:

- Untreated coffee husks was found suitable as sorbent for removal of cationic dyes (e.g. Methylene blue) from aqueous solutions [Oliveira et al., 2008]. In roasted coffees the melanoidins and phenolic compounds have metal chelating properties, which may inhibit iron uptake [Takenaka et al., 2005].
- Coffee grounds were carbonized and claimed to be effective for treatments of waste waters [JP6312194, 19941108].
- Carbonized coffee grounds were claimed as odour absorbing packing medium for gas cleaning deodorizing columns [Yakult, JP9141046, 19970603].
- To remove ammonia odours coffee grounds treated with microwave heating was found to be very effective [Kawasaki, et al 2006].
- Impregnation of coffee grounds with phosphoric acid and subsequent pyrolysis at 450 °C yielded highly porous activated carbons with appropriate efficient sorption of dyes [Reffas et al., 2010]

3.7.4 Other uses

- A method to produce activated carbon from coffee drags that can be used for a body warmer was patented [Eco Carbon KK, JP2009062250, 20090326].
- In another patent carbonized coffee grounds were prepared for use in electrolyte cells or battery [SONY- JP20000327316, 20001128; JP2000268823, 20000929].

3.8 Pyrolysis

- Pyrolysis of coffee waste (grounds) was investigated and compared with other solid residues (brewer spent grains, fibre board). The composition of the product – gas, liquid, and char – are dependent on temperature and heating rate. Higher temperatures yields larger amounts of gasses (CO_2, CO, CH_4, H_2, C_2H_2, C_2H_6, C_2H_4) and less liquid pyrolysis oil [Becidan et al., 2007]. The elemental composition for SCG was reported to be C 51.3, H 6.8, N 3.0, and S 0.2, O 38.7, wt % (dry ash free basis) with a gross calorific value of 19.82 MJ/kg. By fast pyrolysis high degree of conversion can be obtained into volatiles and gasses (88%), which is not affected by the presence of steam [Mašek et al., 2008].

- Pelletized coffee hulls were investigated for pyrolysis at different temperatures using microwave and electrical heating. The quantity of product yields for gas, solids (char) and liquid (oil) were similar with both methods. However, the composition of gasses released were different for both methods. In microwave heating microplasma inducing self-gasification of the char was observed. The amounts of H_2 and CO gas (syngas) released were significantly higher in microwave heating with lower CO_2 and CH_4. [Menéndez et al., 2007].
- By mixing of coffee particles with pyroligneous particles a smoking agent was prepared with coffee aroma and anti-microbial effects [K.K. Maho, JP2000004776, 20000111]

3.9 Composite molded material

Except for a number of older patents [Ligo 1970; Chow 1975] not much research has been published on the use of coffee grounds in composite materials recently. Waste coffee grounds were claimed to act as a filler in thermosetting materials and as a component in reconstituted board products from plant fibre residues. Structural building materials or articles can be manufactured that are combined with polyolefin materials as glue (resin) or matrix (plastic) [Zeisler 1995].

- For the manufacturing of biocomposites and particle boards substitutes for phenolic resin have been investigated. Tannins and polyphenolic residues from agro-industrial production have been evaluated as resins. Coffee husks were tested for the production of particle boards using tannin derived resins [Bisanda, et al., 2003].
- Coffee residue was incorporated by compounding in (synthetic) polymers to produced moulded parts. The heat insulating properties of the material was claimed as well as putrefactive properties and insect damage control, malodour masking agent [Unie Kafue KK, Daicel Huels Ltd, JP5277460, 1993].
- Coffee grounds were incorporated in the core material of a reconstituted board material with plant fibres [Chow Poo, US3927235, 19751216].
- Coffee hulls were used in composite particle boards without the addition of a resin and hot pressing at high temperatures ([US3686384, 19720822].
- Combined with shredded tires the coffee grounds were incorporated in a laminated structure for the manufacturing of a building material composed of recycled materials suitable as insulating panels with a claim for positive effects on indoor climate [WO200216126, 20020228].

3.10 Food applications

3.10.1 Emulsions

Coffee extract was included in a heat stable emulsion with other lipids [Nippon Fats and Oils Co Ltd , JP8080165, 19960236]

3.10.2 Dietary fibre

- Alkaline extraction of coffee grounds has been claimed for the production of soluble dietary fibre (xylan) by means of xylanase degradation [K. Seibutsu, JP3015364, 19910123]
- Method for preparation of mannitol and manno-oligosaccharide alcohols from SCG, by acid hydrolysis, neutralizing and followed by a chemical reduction step of the syrup to alcohol [D.H. Stahl, et al., Gen Foods Corp, EP157043].

3.10.3 Anti-oxidant (food preservative)

- A food preservative was prepared from coffee extract, that was claimed to have anti-microbial and anti-oxidative properties [Dongseo Food Comp Ltd, KR950008466, 19950731].
- Plant sterols (including coffee sterols) as aqueous dispersion in food products (spreads) to provide structure minimizing the use of fats. [Lipton/ Unilever, CA2245467, 19990222].
- The anti-oxidant complex composition extracted from SCG oils containing 5-hydroxytryptamides (5HT, behenic, arachidic, lignoceric acids), phospholipids and glycolipids was claimed [NESTEC, EP0693547, 19960124].

3.10.4 Beverages and energy drinks

- Chlorogenic acid from coffee is described as ingredient for health products and energy drinks [DE102008021586][JP2009165498] having hypotensive effects.
- Nestec has claimed a microorganism or enzyme capable of hydrolysing CGA [WO2009132887], to improve the antioxidant and anti-inflamatory properties of coffee beverage. Caffeic acid and/ or ferulic acids are formed.
- CGA and caffeic acid extraction methods from coffee beans is described in several patents [JP2009297041, CN101602668, WO2009107328, CN101503356].
- The CGA and derivatives (decarboxylated CGA) present in beverages of food products is claimed to have anti-oxidant or anti-inflamatory properties [WO2009132889, 20091105].

3.10.5 Functional Food

A method for preparation of polysaccharides e.g. galactomannans and arabinogalactans extracted from roasted coffee was patented [EP1985635, 20070214] for use as thickener and stabilizer in food products, cosmetic and medical supply

3.10.6 Aroma

- The extraction from roasted coffee of coffee oil by scCO_2 yielding coffee aromas and anti-oxidants [ES2160490, 20011101]

- Solvent extracted defatted coffee grounds are used as absorbent for bad flavour notes [Proctor and Gamble – CA2084572, 19930619] and added to improve the flavour of brewed coffee.

3.10.7 Taste enhancer or modifier

Quinic acid extracted from coffee or tea was applied as taste enhancer for hot (spicy) food [JP200520455, 20050804]. Also as sweetness improving agent and taste masking agent quinic acid from coffee extract was claimed [JP9094080, 19970408; JP2001132115, 20011120]. Taste modifiers based on quinic acid and cinnamic acid were claimed for food products to which chlorogenic acids were claimed to mask bitter taste [WO02100192, 20021219]. Coffee hydrolysate containing quinic acid was claimed as vitaminic odour retarder [JP2001316295, 20021113]. Methods to extract quinic acid from coffee grounds, hydrolysed with alkali or calcium hydroxide was described [JP7008169; 19950113; JP7018256, 19950120].

3.11 Medical, pharmaceutical and cosmetic applications

- Coffee residue was claimed in a drug formulation with beans and Glycyrrhizae radix as medicine against AIDS [S Watari, JP63208533,19880830]
- For treatment of androgenetic alopecia a recipe containing CGA was patented (hair growing formulation) [CN101530407]
- Coffee derived diterpenes cafestol and kahweol have been claimed to possess anticancer properties [KR20060001162] and to be effective in inhibiting angiogenesis [KR20060001161], anti-inflamatory [KR20050107876].
- Treatment and strengthening of the skin (cellulites and selected slimming ('love handles') was claimed to be effected by use of coffee derived diterpenes cafestol and kahweol as cosmetic active ingredients [Sederma, WO2004103334, 20041202, FR2855057, 20041126]. Cafestol was claimed to enhance the lipid synthesis in the skin [EL Management Corp, ZA0908235, 19980303] to prevent dry skin.
- The production of cafestol from kahweol in coffee oil has been claimed by Nestec [GB870145, 19870225] by a chemical hydrogenation step and / or anhydrous methanol esterification. The removal of diterpenes from coffee oil by aqueous isopropanol extraction was claimed [Nestec, GB8417475, 19840815].
- Quinic acid extracted from coffee or tea has been claimed as a cool feeling-reinforcing agent [JP2006104070, 20060420]. Quinic acid preparations have been claimed as medicine for skin treatments [JP4169526, 19920617]

3.12 Uses of chaff (silverskin)

The chaff that is liberated during the roasting or torrefaction process is originating from the green coffee seed cover (= spermoderm or perisperm) found as the thin green testa that is surrounding the endosperm). The chaff imparts a bitter flavour to coffee [M.A. Spiller 1998] and contributes to oil release from the ground bean. When the skin is damaged in the fresh bean this is associated with early staling and quality loss.

- Not much information of the practical commercial use of chaff can be found in the open literature. It has only been referred to as component or assistant material for compost processing [Takata & Sasakura, 2005; Yepsen, 2007] and incorporation in composite materials as short fibres or filler [Ajayi, 2005; Barone 2009]. Antioxidant extracted from green coffee beans or coffee residues (including silver skins) was claimed in a patent to contain N-β-alkanoyl-5-hydroxytryptamine (C-5-HT) as the active ingredient [Okada & Hirazawa 1996].
- The use of coffee silver skin (chaff) was evaluated as dietary fibre [Borrelli et al., 2004]. It has total 60% dietary fibre content with 14% soluble dietary fibre and substantial amounts of melanoidins. Combined with the anti-oxidative activity (small amount of free phenols) and potential prebiotic activity of chaff it was concluded that it has potential as food additive.
- Solid state fermentation of coffee residues (including chaff) as sole carbon source using a fungal strain of *Neurospora crassa* for the synthesis of α-amylase showed coffee pulp and mixed residues to be excellent carbon source [Murthy et al., 2009].

3.13 Other uses

- Media attention was recently drawn for special textiles made out of coffee [Shuo Ting Hung et al., US Patent 2009 0100655]. The patent includes a method for production of yarns with coffee residue incorporated. This patent describes the incorporation of spent coffee residues or carbonized coffee particles in thermoplastic polymers (PP, nylon, PET) (masterbatch 1:9 weight) for yarn production and to impart odour control in fabrics made from it.
- Some discussion forums on ecological friendly printing with coffee residues are found on the web as stated by the Korean designer Joen Hwan Ju. No evidence for patents or commercial approach exploring the use of coffee residues in inks was found.
- Antifoaming agent extracted from chaff [USpat 3,142572 (1964)]

3.14 Summary

The wide variety of smart options for disposal of biomass waste can be derived from the review given here. Some of those investigated uses like animal feed does not seem feasible without costly detoxification or bring restricted value addition as a soil conditioner compost or cheap filler material in building. Other methods of use have been developed and commercialized or may have promise for commercial development such as biotechnological conversion by fermentation and “green energy” purpose, production of activated carbon and composites. The recently marketed coffee fibre textile yarns in odor control fabrics, may be a high-end market for coffee waste of the future.

In food and medical applications many interesting patents can be indentified for coffee consituents that may be more or less easy isolated from currently discarded waste. Further detail investigation is required of their techno-economic feasibility and to what extend these already have found commercial implementation.

