CHAPTER 2 THEORY AND LITERATURE REVIEW

2.1 Green tea

All varieties of tea are produced from the tea plants. *Camellia sinensis*is major varieties of the tea plants. Tea leaves can be processed to black tea, oolong tea, and green tea by fermentation,semifermentation, and nonfermentation.

Generally, to produce black tea, fresh tea leaves are plucked, withered, rolled, fermented, and, finally, dried. The enzyme activities are completely utilized in black tea processing to form the pigments (theaflavin and thearubigin), while the enzyme in the process of green tea are not activated.

Oolong tea has an excellent characteristic with the combination of the freshness of green tea and the fragrance of black tea. It is produced by a special process called green leaf shaking and green leaf cooling. In this process, the moderately withering green tea leaves are bruised at the edges by hand or mechanical shaking and vibrating. The leaf appearance of oolong tea is featured with the reddish edges and green centers.

Green tea has been very popular and used in many applications such as food, cosmetic pharmaceuticals and especially, in beverage. It is made with the fresh leaves. Unlike black and oolong tea productions, green tea production does not involve oxidation of tea leaves. It is produced from steaming fresh leaves at high temperatures, inactivating the oxidizing enzymes and leaving the polyphenol content intact. The polyphenols found in tea are more commonly known as flavanols or catechins, and comprise 30-40 percent of the extractable solids of dried green tea leaves. The four main catechins areepicatechin, epicatechin-3-gallate, epigallocatechin, and epigallocatechin-3-gallate (EGCG). Other polyphenols found in green tea include gallic acid, chlorogenic acids, caffeic acid and the flavonols kaempferol, myricetin and quercetin. Green tea polyphenols have demonstrated significant antioxidant, anticarcinogenic, anti-inflammatory, thermogenic, probiotic, and antimicrobial properties in numerous human.It is composed of compounds such as tea polyphenols, caffeine, theanine, vitamins, etc. as shown in Table 2.1.

However, drinking green tea for a long term can pose harmful side effects such as anxiety and insomnia due to caffeine. An abrupt withdrawal from drinking typically causesfatigue and depression, irritability, tremors, jumpiness, deprivation of deep sleep, and vascular headaches.

Table 2.1 Components of green tea leaves (Camellia sinensis var. assamica) [6]

Type	**Components**	**Dry weight (%)**
Water-soluble	Phenolic compounds	40
	Flavanols	18-30
	Epigallocatechingallate	9-13
	Epigallocatechin	3-6
	Epicatechingallate	3-6
	Epicatechin	1-3
	Gallocatechin	1-2
	Catechin	1-2
	Flavonol glycosides	3-4
	Proanthocyanidins	2-3
	Phenolic acid	4
	Caffeine	3-4
	Amino acids	4
	Theanine	2
	Others	2
	Carbohydrates	4
	Organic acids	0.5
Partially water-soluble	Starch	2-5
	Other polysaccharides	12
	Proteins	15
	Ash	5
Water-insoluble	Cellulose	7
	Lignin	6
	Lipids	4-9
	Pigments	0.5
	Volatiles	0.01-0.02

2.2 Chemical components of green tea

2.2.1 Tea Polyphenols

Green tea leaves are infused with hot water or extracted with solvents providingphenolic compounds which are so-called tea polyphenols. The contents of green tea polyphenols which are composed of six kinds of catechins (Table 2.2) and their derivatives slightly deviate depending on the species of tea and the season of harvesting[7].

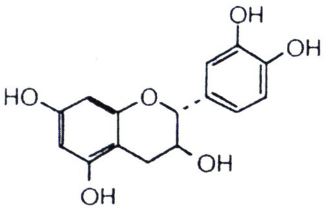
Table 2.2 Contents of polyphenol depending on tea species and seasons (g per 100 g dried leaves) [7].

Polyphenols	**var. sinensis**		**var. assamica**
	Spring	**Summer**	
(+)-Catechins (C)	tr.*	0.07	0.02
(+)-Gallocatechin (GC)	tr.*	tr.*	-
(-)-Epicatechin (EC)	1.50	1.50	1.13
(-)-Epicatechingallate (ECg)	2.80	4.10	3.35
(-)-Epigallocatechin (EGC)	4.00	3.70	0.35
(-)-Epigallocatechingallate (EGCg)	8.80	12.20	12.10

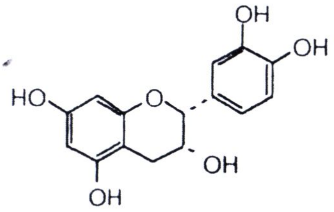
*tr.:trace

The combination of aromatic rings and hydroxyl groups that make up to green tea polyphenols structure related to antioxidant potential because of binding and neutralization of free radicals by the hydroxyl groups.In addition, green tea polyphenols stimulate the activity of hepatic detoxification enzymes, promoting detoxification of xenobiotic compounds and chelating metal ions, such as iron.This can generate radical oxygen species and also other cancer-combating properties [8].