4 Green chemicals production – fragrance, flavour (and fortune?)

4.1 Introduction

Biorefinery can be considered as the agro-industrial digestion tract of the complex biomass that has to be converted effectively to energy and carbon building blocks. A sequence of conversion and extraction steps results in the production of value added products. Cascade extractions of proteins, lipids or sugars can be performed when it yields marketable products. Detailed knowledge of chemistry, physics and biochemistry of these type of digestion processes is available but until recently only scarcely applied in the industrial production of biobased or 'green' chemicals [Boeriu et al., 2005]. Basically biorefinery is thus the metabolic processes of biomass conversion into energy and building blocks on an industrial scale. In this chapter are described the various classes of components present in coffee residues other than caffeine, bearing in mind the properties and potential use and their reported physiological effects. In appendix I additional chemical background for the various components have been included.

4.2 Proteins

The suitability of the proteins in SCG as industrial protein and functional ingredient in food and feed production (emulsifier, gelling properties, nutritional value) is considered poor due to its thermal history and contents of phenolics and melanoidins.

4.3 Phenolic acids and polyphenols

The use of the abundantly present polyphenols in coffee residues has been discussed [Labat et al., 2000]. The use was reviewed of the major phenolic constituents in coffee residues, e.g. cholorogenic acid, caffeic acid and tannin. The contents of these compounds is dependent on coffee species and maturity of the seeds. The biological activities of those compounds have been reported in the medical literature. These compounds are reported to possess a wide range of (contradictory) physiological effects ranging from antitumor and immuno-stimulant/ suppressant activity to antioxidant and analgesic, biocide and carcinogenic properties. The potential use of these bioactive compounds as food additive, cosmetic ingredient or in human health needs further exploration (see appendix I).

4.4 Polysaccharides and monosaccharides

Mannan or galactomannan from plant sources (e.g. guar gum, locust bean gum, konjac gum) are widely used in food industries as hydrocolloid thickeners and are advertised as dietary supplement or dietary fibre. Dietary fibres are for humans non-digestible plant cell wall components. Many references are available for mannose oligomers that have been explored for use as dietary fibre.

The insoluble carbohydrate rich fraction of coffee ground residue is largely composed of β-mannans. Also the undesired insoluble sediments in coffee extracts are composed of (galacto)mannans [Delgado et al 2008].

The digestibility of mannans or mannooligosaccharides from coffee is poor. In the large intestine these are reported to be converted to short chain fatty acids [Asano et al 2003]. Fat accumulation in mice fed with addition of small amounts (1%) of mannooligo's was substantially lower [Takao et al 2006]
The wet process of coffee processing (see appendix B, process A) results in lower free monosaccharide contents in the green beans than the dry process B. Monosaccharides derived from free sugars or hydrolysis of the polysaccharides present in the green and roasted coffee beans may be converted into value added products by fermentation (ethanol, lactic acid, etc.) or by chemical conversion.
Many different procedures to produce oxidized (organic acids) and reduced (alditols) and conjugates from sugars are described [Galbis and García-Martin, 2008] and new renewable polymers based on sugar monomers has been reported.

Fragmented carbohydrates and proteins during the roasting process generate much of the organic acids, flavours and polymerization products present in coffee. Browning reaction products from aldose and amino compounds form decomposition and polymerization products. Also furans are formed from the degradation of sugars during the roasting and high pressure steaming. Too high concentrations are undesirable for the coffee flavour.

4.5 Terpenes and aroma compounds

The volatile aroma compounds produced by plants often belong to the class of monoterpenes (C_{10}). The aroma of robusta coffee is affected by the presence of 2-methyl isoborneol, one of the volatile monoterpenes that can be smelled in very low concentrations (ppb). In coffee flavour numerous chemicals have been identified. These will not be considered here.

Most commonly known terpenes in coffee grounds and processing streams are the diterpenes. Diterpenes (C_{20}) present in green beans are predominantly cafestol and kahweol. Also in coffee grounds these are remaining (1-2%) or are retained in the filtering process. They were shown to have effects on cholesterol concentrations in human blood.

Other diterpenes recognized in green coffee beans are atractyligenin derivatives in free or conjugated form. The actractylosides are water soluble and found in the early extraction fractions during coffee beverage production. These are predominantly present in arabica.
Some more structures have been published of related compounds; no physiological or functional properties were found to be described.

4.6 Fatty acids

The polyunsaturated fatty acids in the coffee residue extracted oils can crosslink and form polymeric networks with hydrophobic barrier properties that are suitable as protective coating layers (compare linseed oil, varnish, coatings). Such drying oils may be interesting for copolymerization with vinyl or for the manufacturing of alkyd resins, polyamide and polyurethanes production. Good film forming properties of lipids may find use in novel paint formulations.

4.7 Sterols

Sterol composition is different between coffee varieties. Such compounds (phytosterols) have potential biomedical, pharmaceutical, hygienic or toxic effects when right or wrongly applied. Searching in the patent literature on camposterol alone over 200 patents are found in cosmetics (dermopharmceutical moisturing composition), nutraceutic preparations (anti-obesitas), immuno-modulating, herbicide. Searches on stigmasterol results in more than 300 patents with applications such as water soluble bioactive lipohillic compounds.

4.8 Flavanols

Catechin (almost 1500 patents) is widely applied as food supplement (beverage), blood glucose content control, anti-viral compositions, mosquito repellents, antibacterial formulations, but also as anti-oxidant in rubber (tires), inhibitor of furan formation (food heating and baking). It is present in the coffee pericarp and pulp and hulls, but not in coffee beverage [Arts et al., 2000].

4.9 Hydroxytryptamides

In coffee bean wax components are present that are associated with occurring stomach problems in coffee consumers. Patents have been filed for the conversion of these residues isolated from coffee wax to serotonin [Neunhoeffer et al., 1973]. Serotonin or 5-hydroxytryptamine is a well known biochemical responsible for neurotransmission in the brain and applied as anti-depressive.

4.10 Summary

In coffee residues numerous components have been identified with interesting properties as ‘green chemicals’ for technical use as antioxidant, or as functional food additive and for the bioactive components in biomedical use. The economic feasibility is dependent on the ease of extraction and the purity (quality) of the ‘green chemical’ as well as the available quantities in relation to the market demand. The most promising route appears to be a combined extraction from SCG of lipids, including the bioactive unsaponifyable fraction, followed by carbohydrate fraction purification. The wax that is found concentrated in the chaff fraction may be of interest for biomedical application development. In the next chapter these options are further elaborated.

5 Selection of feasible value addition for coffee residues

5.1 Economic extraction of compounds from coffee residues

The main products estimated to be liberated in the Dutch manufacturing industries of coffee products are listed below in Table 4. Starting from 160.000 tons of green beans this results in 95.000 tons of SCG.

The roasting process is performed at different bigger and smaller companies who are all producing chaff as a residue, in total 2.000 tons.

Table 4 Coffee residues liberated in Dutch coffee industries (data from CBS /VNKT)

	Volume /y	
Green beans	160.000 ton	Roasting 15 wt% loss (-24.000 ton)
Roasted beans	136.000 ton	Coffee brewing 30 wt% loss (-41.000 ton)
Total residue	95.000 ton	

Residue	**Volume /y**	**Current value**
SCG[a]	80.000 ton	nil
SCG[b] (including chaff)	15.000 ton dry weight (400 ton)	€2.000.000 (133 €/t)
Press water	100.000 m^3	-/- €400.000
Chaff[a]	1.500 t	-/- €120.000
Chaff[b]	65 t	-/- €6500 (100 €/t)

a liberated, dispersed
b liberated at identified coffee processing industries

Except for Sara Lee (Joure), companies do not extract the roasted beans for instant coffee or soluble coffee production for use in coffee machines. In the process of coffee extraction, SCG is liberated and accumulate on site of production in substantial quantities. However, the majority of SCG (almost 80.000 t/y) is dispersedly available in catering and household waste and does not have any economic value. Recollection of this residue is not performed at this moment. The current value of SCG is calculated as the energy value for fuel in steam boilers and is 6 €/GJ. From the literature review in the previous chapters it can be derived that SCG is composed of hydrophobic lipids and terpenes (16 %), polymeric insoluble polysaccharides (33 %), proteins (10 %) and melanoidins (38 %).
In the current process at Sara Lee besides the SCG also press water is released with a high content of organics (BOD), requiring costly waste water treatment.

5.2 Lipids, terpenes and sterols

Extraction of the lipid fraction from 15.000 t SCG would reduce the calculated energy value with ca 10% from 22.3 GJ/ton to ca 20 GJ/ton (dry basis). Total energy yield loss per ton SCG when 15% weight loss from extracted lipids leaves 17 GJ of the original 22.3 GJ per ton SCG. The energy value loss can be estimated at ca <u>500.000 € /y</u> when all lipids are extracted from the SCG and a value of 6€/GJ can be counted.

When all the lipids from the SCG fraction could be extracted a volume of 2250 ton/y oil would be isolated. The world food oil prices are currently high at ca 750-775 $/ton. As a food grade oil the value of the extracted fraction equals 1.250.000 €. However, the composition of the oil fraction contained in SCG does not allow use for food or feed. Value addition can be derived from further refining of the fraction.
The unsaponifiable fraction (270 ton/y) in coffee oils contains highly bioactive components such as the diterpenes (cafestol and kahweol) and phytosterols. Cafestol and kahweol preparations are marketed by pharmaceutical industries (anti-carcinogenic) in skin care applications at high prices (>> 10€/kg). When 150 t of diterpenes can be isolated and purified the estimated value is more than 1.500.000 €.
Also the phytosterols find application in food industries as additive in functional foods in beverages, dairy products, margarines, fruit juices (Unilever, Cargill, Coca Cola). The cholesterol lowering effects of sterols have given a boost to the market: US sterol market is estimated at $75 million, compared to $600 million in Europe and $130 million in Japan [Functional Foods Magazine, April 2006]). The current market price estimation for sterols (soy bean sterols/ tall oil sterols) is ca 13 €/kg. A conservative estimation of 100 t/y yield for phytosterols from this fraction could value 1.300.000 €.
The value of the triglyceride fraction (85% of the lipids, 1900 t/y) can be estimated as for vegetable oil prices applicable for biodiesel production at 500 €/t. The conversion to biodiesel requires a trans-esterification step to methylesters. The presence of free fatty acids may complicate the conversion efficiency. The high content of long chain unsaturated fatty acids and especially EPA in this fraction may affect its preferred use. In the conversion of triglycerides to fatty acid methyl esters (FAME) ca 10% of the biomass is liberated as glycerine (35 €/t). The remaining biodiesel product yields provide 900 €/m^3.

Table 5 Possibilities residue valorisation lipids, terpenes and sterols

Possibilities residue valorisation	Volume	Value
Extraction lipid fraction of 15.000 ton SCG	2250 ton	-/-500.000 €
Lipids food grade	2250 ton	1.250.000 €
Diterpenes for pharma	150 ton	1.500.000 €
Phytosterols for food	100 ton	1.300.000 €
Biodiesel from triglycerides	1900 ton	950.000 €
Conversion of triglycerides to FAME	190 ton	6650 €
remaining biodiesel product	1700 ton	1.360.000 €

5.3 Carbohydrates for dietary fibres and bioplastics

The lipid-extracted SCG has a remaining heating value of ca 20 MJ/kg. The defatted SCG fraction still has an estimated energy content value (6€/GJ) of ca 1.500.000 €.
Over one third of the SCG dry weight are insoluble polymeric carbohydrates, largely (70%) polysaccharides of the mannan type and some cellulose (10-15%) that are resistant to heat treatment and remain unaffected during roasting. Selective extraction of mannan from the

defatted SCG would yield ca 5000 t mannan. This reduces the energy value of the remaining fraction with (5100t x 18 GJ/t x 6 €/GJ =) 550.000 €.

Table 6 Carbohydrates from SCG

	Volume	Value
Lipid-extracted SCG (85% of 15.000 ton)	12.750 ton	1.500.000 €
Extracted Mannan (40% of 12.750 ton)	5000 ton	-/- 550.000€
Mannan to bioplastics		3.570.000€[1]
Mannan to dietary fibre		7.140.000€[2]
Mannan to mannitol		3.570.000€[3]
Melanoidins	7650 ton	-/- 950.000€

5.3.1 Bioplastics

Mannans can be converted to different value added use, depending on its structural features (DP, substitution) and physical properties. Polymeric mannans are commonly used as texturizing additives in food and pharmaceutical products. Besides hydrocolloids (gels, thickener) in foods some literature on film formation and barrier properties can be found. Polymeric (gluco- or galacto-)mannan may cost up to 25 €/kg (Konjac glucomannan retail bulk price). However, the functional properties of SCG derived mannan are not explored in detail and its low branching and poor dissolution behaviour are of interest for biomaterials development.
Methods to isolate mannan in polymeric form from SCG have not been published. The similarity of linear polymeric mannan properties with purified α-cellulose (dissolving pulp) and the available novel technical knowledge of cellulose dissolution (e.g. ionic liquids) and chemical behaviour can be explored in a R&D project. Its utilization as polymer for bioplastic production has not been addressed, largely because of the lack of suitable sources of linear mannan. The properties of mannan derivatives (e.g. ester and ethers) will be very comparable with highly valued cellulose derived plastics that are applied in many products from membranes, textiles yarns, cigarette filters to computer screens. Current market price for bioplastics such as polylactic acid (2 €/kg) and cellulose diacetate (3€/kg) are still relatively high as compared to petrochemical plastics. In special niche (packaging) markets these products are more and more adopted.

[1] *For comparison the (bulk) market value of dissolving cellulose pulp (1000-1300 $/ton [2007]), which is the raw material for CDA production is estimated at 750-1000 €/ton. A value addition of this fraction can be estimated when mannan could be used for similar purpose bioplastic production at 1€/kg or in total calculated as 12.750 t x 0.40 x 0.70 x 1€/kg = 3.570.000 €.*

[2] *12.750 t x 0.40 x 0.70 x 2€/kg = 7.140.000 €.*

[3] *Calculating the added value of the mannan fraction in SCG (as 40wt % of 70% mannan) and converted to mannitol: 12.750 t x 0.40 x 0.70 x 1€/kg = 3.570.000 €.*

5.3.2 Dietary fibre and food additives

Depolymerisation and dissolution of the mannans can be achieved with hydrolytic enzymes or controlled (acidic) catalysed depolymerisation. Oligomers and monomers that easily dissolve in water are obtained. Dissolved and extracted mannose oligomers find applications in functional food as dietary fibre. Manno-oligosaccharides (MOS now often derived from hydrolysed yeasts) is frequently used in health products and dietary fibres and animal feed. The market prices of dietary fibre are varying much, depending on the purity, and functional properties but also in volumes. Raw bulk fibre used in animal feed formulations is sold at only 100-120 €/t. On the other hand pure insoluble dietary fibre may have a price of 2000€/t, while soluble fibre even could give 2500-3000 €/t.

Depolymerized and hydrogenated mannan yields mannitol, a low calorific sweetener widely used in pharmaceutical industries and items like chewing gums and other sugar free products. Mannitol was found to be marketed at prices up to 10 €/kg, which is extremely high. Sorbitol, a similar product, is considered competitive at 1100 €/t.

5.3.3 Browing products (melanoidins)

The 60% residue of SCG after defatting and mannan extraction contains proteins and melanoidins. The biomass still represents an energy value of 950.000 €[4]. The materials will be enriched in nitrogen and phenolics. Extraction of crude proteins from this material does not seem suitable, because of the thermal deterioration and chemical cross-linking that occurs during the roasting process. Controlled hydrolysis could yield (mixed) amino acids, peptides and liberate other organic compounds such as phenolic acids (CGA) and flavours.

In literature no specific mentioning of value added utilization of this fraction has been found except for the anti-oxidant effects that have been ascribed to phenolics in SCG and its value (detoxified SCG) as feed additive. Quantification of yields of such compounds is not possible without experimental evidence of yields of extractable components or data on nutritional feed value. Bulk feed prices for oil seed press cakes and other agroresidues with high nitrogen content may yield up to 200 €/t.

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[4] *The 7650 t biomass still represents an energy value of (7650t x 21.15 GJ/t x 6 €/GJ =) 950.000 €*

5.4 Business case biorefinery scheme

From the above the following biorefinery scheme can be derived. This scheme does not yet include the investment costs for the extraction/ purification and conversion processing steps to biodiesel, bioplastics and other marketable products.

	SCG				
	↓				
solvent	extraction	→	lipids	separation	
	↓			purification	→
	defatted SCG			esterification	→ biodiesel
	↓				
solvent	extraction	→	mannan	purification	
	↓			derivatisation	→ bioplastic
	residue				
	melanoidin	→	phenolics		
	protein	→	amino acids		

Product	volume	energy value	market value
SCG	15.000 t	2.000.000 €	
Lipids extraction	2250 t	500.000 €	4.166.000 €
Mannan extraction	5100 t	550.000 €	3.570.000 €
Melanoidin/protein	7650 t	950.000 €	1.530.000 €
total			9.266.000 €

From the dissolving cellulose price (1€/kg) in relation to the CDA price (3€/kg) an impression can be obtained from the cost involved in the conversion process. On the other hand the scale of production is of strong influence on the market penetration. Competing on the bulk market for commodity plastics is difficult due to the high pricing of bioplastics and the market adoption is successful only for selected niche markets.

5.5 Logistics of coffee grounds

In the above paragraph the technical options for valorisation have been described and as much as possible related to the value of existing comparable market products. The concentrated availability of SCG at the site of industrial coffee extraction makes the options for valorisation better feasible. The majority of the SCG is however dispersedly available in catering and as fraction of household waste. Recollection of the coffee drags from the catering sector (hotels, restaurants, canteens, offices, hospitals, etc) could be organized when sufficient added value can be generated. In The Netherlands 30% of the coffee is consumed not at home [VNKT jaarverslag 2008].

The coffee sector as one of the most ecologically conscious and social responsible industries may be ready to adopt a responsibility for the residue recovery and value addition.

5.6 Chaff

Chaff can be collected from the various coffee roasting companies as waste residue. It is estimated that 2000 t per year is liberated in total in the Dutch coffee industries. Currently this is compressed and further disposed of as fuel or compost at a negative value for the industry of ca 100 €/ton. Apart from the presence of some fibre and bioactive components (lipids, anti-oxidants) especially the wax content is of interest. The content of 400-500 μg/g of alkylated 5-hydroxytryptamides that may be converted to serotonin, which is a well known neurotransmitter in the brain and applied as anti-depressivum. Purified serotonin HCl is marketed at 55 €/g
At a 50% conversion efficiency or 0.2 kg/ton of serotonin yield this could be a very profitable value addition of 16.500.000 €[5].

5.7 Aroma

The extraction and recycling of coffee aroma components has not been addressed in this study largely because of lack of suitable data on real composition of available fractions and the vast amount literature on the core business of coffee beverage production dealing with its taste and aroma, which was considered besides the scope of this study.

[5] *1500t x 0.2 kg/t x 55.000 €/kg = 16.500.000 €!*

6 Enquiry coffee manufacturers

6.1 Questionnaire

- Which of the coffee manufacturing processes (A, B, C, D or E) are performed by your company
    - Input raw material
        - Green beans, varieties, quantity, quality control, process A or B
        - Roasted beans
        - Ground coffee
    - Out put products
        - Roasted beans
        - Ground coffee
        - Coffee blends
        - Coffee extracts (instant)
        - Coffee flavours
        - Other coffee products

- What are the residues liberated in the process of conversion of green beans to beverage
- How much of these residues per annum (as dry and wet weight in tons per annum)
- Where are these liberated in the process
- What is known of its composition
- What is the current method of use (steam generators) or disposal
- What is the economic value / costs?

Industrial coffee grounds

Coffee roasting companies

Coffee extraction

Coffee grounds liberated in Retail (Hotels, Restaurants and Café's)

Consumers (home brewing) logistically difficult to recollect the

How a logistic process for collection of SCG can be organized.

The paragraphs describing the interviews with the different companies have not been included in this document for confidentiality reasons….

7 Conclusions and recommendations

The coffee sector as one of the most ecologically conscious and social responsible industries may be ready to adopt a responsibility for the residue recovery and value addition. In the production chain of coffee most of the biomass residues are produced in the coffee cultivating countries, where limited value addition is obtained in mulching or boiler fuel use.

In the consuming countries the main residues liberated in the coffee production are spent coffee grounds (SCG) and chaff. The majority of these biomass residues are released dispersedly at the site of consumption. Hoewever, the industrial coffee roasting process is liberating the chaff as substantial residue. In the Netherlands it can be estimated that in total maximum 2000 tons per year can be collected for value addition. Currently this is disposed of at the cost of ca 100 € per ton and used as fuel for co-firing in the electricity production.

Most of the discarded biomass from coffee consumption is liberated as the spent coffee grounds (SCG) in households and catering. In more concentrated form SCG is available in the coffee brewing industry (15.000 tons per year in The Netherlands), where it is partly used as fuel for the steam boilers and the excess (ca 50%) is sold for use as fuel for co-firing in electricity production. In this process the waste water that is liberated has a high costs for cleaning as it contains substantial amounts of organic components (e.g. lipids, amino acids, organic acids, etc).

In this study the current knowledge of the coffee residues composition and the current state of the art of coffee residue utilisation is described. Many of the uses that are described in the open literature and patents are low value compost, mulching or fermentation feedstock. Other patents are seeking value addition of residues for the energy content (briquettes, biodiesel) and manufacturing of activated carbon. Many patents for higher value added use are addressing food additives, medical and pharmaceutical or cosmetic uses of selected fractions. From the open literature records it cannot be concluded which applications actually have been implemented successfully. Further investigation of the commercialisation potential is recommended.

Based on the literature survey and existing patents a number of options were identified for value addition taking into account the effects of the current practice of use in steam boilers.

Conservative estimations on the value addition of fractions in coffee residues were based on current market values of comparable market products. The effects of scale of operations or required investment for process design and implementation needs further elaboration in cooperation with the industries. Based on these data no estimation can be based yet for a real business plan with realistic RoI time frames.

Biorefinery and stepwise extraction of valuable components from coffee residues (SCG, chaff) needs to be investigated for its technical and economic feasibility. The cascading of lipid extraction, followed by extraction of polymeric carbohydrates (mannan) as integrated process in coffee waste recovery may prove to be profitable and reduce the environmental impact (LCA) of coffee production and thus enhance the sustainability of the coffee consumption.

Extraction and value addition of lipid fractions remaining in the SCG after brewing process may yield economic value as pharmaceutical preparation and/or biodiesel feedstock. The waste water from coffee brewing industries is currently disposed off at high costs. Its lipid content and possibly other relevant organic constituents may provide value for water precleaning and economic recovery of 'green chemicals' from this fraction.