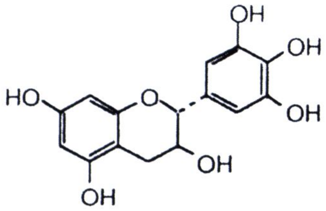
The catechins in fresh tea leaves undergo enzymatic and chemical oxidation leading to oxidized, condensed, and polymerized polyphenols known as theaflavins and thearubigins, which contribute to the color and taste of liquors of black tea. The oxidative fermentation of catechins results in the development of appropriate flavor and color. It will cause a darkening of the leaf and a decrease in astringency.



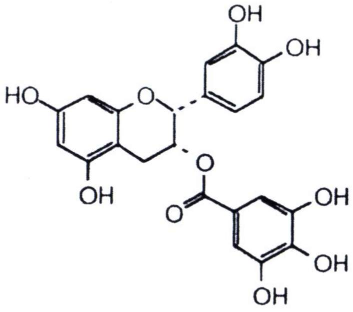
(+)-Catechin



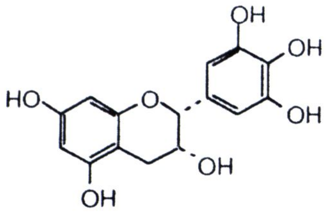
(-)-Epicatechin



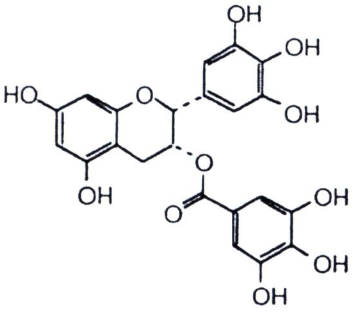
(+)-Gallocatechin



(-)-Epicatechin gallate



(-)-Epigallocatechin



(-)-Epigallocatechin gallate

Figure 2.1 Chemical structures of catechins

2.2.2 Tannin

Tannins are water-soluble polyphenols that are present in many plant foods. They can be divided into hydrolysable and condensed tannins. Tannins have been found in a variety of plants utilized as food and feed. These include food grains such as sorghum, millets, barley, dry beans, faba beans, peas, carobs, pigeonpeas, winged beans, and other legumes. Fruits such as apples, bananas, grapes, and strawberries also contain an appreciable quantity of tannins. Likewise, tannins are present in tea.

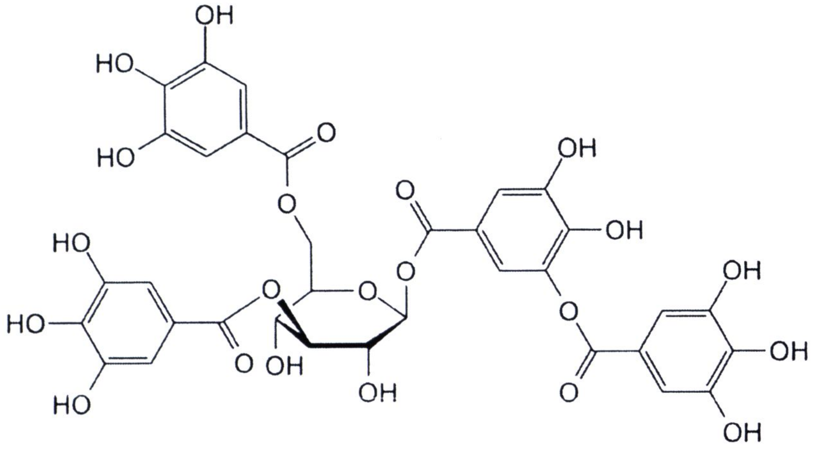


Figure 2.2 Chemical structures of the tannins

Condensed tannins are the polymerized products of favan-3-ols and favan-3, 4-diols, or a mixture of the two. The polymers, referred as "favolans", are popularly called condensed tannins. Its molecular weight is between 500 and 3000 Daltons [9].

Tannins are considered nutritionally undesirable because they precipitate proteins, inhibit digestive enzymes and affect the utilization of vitamins and minerals. Tannins have special properties, such as the ability to precipitate alkaloids, gelatin and other proteins [10, 11].Tannins form complexes with proteins, starch and digestive enzymes and reduce the nutritional values of foods.They interfere with the digestion and/or absorption of carbohydrates from sorghum.However, it is generally believed that the major dietary effect of condensed tannins within the digestive tract is due to the formation of less digestible complexeswith dietary proteins, rather than by inhibition of digestive enzymes.