The perspective of value addition of fractionated coffee residues seems worth while for further exploration. Especially the lipids fraction may find value in the non-sponifyable fraction, e.g. diterpenes and saponins. These bioactive compounds may find high value by use in pharmaceutical and cosmetic products. The triglyceride fraction composition contains valuable long chain omega fatty acids, known for their promoted use in health foods.

The remaining deoiled SCG fraction is composed of the polymeric carbohydrate fraction (mannans) that when isolated may find applications as dietary fibre or mannitol in health food industries.

Unexplored yet is the use of polymeric linear mannans in bioplastics production. Its intrinsic properties known from other sources invites for investigation of this option to convert this residue into disposable bioplastics, that can be thermoformed and is heat stable. Disposable coffee cups based on coffee residues would make a strong marketing. Another use of this component may be found as bioplastic or coating in packaging films.

The most complicated fraction in SCG is the melanoidin residue, which except for anti-oxidant properties has not been explored in detail for other value addition than its energy value.

The use of coffee chaff should be explored for its content of waxy material containing potential high value precursors for serotonin manufacturing, which is well known for its importance as neurotransmitter in medical literature.

Many other components may be liberated from this biorefinery process for 'green chemicals' production like anti-oxidants, surfactants, dietary fibre or food additives. Further investigation of the different fractions and the feasibility of their potential uses is recommended.

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Appendix A: Coffee production chain

Approximately eight million tons of raw coffee beans are grown and harvested annually throughout the tropics. The best quality coffees are obtained from tropical highlands where Arabica coffee varieties grow best, yielding better quality and higher price. The berries or cherries are harvested from the shrubs of mainly *Coffea arabica* and *C. canephora* (resp known as Arabica and Robusta) and some minor species (*C. excelsa* / *C. liberica*).

Coffee is grown throughout the tropics. The best quality crops of Arabica are harvested at farms with shade grown shrubs in the mountainous highlands (e.g. Colombia, Ethiopia, Mexico). Brazil is by far the largest producer, followed at distance by Vietnam and the traditional coffee growing countries such as Colombia and Ethiopia. A list of the largest coffee producers is given in Table 7, and a complete overview of coffee producing countries in given in Table 8, including specification of coffee variety (i.e. Arabica (A) or Robusta (R)).
Small holder farmers produce ca 300 kg green beans ha/y, while most efficient modern plantations of Arabica or Robusta coffees may yield 2000 and 3500 kg green beans ha/y, respectively. Yields of up to 5t ha/yr green beans have been reported for special new cultivars [Söndahl et al., 2005].

Table 7 Largest coffee producers worldwide

Country	Production 2008 (million bags @60kg)	kt /y	% of total production
Brazil	46	2.760	36.2
Vietnam	16	960	12.6
Colombia	10	600	7.9
Ethiopia	6.1	366	4.8
Indonesia	5.8	348	4.6
India	4.6	276	3.6
Mexico	4.6	276	3.6
Peru	4.1	246	3.2
Honduras	3.8	228	2.9
Uganda	3.5	210	2.8
Guatemala	3.4	204	2.7
Total		**6.474**	**84.9**

Coffee industries are challenged to improve their social responsibility and reduce the impact on the environment. One option to enhance the value chain is to explore the use of biomass waste. Only 6% of the fresh harvested crop weight is used for the production of the beverage. The remaining 94% is water and by products that cause often environmental pollution and problems with disposal (Zuluaga 1989). This statement is made 20 years ago and is still actual. Then the question arises how much biomass is released in the production chain and is accumulated as waste or used for economic value addition? What are the properties, composition and potential uses of the residues and where are these available in the producing countries and at the site of consumers?

Starting from the red berries to grains half of the dry weight is lost, and from grains to roasted and ground beans up to final cup of coffee from the machine just a few milligrams of characteristic flavour and bitter taste and between 40 and 180 mg caffeine per cup is sufficient for suiting the daily addiction. It can be concluded that most of the crop weight is not consumed but disposed off or somewhere piling up in the environment.

Analysis of composition of fresh and roasted coffee beans [Vitztum 1976; Spiller 1990] provides long listings of practically all known types of organic constituents commonly found in plant tissues. Furthermore, coffee contains smaller or larger quantities of typical components that are exclusively found in coffee and some related species.

Table 8 TOTAL PRODUCTION OF EXPORTING COUNTRIES

(000 bags / 60 kg)		Crop year	2003	2004	2005	2006	2007	2008
WORLD PRODUCTION			103 912	115 558	110 131	127 653	117 882	127 005
Angola	(R)	Apr-Mar	38	15	25	35	36	100
Benin	(R)	Oct-Sep	0	0	0	0	0	0
Bolivia	(A)	Apr-Mar	125	165	135	157	139	135 1/
Brazil	(A/R)	Apr-Mar	28 820	39 272	32 945	42 512	36 070	**45 992**
Burundi	(A/R)	Apr-Mar	338	437	285	387	169	412 1/
Cameroon	(R/A)	Oct-Sep	900	727	849	836	795	800 1/
Central African Rep.	(R)	Oct-Sep	43	45	46	78	64	60 1/
Colombia	(A)	Oct-Sep	11 197	12 033	12 329	12 153	12 515	**10 500**
Congo, Dem. Rep. of	(R/A)	Oct-Sep	427	360	336	378	416	400 1/
Congo, Rep. of	(R)	Jul-Jun	3	3	3	3	3	3 1/
Costa Rica	(A)	Oct-Sep	1 783	1 887	1 778	1 580	1 791	1 594 1/
Cote d'Ivoire	(R)	Oct-Sep	2 689	2 301	1 962	2 847	2 150	2 500 1/
Cuba	(A)	Jul-Jun	224	154	125	100	70	133 1/
Dominican Republic	(A)	Jul-Jun	351	491	310	387	465	500 1/
Ecuador	(A/R)	Apr-Mar	766	938	1 120	1 167	1 110	657
El Salvador	(A)	Oct-Sep	1 477	1 437	1 502	1 371	1 626	1 369
Ethiopia	(A)	Oct-Sep	3 874	4 568	4 003	4 636	4 906	**6 133**
Gabon	(R)	Oct-Sep	0	0	1	1	0	0 1/
Ghana	(R)	Oct-Sep	13	16	20	29	30	25 1/
Guatemala	(A/R)	Oct-Sep	3 610	3 703	3 676	3 950	4 100	**3 370** 1/
Guinea	(R)	Oct-Sep	366	316	525	473	415	335 1/
Haiti	(A)	Jul-Jun	374	365	356	362	359	350 1/
Honduras	(A)	Oct-Sep	2 968	2 575	3 204	3 461	3 842	**3 833**
India	(A/R)	Oct-Sep	4 508	4 592	4 396	5 079	4 148	**4 610**
Indonesia	(R/A)	Apr-Mar	6 404	7 536	9 159	7 483	7 751	**5 833** 1/
Jamaica	(A)	Oct-Sep	37	21	34	41	20	40 1/
Kenya	(A)	Oct-Sep	673	736	660	826	652	950 1/
Madagascar	(R/A)	Apr-Mar	435	522	599	587	604	600 1/
Malawi	(A)	Apr-Mar	48	21	24	17	19	25 1/
Mexico	(A)	Oct-Sep	4 201	3 867	4 225	4 200	4 150	**4 650** 1/
Nicaragua	(A)	Oct-Sep	1 547	1 130	1 718	1 300	1 700	1 600 1/
Nigeria	(R)	Oct-Sep	46	45	69	51	42	50 1/
Panama	(A)	Oct-Sep	172	90	176	173	166	160 1/
Papua New Guinea	(A/R)	Apr-Mar	1 155	998	1 268	807	968	850 1/
Paraguay	(A)	Apr-Mar	52	26	45	20	29	25 1/
Peru	(A)	Apr-Mar	2 616	3 355	2 419	4 249	2 953	**4 102** 2/
Philippines	(R/A)	Jul-Jun	293	252	309	298	431	700 1/
Rwanda	(A)	Apr-Mar	266	450	300	254	252	367 1/
Sierra Leone	(R)	Oct-Sep	36	15	60	31	39	20 2/
Sri Lanka	(R/A)	Oct-Sep	37	32	35	33	32	35 2/
Tanzania	(A/R)	Jul-Jun	612	763	804	822	810	917
Thailand	(R)	Oct-Sep	827	884	999	766	653	825 1/
Togo	(R)	Oct-Sep	144	166	140	134	125	130 1/
Trinidad and Tobago	(R)	Oct-Sep	16	15	15	12	0	15 2/
Uganda	(R/A)	Oct-Sep	2 599	2 593	2 159	2 700	3 250	**3 500** 1/
Venezuela	(A)	Oct-Sep	780	629	760	813	897	880 1/
Vietnam	(R)	Oct-Sep	15 231	14 174	13 542	19 340	16 467	**16 000**
Zambia	(A)	Jul-Jun	100	110	103	56	61	70 1/
Zimbabwe	(A)	Apr-Mar	92	120	66	45	29	50 1/
Other producing countries	3/		603	608	513	616	563	801

1/ Estimate to be confirmed by the Member unless otherwise indicated 2/ Estimated 3/ Equatorial Guinea, Guyana, Lao (PDR of), Liberia, Timor-Leste and Yemen

http://www.ico.org/prices/po.htm

Appendix B: Coffee processing chain

Introduction

Most of the biomass is released at the beginning of the chain. In the literature no specific mentioning is found of the management of crop residues at the farm level, except burning of pruning/ trimming residues and return of carbon/ nutrients to the soil by mulching of hulls.

Six tons of fresh berries is yielding 1 ton of green beans and 1,25 t dry pulp and parchment. The pulp and parchment that is liberated at the processing facilities is commonly not returned to the field. Parchment may be used as fuel for boilers in the wet process for curing. The average composition of fresh dried coffee beans is given in Table 9.

Table 9 Composition of fresh dried coffee bean (endosperm) [Van der Vossen & Wessel 2000]

Component	wt%
Water	10-13
Proteins and free amino acids	11-16
Lipids	12-14
Sucrose and reducing sugars	34-48
Cellulose and other polysaccharides	32-48
Chlorogenic and other acids	10-15
ash and minerals	4
Caffeine	0.6-1.7% (Arabica) 1.5-3.3% (Robusta)

Literature is providing many reports with details on the structures and long lists of compounds that were chemically analyzed and structurally identified to be present in fresh or roasted coffees [M.A. Spiller 1998b]. Many of those are found only in very small amounts (expressed in ppm or bpm; or μg/kg and ng/kg) specifically in fresh or just in different grades of roasted beans.

It is of interest to know which compounds of potential economic value can be identified in this complex mixture to explore economically. Therefore the chain of processes of coffee manufacturing is followed from the harvest to the disposal of the coffee ground. To visualize and quantify how much of residues are available at which stage of the process, schemes are given. Five processes of coffee manufacturing are described here: the wet method, the dry method, coffee roasting, instant coffee production and decaffeination process.
In the process of green coffee bean production several steps are required to remove the surrounding fruit tissue. Two methods have been used in coffee production to obtain the proper coffee bean from the fresh berries (or cherries) , i.e. the wet and the dry method. About 40% of the world coffee is produced according to the wet process, including most of the organic coffees. These washed coffees are considered of superior quality.

Wet method (process A)

The wet method commonly starts with handpicked beans of uniform quality and cleanness that are washed/ soaked in water and directly (within 12-24 hrs) mechanically depulped by removing the outer skin and mesocarp (pulp). The more resistant mucilage layer is removed by fermentation of the depulped seeds that are submerged in large tanks. This is exposing the parchment layer (endocarp) that is mechanically removed after (sun) drying [Bicchi et al 1997; Martin et al., 1996; Suchánek et al., 1996].

Six tons of fresh berries yield 1.1 ton parchment coffee, 2.7 ton fruit pulp, and 25000 liter of waste water [Van der Vossen, 2005].

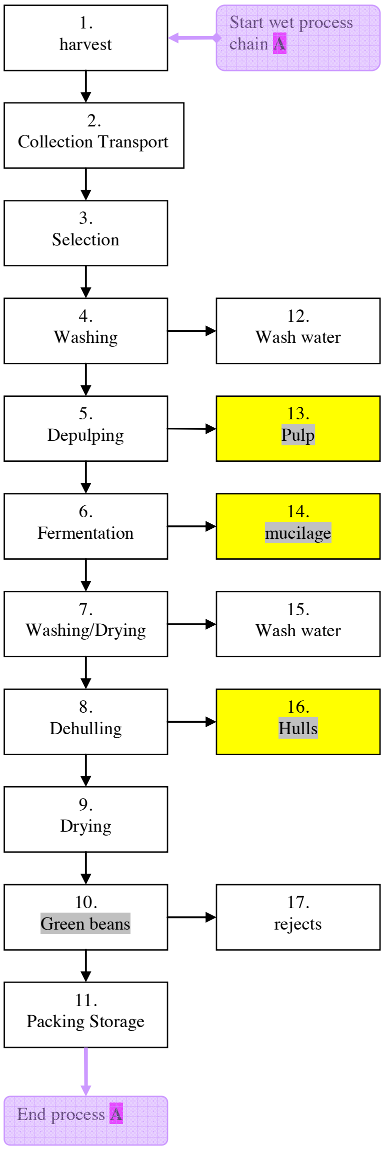

Figure 1 The wet method (process A)

Dry method (process B)

Mechanically strip harvesting is commonly applied in modern coffee production applying the dry method. All berries of different ripeness are collected at once and dried by spreading them in the sun (3-4 weeks). The skin, pulp and mucilage layers are fusing into the coffee hull. By dehulling the layers are mechanically removed from the seeds. The remaining of the silver skins that is left can be removed by moistening the beans and mechanical action (polishing). The drying is then again required before storage and shipping.

Transportation and storage of the green coffee beans is done at low moisture contents (10-12%) and preferentially low air humidity (RH 40-60%)and temperature (<21°C) to avoid molds development and quality degradation.

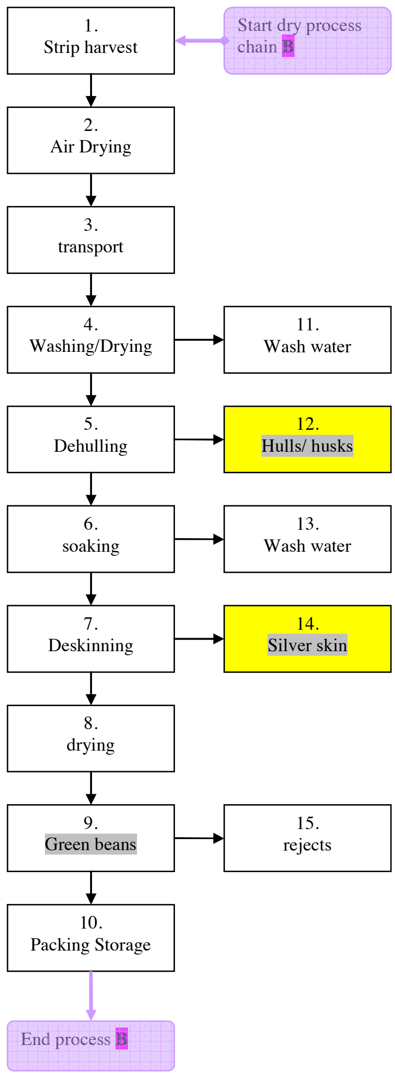

Figure 2 The dry method (process B)

Coffee roasting (process C)
Coffee roasting is performed at different temperatures and times to obtain the desired coffee flavour. Commonly the roasting is performed between 190 and 240 °C and the coffee beans are obtaining the desired shade of brown colour and taste. Other methods use temperatures up to 450 °C. The residence time in the roasting drums is also critical. Some coffee flavours (espresso) may be heated twice. The components lost from the coffee beans in this way form minor amounts of tar and soot (polycyclic and aromatic compounds).
The chaff or silver skin that is dried and liberated in the roasting process can be collected and pelletized. The chaff is sometimes (partly) returned to impart taste to the roasted beans. Recycling of effluent gasses affects the final character of the coffee roast. The roasted beans are cooled and need to be brittle for grinding. During the grinding process volatile aroma components are released.
The ground coffee is (vacuum/air tight) packed and stored. During the roasting process part of the sugars present are caramelized and the polysaccharides partly depolymerise. Many chemical conversions occur such as dehydration and Maillard reactions (browning) (see 2.2.2) liberating typical flavours.

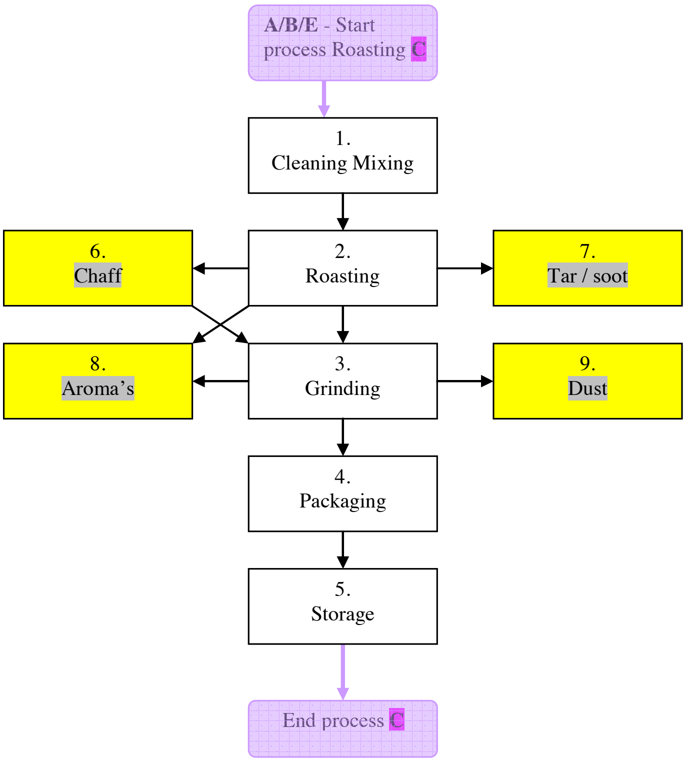

Figure 3 Coffee roasting (process C)

Instant coffee production (process D)

The production of instant coffee usually involves percolation of the roasted and ground coffee beans with pressurized water (170 °C). This dissolves the water soluble components such as carbohydrates, flavours and fragrances, and part of the depolymerised polysaccharides. In total ca 25-35% of the weight is extracted. Under normal conditions for coffee extraction with hot water (100 °C) ca 21 wt% is extracted.

The extract is subsequently dried either by spray drying or freeze drying. Some of the aroma's may get lost in the drying processes. Flavour and aroma addition (coffee oil) after the drying process is common practice.

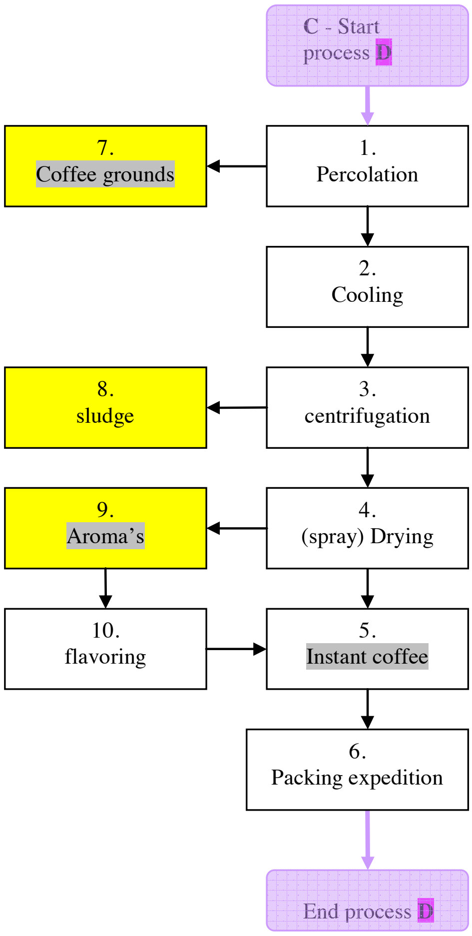

Figure 4 Instant coffee production (process D)

Decaffeination (process E)
The decaffeination process is performed on steamed green beans with aid of solvents. Mostly methylene chloride is used and sometimes other organic compounds such as ethylacetate, ethanol, methanol, acetone or supercritical CO_2. The coffee beans lose the waxy layer by solvent extraction as well as some flavours. Decaffeinated beans are more susceptible to fungal attack. All other components that are removed in this way except for caffeine are preferentially reabsorbed on the beans (saturated solvent method with selective caffeine removal). The extracted caffeine finds a high price in the manufacturing of some soft drinks.

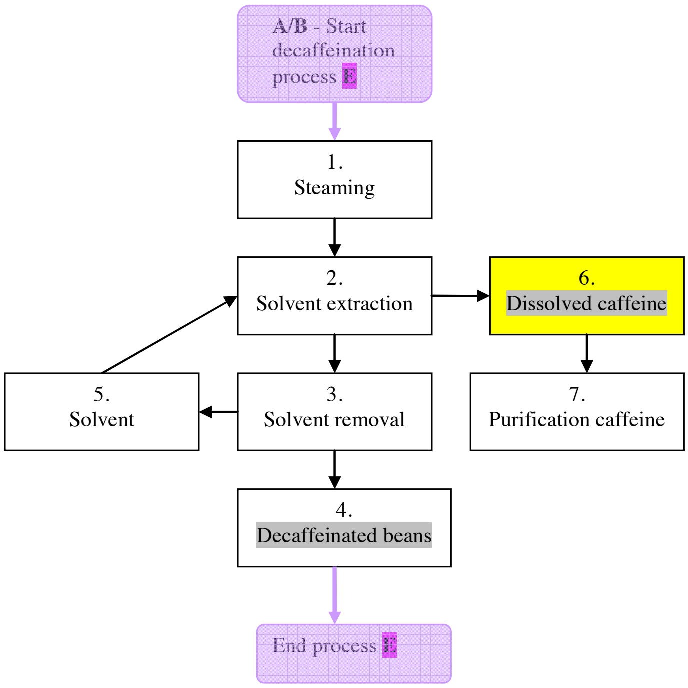

Figure 5 Decaffeination (process E)

Appendix C: Residues of coffee processing

Introduction
In the process of coffee production various residues are obtained. Biomass residues can be categorised into three main groups: primary biomass residues, available at the farm; secondary biomass residues released in the agro-food industry and tertiary biomass that remains after use of the product [Rabou et al., 2006].
The volume of primary residues such as branches, stalks, leaves, prunings, and uprooted crop is difficult to estimate and less relevant for this study. More of relevance is an estimate of the volume of secondary residues like seed hulls, pulp, and chaff that are released from the commodity processing at different stages. Differentiation is relevant between secondary residues liberated in the country of green beans production and in consuming countries at the site of roasting and retail. Quantification of available tertiary residues (i.e. spent coffee grounds SCG) is possibly more complicated and dependent on the economics of recollection.

Secondary residues
The coffee bean is the endosperm of the coffee fruit or berry that is surrounded by endocarp or hull and a mucilage layer or mesocarp enclosed by spongy cells (pulp) and the mostly red colored epicarp. The fresh coffee beans are liberated from the fruits releasing coffee pulp (29% dry weight), mucilage (5%) and coffee hulls (12%) in a sequence of wet and dry processing steps (see process A and process B) [Bressani et al 1972].
The mucilage is either mechanically removed or through fermentation. The weight percentages may differ depending on the variety of coffee. In coffee producing areas the availability of large quantities of coffee pulp has evoked research into its use. Animal feed and fertilizer were the main outlets identified, but the presence of alkaloids (caffeine) and free phenols (caffeic, chlorogenic and tannic acids) contribute to the anti-physiological effects in animals and therefore have so far resulted in little commercial interests. Hulls (or husks) are used to provide energy for drying of the beans.

Coffee pulp
The coffee pulp that is released from the wet process (process A) has been studied for its utilization as fertilizer, livestock feed or compost [Braham and R. Bressani, 1979] [EU – INCO-DC programme IC18*CT970185] [CFC /ICO projects (2007)]. Since coffee pulp contains a number of components such as caffeine and tannins (Table 10) it is toxic and gives problems with disposal.
Biotechnological methods to detoxify the coffee pulp have been reviewed [Pandey, et al., 2000]. The use of these waste streams with novel biotechnological methods has been proposed for the production of bulk chemicals and value added products such as single cell protein, ethanol, organic acids (citric acid, gibberellic acid), amino acids, secondary metabolites (aroma compounds), mushrooms and enzymes (see chapter 6.3.4).

Table 10 Composition of secondary coffee residues*

	Pulp		Mucilage		Hulls*	
Moisture		6.9			12.0	
Caffeine		0.6-1.3			1.2	
Chlorogenic acid		0.2-3.2				
Caffeic acid		0.3-2.6				
Fat/lipids		2.5	2.5		1.5-2	
Fibres	21.0				31.8	
Hemicellulose		2.3				20.3-38
Cellulose		17.7	27.6			45.9-50
Carbohydrates	59.1				26.5	
Pectins			6.5			12.4
Reducing sugars		12.4		30.0		
Non-red sugars		2.0		20.0		
Tannin		1.8-8.6	1.8-8.6			4.5
Lignin		17.5			24.4	
Lignified protein		3.0			9.2	
Crude protein		8.3-10.1			6.8	
Ash		8.3			6.0	

* lit data are giving contradictory data due to different analytical methods and different preparations (process A or B). More accurate determination seems required.

Reduction of the cellulose content and removal of the anti-nutritional factors (ANF's: phenols, tannins, caffeine) was elaborated to enhance the nutritional value of coffee pulp [Ulloa Rojas et al., 2003]. The aerobic (bacterial inoculated) degradation gave better improvement of the nutritional value than ensilage. Lactic acid bacteria were investigated to enhance the detoxifying effects of fungal enzymes on coffee pulp silage and solid state fermentation [Gaime-Perraud, 1995]. The potential use of these residues in fish feed was also evaluated [J.B. Ulloa et al., 2004] but it was concluded that due to its low nutritional value and content of ANF's more research is needed. The dissolved (reducing) sugar content in the pulp is 50% fructose, 30% glucose and some galactose and sucrose.

The polyphenols in coffee pulp were analyzed and characterized [Ramirez-Coronel et al., 2004]: Dominant in this fraction (>50%) are the flavan-3-ols (monomers and proantocyanidins; e.g. epicatechin, monomers to hexamers), with substantial amounts (40%) of hydroxycinnamic acids

(caffeoylquinic acid, and trace p-coumaroylquinic acid) with traces of flavonols, and anthocyanidins (total ca 4% wt).
Coffee pulp contains high amounts of potassium that contributes to the anti-nutritional effects in animal feeds [Campabadal, 1987].

Coffee hulls/ husks
The hulls or husks that are liberated in the wet or dry process are currently often burned for generation of processing energy. Hulls have been reported to contain lignocellulose: cellulose (50%) and hemicellulose (38%) and lignin, with some alkaloids (caffeine) and tannins. Sometimes these are returned and used as mulch in the coffee fields. The hulls derived from process A or B are different in composition and quantitative mass yield percentage. In case of the dry process the term husk is more often applied.

Hydrolysis of coffee hulls was investigated to recover the fermentable sugars [Woiciechowski et al., 2000]. The hydrolysate that is obtained after enzyme assisted, autocatalysed or controlled acid catalytic pretreatment could be applied as fermentable sugar. Optimum condition for obtaining high reducing sugar concentrations was autocatalytic hydrolysis for 10-15 min at 120 °C. By addition of acid catalysts (HCl) or reaction at higher temperatures degradation of sugars occurs and furfural and HMF are formed.

Immature and defective beans (triage)
The presence of immature green and defective beans has a negative influence on the quality of the coffee beans [Mazzafera 1999]. Immature beans are more acidic and contain less sucrose. Polyphenol oxidase activity is especially present in defective (black) beans. The relation with the content of 5-caffeoylquinic acid (5CQA) and enzyme activity was suggested. Defective beans comprise ca 20% of the beans in strip harvesting practice and need to be separated for quality coffee production. Alternative uses are therefore of interest. Coffee oil content and composition was determined and found to be similar to normal coffee beans [Franca et al., 2005; Oliveira et al., 2006]. The extracted oil can be used as food grade oil after processing. Extracts from low-grade coffee beans were examined for the antioxidant properties. The methanol extract gave highest yields of radical scavenging capacity and antioxidant activity [Ramalakshmi, et al., 2008].

Overview of residues

Type of residue	Process		Products
Primary			
		Growing	Biomass (leaves, branches, uprooted crop), mulch
		Harvest	Fruits (cherry / berry)
Secondary			
	Process A	Rinsing	waste water
		Depulping	pulp (29%)
			56-60 kg fresh or 12-15 kg dry pulp
		Fermentation	mucilage (4-5%)
		Dehulling	Grains / seeds (55%)
		Wet processing	39 kg fresh pulp = 16 kg dry pulp
			22 kg mucilage
			39 kg parche or 20 kg traded coffee +19 kg hulls
	Process B	Cleaning	defective and green immature beans (triage)
			stones, leaves, branches
		Preprocessing (sun / air drying)	100 kg fresh cherries
		Dry processing	40-45 kg dry berries
		Dehulling	hulls (husk) (12%)
			20 kg husks
	Process C	Torrefaction / Roasting	tar and soot
		(ca 15% weight loss on roasting)	silver skins /chaff
		Grinding	aroma, dust
Tertiary			
	Process D	Brewing	spent coffee grounds (SCG)

Appendix D: Lipids and oils in SCG

Fatty acids

Coffee seed oil has a low melting point (ca 8 °C), which is attributed to the content of unsaponifiable lipids present in the oil (Table 11) [Hartman et al, 1968].

The residual triglycerides in coffee grounds have been extracted and used to manufacture soap but potentially can be converted into other commercial products such as coatings or biodiesel. The composition of fatty acid methylesters mixture derived from coffee grounds is different from coffee seed oil analytical data. Especially the long chain fatty acids eicosapentaenoic 11.4% (20:5, EPA) and eicosanoic acid 12.6% (20:0, Arachidic) were not reported previously and are substantially higher (Table 11) [Oliveira et al., 2006]. Probably the higher unsaturated fatty acids were not separated from linoleic acid in older literature.

Table 11 Fatty acids composition of coffee seed oils (% weight)

Component	Hartman et al 1968	Kaufmann and Hamsagar 1962;	E.W. Eckey 1954;	Oliveira 2006
Myristic (14:0)	-	3		
Palmitic (16:0)	25	28		7.2
Stearic (18:0)	7-10	13	13	9.4
Oleic (18:1)	8-9.5	17	17	9.7
Linoleic (18:2)	39	36		10.4
Arachidic (20:0)				12.6
EPA (20:5)				11.4
Other	4-6	5	3	

Unsaponifiable lipids and diterpenoids

The main constituents of the unsaponifiable fraction (12% of the oil extract) are diterpenoid alcohols cafestol ($C_{20}H_{28}O_3$) and kahweol ($C_{20}H_{24}O_3$), besides lower quantities of phytosterol and phosphatides [Kaufmann and Hamsagar, 1962]. In unfiltered coffee these diterpenes are present in oil droplets and floating fines. In the filtering process these compounds are retained in the paper filter. These lipids have an effect on the cholesterol content in serum and elevate alanine aminotransferase activity [Urgert et al., 1995; Urgert and Katan 1997]. The lipid fraction of Arabica coffee is typically higher in content of 16-O-methyl cafestol [Speer et al., 1991; Trouche et al., 1997].

Sterols

Composition of blends may be derived from the composition of the lipid fraction [Muratore et al. 1998; Valdenebro et al., 1999]. Sterol composition has been shown to be different between coffee varieties. Capesterol (CPR 16%), stigmasterol (STR 19%) and β-sitosterol (BSIT 50%) are the major sterolic constituents in both arabica and robusta. Δ^5-avenasterol (D5) is significantly more pronounced in robusta (11%).

Volatile (aroma) components

Several hundreds of volatile constituents have been indentified in coffees (acyclic, isocyclic, and hetrocyclic substances) that are contributing to the flavour of the brew. The physiological effects or pharmacological activity of such complex of components is unclear and the value of isolated components may be of interest for further exploration. The quantity of those volatile components is however relatively low (ca 0.05 wt%). In SCG these components are largely extracted.

The composition of the volatile fraction can be classified as aldehydes (50%) (di)ketones (20%), esters (8%) and heterocyclic (7%) with ca 2% dimethyl sulphide and other odorous sulphides, and many more low molecular weight organic compounds (nitriles, furans, alcohols, acids) [Sivetz and Desrosier 1979]. Most prominent components identified typically for coffee aroma are for example furfurylmercaptan, kahweofuran, cyclotenes, maltol (sweet caramel flavour). Kahweaofuran and related constituents are exclusively found in coffee.

The aroma of the roasted coffee determines its quality. Analytical methods have been developed to distinguish between different origins or mixture compositions [Bicchi et al. 1997]. Important discriminator flavours were identified to be methylpyrazine and 2,3-butanedione [A. Murota 1993)]

The aromas liberated during the roasting of coffee were analyzed [Mayer and Grosch, 2001]. In a model mixture of 22 identified odorants in roasted coffee the similarity of the aroma could be approached. The volatile compounds that are released during the grinding of roasted coffee were analyzed by sampling of headspace using SPME and GC/MS [Akiyama, et al. 2003].

Appendix E: Carbohydrates in SCG

Polysaccharide composition of coffee beans
Coffee beans contain besides lipids a substantial part of carbohydrates. The polysaccharide composition (4.9 g/10 g) of different coffee beans are very similar.

Table 12 Monosaccharide content of green coffee beans

Component	Wolfrom et al 1960 mg/10 g fresh	Bradburg and Halliday 1990 %
Rha	13.5	0.3
Ara	396	4.0
Xyl	22.0	0.2
Man	2370	22.4
Gal	1176	12.4
Glc	725	8.7
GalA	136	

Water insoluble polysaccharides are the main components in coffee beans, approximately 48% of the dry weight [Wolfrom et al., 1960]. It contains arabinogalactan, mannan and cellulose [Bradburry and Halliday 1990]:

<u>Arabinogalactan</u> (type II): β (1→3) D-Galp main chain with frequent Ara β (1→3) D-Galp (1→ side chains linked to C6. Arabinogalactans commonly are associated with protein.

→3)-D-Gal*p*-β(1→3)-D-Gal*p*-β(1→3)-D-Gal*p*-β(1→3)-D-Gal*p*-β(1→3)-D-Gal*p*-β(1→
6
Ara β (1→3)-D-Gal*p*-β-1

<u>Mannan</u>: linear β (1→4)-D-Man*p* chain with occasionally D-Gal side chains (low Mw 7000); The ration of sugars in Galactomannan was found to be Man : Gal 45: 1 [Hashimoto and Fukomoto, 1969].

→4)-D-Man*p*-β(1→4)-D-Man*p*-β(1→4)-D-Man*p*-β(1→4)-D-Man*p*-β(1→4)-D-Man*p*-β(1→
6
D-Gal*p*-β-1

<u>Cellulose</u> is determined to be below 10% of the coffee bean weight. Coffee beans have a negligible starch content.

→4)-D-Glc*p*-β(1→4)-D-Glc*p*-β(1→4)-D-Glc*p*-β(1→4)-D-Glc*p*-β(1→4)-D-Glc*p*-β(1→

Green beans of Arabica contain slightly more mannose, while Robusta has slightly higher (3%) arabinogalactan [Fischer et al., 2001]. The branching of mannan with Gal residues is found to be higher and between 14:1 and 30:1. The arabinogalactans are heterogeneous with regard to branching and polymerisation degree. In robusta the side chains are longer.

Effect of roasting on polysaccharides

In the roasting process the carbohydrate composition is affected. The polysaccharides present in green beans are partially degraded by roasting. The effect of the degree of roasting on the extractable polysaccharides was investigated [Nunes et al., 1997]. Extractable and unextractable polysaccharide fractions were shown to be affected by the degree of roasting. The arabinose is more susceptible to degradation at elevated temperatures and especially the arabinogalactan content declines with more severe roasting.

The polymerization degree (Mw) of the polysaccharide fractions in the coffee affects the foam properties. Crosslinks with protein (Maillard reactions during roasting) and lignin make it impossible to isolate polysaccharides from roasted coffee without chlorite treatment [Nunes et al., 1998]. The thermal stability during roasting of arabinogalactans is less (60%) than mannans (36%), while cellulose is unaffected [Redgwell et al., 2002]. This leads to significant better solubility of the arabinogalactans and mannans. Roasting results in breaking of galactan backbone and arabinose loss. Depending on the degree of roasting the polymerisation degree and branching decreased [Nunes and Coimbra, 2002]. The soluble galactomannans are of lower polymerisation degree and have a higher branching (1:8) than unextractable fractions (1:15-24) [Oosterveld at al., 2003a]. Only a minor fraction of the degraded polysaccharides during roasting is found as oligomers or monomers [Oosterveld et al., 2003b]. These are quickly converted by Maillard reactions and formation of thermolysis (pyrolysis) products. It was found that the mannans are frequently acetylated especially at O-2 of Man residues [Nunes et al., 2005]. In green beans minor substitution (2%) with branches of Ara was found which decline upon roasting. In the mannan backbone β-(1$\rightarrow$4)-D-Glc (6%) was present. In roasted beans D-Glc was found (1%) only at the reducing end of the mannan chain.

Maillard reaction products, browning compounds and melanoidins

The effect of roasting on the coffee bean composition involves the darkening of the colour and the liberation of aroma compounds. The dark colored compounds that are formed as reaction between proteins and sugars (Maillard reaction) while also chlorogenic acid was found to be involved in the reaction [Heinrich & Baltes 1987] [Bekedam et al 2008c]. Arabinogalactans are more involved in the formation of high Mw melanoidins than galactomannans. The low Mw melanoidins were extracted and separated and analysed for their composition. The apolar character of the melanoidins was confirmed and incorporation of proteins or amino acids demonstrated and high glucose contents were shown. This glucose was suggested to be derived from sucrose. Also phenolics were incorporated (chlorogenic acid) providing apolarity to the melanoidins. [Bekedam et al 2008a]. The formation of melanoidins in roasted coffee is linked to the induced antioxidant properties of the high Mw fractions [Bekedam et al 2008b].

Appendix F: Organic acids and phenols in SCG

Chlorogenic acid (CGA) occurs in relative high quantities in coffee tissues and is considered to be a promising source of biofunctional dietary supplement. In green beans the presence of non-volatile organic acids that are water soluble has been found up to 8.2 % on dry weight basis. Chlorogenic acid is with ca 7.0 % the main component of this fraction. The remaining 1.2 % includes oxalic acid, malic acid, citric acid, and tartaric acid [Sivetz & Desrosier 1979]. After roasting the amount of soluble chlorogenic acid has decreased to 4.5% while caffeic acid and quinic acid are liberated.

Extraction of chlorogenic acid from SCG was studied. Highest yields of phenolics were obtained by extraction with aqueous ethanol (60%) from the smallest particles (up to 400 mg/l CGA). The addition of the enzyme cellulase was reducing the liberation of phenolics [Pinelo et al 2007].

Chlorogenic acid (up to 300 mg / cup) or 5-caffeoylquinic acid, stimulates stomach (gastric) secretion and enhances hydrochloric acid production. Caffeic and chlorogenic stimulate intestinal motility; thiamin content in serum decreases. Numerous patents have been filed for extraction and use of chlorogenic acid in energy drinks and as functional additive in food products.

Chlorogenic acid and related metabolic derivatives (caffeic / ferulic acids) have been associated with anti-oxidant properties and inhibition of tumor growth [Huang et al., 1988]. Caffeic acid is an effective inhibitor of lipid oxidation [Chen & Ho, 1997] and reduces leukotriene biosynthesis [Koshihara, et al, 1984] and its phenethyl ester has been identified as lipoxygenase inhibitor [Sud'ina et al., 1993].

The presence of other phenolics such as tannins and lignins in coffee is poorly documented. In many cases the melanoidins formed during roasting are classified as such.

Appendix G: Alkaloids in SCG

Purine alkaloids
Alkaloids are among the most prominent biologically active substances. The purine alkaloids present in coffee and tea are the most valued. Besides the predominant presence of caffeine in coffee beverages other related alkaloids are present in minute amounts. These are of similar purine alkaloid structure and are metabolites of caffeine (theobromine, theophilline, paraxanthine, theacrine, libertine, methylliberine [Viani, 1988]). The alkaloids are extracted in the production of the coffee beverage. Remaining residues of caffeine in SCG are low and not considered economically worth while to extract. In the decaffeinated coffee production the highest value (more than the decaf coffee) is obtained from the extracted caffeine that is used in energy drinks industry.

Pyridin alkaloids
<u>Trigonelline</u> [CAS 535-83-1] is an alkaloid present in coffee with a pyridinium-carboxylate structure related to nicotinic acid or niacin. It is easily soluble in water. Its presence in coffee has been associated with the reduced risk of diabetes in coffee consumers. It has been reported to prevent dental caries by hindering bacterial adhesion (*Streptococcus mutans*). It is found in green and roasted coffees [Martin et al., 1997] and may be transformed by roasting into alkylpyridines [Casal et al., 2000]. Its presence (up to 1% dry roasted beans) has been identified as an effective phytoestrogen, even at low dose [Allred et al., 2009].

<u>Niacin</u> or vitamin B3 / PP (=nicotinic acid, pyridine-3-carboxylic acid) is found widely in plants and also in coffee it has been reported to be prominently present. As a precursor for nicotinamide and NAD and NADP in vivo it is essential as food ingredient.

<u>Quinolinic acid</u> is a pyridine-2,3-dicarboxylic acid found in coffee along with other alkaloids in minor qualtities.

Appendix H: Mineral and metal content in SCG

Coffee is known for its high potassium (K) content. Brewed coffee is rich in potassium (up to 200 mg/cup), magnesium (up to 20 mg/cup) and relatively high amounts of manganese (0.2 mg /cup) [Clarke &Macrae 1989]. Discriminative differences in mineral content have been shown between different varieties [Martin et al., 1998] and brews [Haswell & Walmsley 1998]. Phosphorus (P) and copper (Cu) are higher in robusta while arabica contains more manganese (Mn) (table 2.4).

Table 13 Mineral content in different coffee types [Martin et al., 1998]

Mineral	Arabica (wt%)	Robusta (wt%)
K	1.5	1.7
P	0.152	0.20
Ca	0.107	0.130
Cu	$1.6.10^{-3}$	$2.2.10^{-3}$
Mn	$3.1.10^{-3}$	$1.6.10^{-3}$

The elemental composition of coffee grounds is also given by the Phyllis data (total ash 0.2%) (Table 14). The mineral composition of SCG declines to ca 1.5 % since a large part of the mineral content is extracted in the brewing process [Sivetz & Desrosier, 1979].

Table 14 Major elemental composition of coffee ground ash [Phyllis data base]

Element	mg/kg dry sample
Al	100
Ca	900
Co	10
Cu	14
Fe	50
K	200
Mg	200
Mn	14
P	100
Si	100
Zn	4

Appendix I: Green chemicals production

Most of the methods described in the literature for utilisation of coffee residues are focussed on just one component or ingredient while neglecting or discarding the larger part of the biomass. Selected extraction of 'green chemicals' from biomass requires process design and technological innovation. Technologies that have been developed for conversion of agro-industrial waste streams into (intermediate) products of value may be suitable for application on coffee residues as well for production of 'green chemicals'. Some examples of ongoing developments in this area are:

- Fisher-Tropsch conversion of biomass for bio-diesel production (DOE Biomass Power program funding)
- Conversion of biomass for ethanol production via fermentation (Sugarcane, Brazil) [Borrero et al., 2003]
- Enzyme technology (Iogen Corp, Canada)
- Thermolytic conversion of biomass for the production of fuels by pyrolysis, liquefaction, hydrocracking (Ensyn Inc, DynaMotive, Canada; HTU, BTG, The Netherlands)
- Thermolytic conversion to bio-oil, biocrude, or syngas [Czernik & Bridgwater 2004; Zhong-ming & Li, 2002; Goudriaan et al., 2000].

Background information found in literature on the relevant fractions present in different coffee residues and their use as 'green chemical' or food / pharma ingredient is given in this appendix.

Phenolic acids and polyphenols

Tannin

Tannins occur as hydrolysable and condensed structures in many plants. Tannins are polyflavonoid condensed structures or mixtures of hydrolysable phenols (gallic and ellagic acids and esters). Tannins are present in various tissues of the coffee crop and play an important role in the anti-nutritional properties of the residues (hulls & pulp). The presence of tannins in feed reduces the iron uptake considerably [De Rozo et al. 1985].

Tannins are highly reactive compounds that are likely to condensate and polymerize rapidly under certain conditions giving insoluble dark coloured residues. Especially at elevated temperatures they readily react with proteins, anthocynanidins and other components in the medium. In SCG tannins are not prominently present, but may be incorporated in the melanoidins.

Industrial qualities of tannins are extracted mainly from barks (quebracho, mimosa, oak) traditionally for leather making. Besides substantial quantities consumed in leather tanning industries the main use currently is found in wood adhesives formulations. Tannin use is reported as plasticizer in cement processing. Also food additives (wine, fruit juice) and medical or pharmaceutical uses of tannins are currently explored.

Anti-oxidant and chlorogenic acid

- The presence of strong antioxidants in coffee beans like tocopherols (α, β and γ) and caffeic acid contribute to the resistance of the coffee against oxidation in atmospheric conditions [Lehmann et al., 1972ab, 1979]. Chlorogenic acid (CGA) is recognized as an important determinant of coffee flavour and as the main component of the phenolic fraction.
- In green and roasted coffee beans the presence of substances with antioxidant activity was demonstrated. The presence of high amounts of CGA, caffeic acids and other (poly)phenols (up to 14%) have been associated with the strong antioxidant activity. The protective activity in lipid peroxidase tests only was significantly lower in unroasted beans [Daglia et al., 2000]. In the roasting process these activities are affected due to chemical degradation of CGA (isomerization, hydrolysis and maillard reactions, melanoidins formation) [Farah & Donangelo 2006]. In roasted coffee CGA content depends on the conditions but may still reach up to 7% of CGA derivatives present.
- The beneficial effects of CGA compounds on human health have been reported, but the metabolism is poorly understood [Monteiro et al 2007; Farah et al 2008].
- Besides the antioxidant properties of phenolic compounds in food, concerns have been raised about the pro-oxidant properties that may cause deterioration of food products [Anduaeza et al 2009].
- Patents for extraction of caffeic acid or quinic acid from coffee grounds by using microbial enzymes (chlorogenic acid hydrolase) were filed [WO2009107328, 20090903]. The same was claimed from extracting burdock leaves [JP2009100760, 20090514].

Guaiacol derivatives

Antioxidant activities were measured in brewed coffees and ascribed to the presence of guaiacol derivatives (H, ethyl- and vinyl-guaiacol) besides the chlorogenic acids (caffeoyl and feruloyl quinic acids) [Fujioka & Shibamoto 2006]. The formation of volatile phenolics was measured during the roasting process. These VOC's are important aroma compounds in coffee [Dofner et al 2003].

Acetophenone derivatives

From coffee beverage antimicrobial substances can be extracted that are present at very low dose [Daglia et al 1998]. Acetophenone and its derivatives are among the components that are associated with this effect [Nishina, et al. 1994; Spiller 1998; Fujioka & Shibamoto 2006].

Polysaccharides

- The insoluble carbohydrate rich fraction of coffee ground residue is largely composed of β-mannans. Also the undesired insoluble sediments in coffee extracts are composed of (galacto)mannans [Delgado et al 2008]. In the coffee beverage soluble dietary fibre contents are reported to be present [Díaz-Rubio & Saura-Calixto 2007]. The viscosity of the coffee extracts (in instant coffees) is ascribed to the polymeric mannan content and can be reduced by hydrolysis with mannanase [Sachslehner et al 2000].

- Mannan oligomers (DP 1-10) were produced by hydrolyzing coffee grounds with acid [US4508745, 19850402]. The production of a mixture of mannitol and mannosaccharide alcohols from coffee residue by acid hydrolysis, neutralizing and reduction to alcohols has been filed as patent [Stahl et al., EP157043].
- Mannan or galactomannan from other plant sources (e.g. guar gum, locust bean gum, konjac gum) are widely used in food industries as hydrocolloid thickeners and are advertised as dietary supplement / dietary fibre. Dietary fibre are for humans non-digestible plant cell wall components. Many references are available for mannose oligo's that have been explored for use as dietary fibre. The digestibility of mannans or mannooligosaccharides from coffee is poor. In the large intestine these are reported to be converted to short chain fatty acids [Asano et al 2003]. Fat accumulation in mice fed with addition of small amounts (1%) of mannooligo's was substantially lower [Takao et al 2006]
- The most pronounced biological activity of mannans has been identified as the immunostimulant potential [Tizard et al 1989].
- The Japanese patent to extract and convert xylan from coffee ground with xylanase to produce soluble dietary fibre [JP3015364, 1991, Yamamoto Sangyo KK] seems unrealistic considering the coffee ground composition and the absence of xylans.
- Arabinogalactans (typeII) have been isolated [Gniechwitz et al 2008] from roasted coffee and shown to be poorly digestible in the human colon. The arabinogalactan-protein fraction (15% of the green bean) was shown to possess hydrocolloid and foaming properties [Redgwell et al 2005].

Sugars

The wet process of coffee processing (process A) results in lower free monosaccharide contents in the green beans than the dry process B which are affecting the sensorial differences between the two processes [Knopp et al 2006]. Monosaccharides derived from free sugars or hydrolysis of the polysaccharides present in the green and roasted coffee beans may be converted into value added products by fermentation (ethanol, lactic acid, etc.) or by chemical conversion. Selected strains may be capable of fermenting mannose into ethanol and other products.
Many different procedures to produce oxidized (organic acids) and reduced (alditols) and conjugates from sugars are described [review: Galbis and García-Martin, 2008]. New renewable polymers based on sugar monomers have been reported.

Sugar degradation products

Fragmented carbohydrates and proteins during the roasting process generate much of the organic acids (formic, acetic, oxalic, malonic, citric, and succinic acids), flavours (aldehydes) and polymerization products present in coffee. Browning reaction (Maillard) products from aldose and amino compounds form decomposition and polymerization products. Also furans are formed from the degradation of sugars during the roasting and high pressure steaming. Too high concentrations are undesirable for the coffee flavour.

- Maltol and 5-hydroxymaltol are well known caramel flavours that are formed from sugars during the roasting process and contribute to the coffee flavour [Flament & Bessière-Thomas, 2002].
- Maillard reaction products formed during the roasting process from the reaction of proteins with sugars are complex molecular structures that are difficult to separate and identify. These complexes of variable molecular size and solubility are referred to as melanoidins [Bekedam et al 2008].

Terpenes

The volatile aroma compounds produced by plants often belong to the class of monoterpenes (C_{10}). The aroma of robusta coffee is affected by the presence of 2-methyl isoborneol, one of the volatile monoterpenes that can be smelled in very low concentrations (ppb).

Most commonly known terpenes in coffee grounds and processing streams are the diterpenes. Diterpenes (C_{20}) present in green beans are predominantly cafestol and kahweol. Also in coffee grounds these are remaining (1-2%) or are retained in the filtering process. They were shown to have effects on cholesterol concentrations in human blood.

Other diterpenes recognized in green coffee beans are atractyligenin derivatives in free or conjugated form (<1g/kg, kaurenols/ furokauranes / furokaurenes). The actractylosides (or acatractyligenin glycosides) are water soluble and found in the early extraction fractions during coffee beverage production. These are predominantly present in arabica.
Some more structures have been published of related compounds such as: Ent-16-kauren-19-ol, cofarol and 16,17- dihydroxykaur-9-(11)-en-18-ioc acid. No physiological or functional properties have been described.

- In medical patents for diterpenes from coffee the cafestol (and/or kahweol) has been included in immuno-modulating recipes with synergistic effects with other chemotherapeutic agents in anti-cancer treatments [WO2010008726].
- Also in pharmaceutical and cosmetic formulations cafestol was claimed for contribution to the formation of a protective lipid barrier for skin treatments [US6716437, 2004].
- Controlled release of anti-angiogenic compounds (tyrosine inhibitor) [US2007149480, ALCON Inc]
- Hair loss prevention shampoos [S. Commo, FR2879444, Oreal, 2006]
- Prevention and treatment of cancers [KR2006 0001162 Jansaeng, Doraji Co Ltd].
- Processes for the preparation of cafestol from kahweol by hydrogenation and extraction of mixtures from coffee oil was claimed [GB8701415, 19870225]
- Removal of diterpenes from coffee oil by isopropanol extraction [GB8417475, 19840815] is patented.

- In processing industries diterpenes with structural similarities like rosins or resin acids from wood are used for paper sizing, emulsifiers, adhesive tacking agent and in printing inks.

Fatty acids
The polyunsaturated fatty acids in the coffee residue extracted oils such as linoleic and EPA (Table 11) can crosslink and form polymeric networks with hydrophobic barrier properties that are suitable as protective coating layers (compare linseed oil, varnish, coatings). Such drying oils may be interesting for copolymerization with vinyl or for the manufacturing of alkyd resins, polyamide and polyurethanes production. Good film forming properties of lipids may find use in novel paint formulations.

Sterols
Sterol composition is different between coffee varieties (see 4.7). Such compounds (phytosterols) have potential biomedical, pharmaceutical, hygienic or toxic effects when right or wrongly applied.
Searching in the patent literature on camposterol alone over 200 patents are found in cosmetics (dermopharmceutical moisturing composition), nutraceutic preparations (anti-obesitas), immuno-modulating, herbicide. Searches on stigmasterol results in more than 300 patents with applications such as water soluble bioactive lipohillic compounds.

Flavanols
Catechin (almost 1500 patents) is widely applied as food supplement (beverage), blood glucose content control, anti-viral compositions, mosquito repellents, antibacterial formulations, but also as anti-oxidant in rubber (tires), inhibitor of furan formation (food heating and baking). It is present in the coffee pericarp and pulp and hulls, but not in coffee beverage [Arts et al., 2000].

Hydroxytryptamides
In coffee bean wax the presence of different alkylated 5-hydroxytryptamides has been reported [Hunziker & Miserez 1994; Lang & Hofmann 2005; Lang et al., 2009] and in total ranging between 400 and 500 μg /g. These components were associated with occurring stomach problems in coffee consumers. Patents have been filed for the conversion of these residues isolated from coffee wax to serotonin [Neunhoeffer et al., 1973]. Serotonin or 5-hydroxytryptamine is a well known biochemical responsible for neurotransmission in the brain and applied as anti-depressivum.

Contaminants
Ochratoxin A (OTA) is a mycotoxin or a contaminant derived from microbial spores occurring on the green beans. OTA is occurring in concentrations between 4-13 μg/ kg on the beans [Napolitano et al., 2007]. OTA is largely removed during roasting by thermal degradation and physical removal with chaff [Blanc et al., 1998][Van der Stegen et al., 2001][Ferraz et al., 2010].

Appendix J: Coffee research and networks

Coffee networks and associations are largely concerned with product promotion, marketing and beverage quality aspects.

KNVKT is a member of the European Coffee Federation: www.ecf-coffee.org

There are different other organizations dealing with various aspects of coffee agriculture, science, politics and markets (www.coffeeresearch.org/links/organizations.htm). One prominent European example is the Speciality Coffee Association Europe: http://scae.com/

The Association for science and information on coffee ASIC: www.asic-cafe.org/index.php

ASIC organizes scientific conferences that are concerning the scientific findings and technological developments in the coffee production: www.coffeeresearch.org/science/asic.htm

Information about the Global coffee research network GCRN is found at: www.asic-cafe.org/htm/GCRN/index.php

As a non-member the accessibility of information is restricted

The European coffee science information centre CoSIC (ISIC 1990) for the coordinated investigation of health related issues of coffee consumption: www.cosic.org/

The International Coffee Organization ICO www.ico.org/coffee_story.asp is the main intergovernmental organization for coffee commodity trade. ICO initiates development projects to encourage sustainable production and improve marketing.