2.2.3 Caffeine

Most of the caffeine consumed comes from dietary sources such as coffee, tea, cola drinks, and chocolate. It is most commonly consumed by humans in infusions extracted from the cherries of the coffee plant and the leaves of the tea bush.Caffeine is also widely used as drugs.

The consumption of caffeine is most often correlated with the positive effects following its ingestion, namely increased alertness, energy, and ability to concentrate. However, caffeine activates the central nervous system (CNS), leading to behavioral, autonomic, and endocrine responses. Effects of caffeine on peripheral functions are widespread and are mediated by direct tissue effects along with hormonal and autonomic outputs.

Caffeine is a trimethyl derivative of purine 2, 6-diol as shown by Figure 2.3 and is synthesized mainly in leaves of the tea plant. Caffeine (3, 7-dihydro-1, 3, 7-trimethyl-1H-purine-2, 6-dione) has the chemical formula is $C_8H_{10}N_4O_2$.

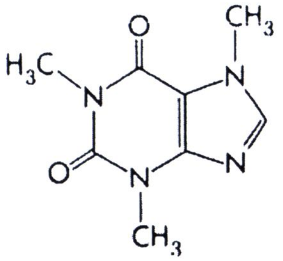


Figure 2.3 The molecular structure of caffeine

2.3 Corn cob

Corn cobs are one of the biomass feedstocks for renewable energy industries in the U.S. to reduce the current energy and the greenhouse gas problems. In the United States, corn cobs are used to produce ethanol [12]. It can also be used for producing heat, power, fuels, and a wide variety of chemical products.

Corn cob comprises three natural parts. They are the chaff and the pith forming the light part and the woody ring which forms the hard part of the cob. The corn cob has both absorbent and abrasive properties. The chaff is on the outside, pith is the soft spongy center and the tough woody ring is formed in between. The chaff and pith provide absorbency while the woody ring has major abrasive properties [13].

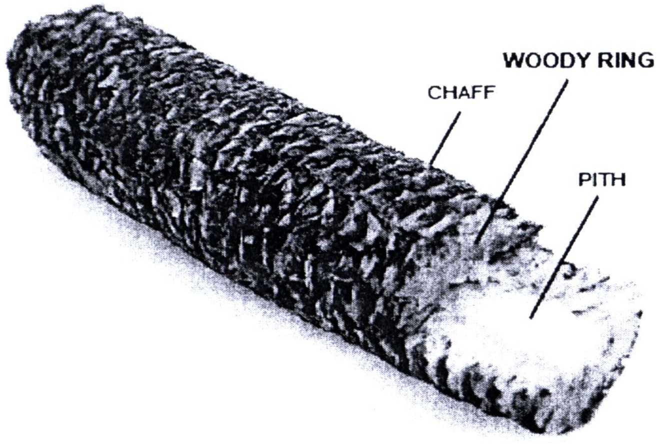


Figure 2.4 Corn cob [14]

Cellulose is the major chemical component of fiber wall and contributing 40-45% of the wood's dry weight. The cellulose is composed of linear chains of D-glucose linked by ß-1,4-glycosidic bonds (Figure 2.5) with the degree of polymerization from 10,000 in native wood to 1,000 in bleached kraft pulps. Each D-anhydroglucopyranose unit possesses hydroxyl groups at C2, C3, and C6 positions. The molecular structure imparts cellulose with its characteristic properties: hydrophylicity, chirality, degradability, and broad chemical variability initiated by the high donor reactivity of hydroxyl groups [15].

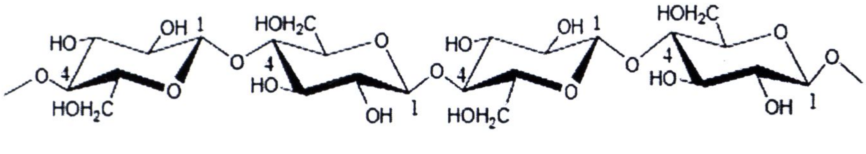


Figure 2.5 The structure of cellulose

Cellulose has a strong tendency to form intra- and inter-molecular hydrogen bonds by the hydroxyl groups on these linear cellulose chains, which stiffen the straight chain and promote aggregation into a crystalline structure and give cellulose a multitude of partially crystalline fiber structures and morphologies

Hemicelluloses have degree of polymerization only 50-300. Hemicelluloses are essentially amorphous because it is composed of side groups on the chain molecule. As a result, hemicellulose is branched whereas cellulose is unbranched. Hemicelluloses were hydrolyzed or removed by acid or base [3].

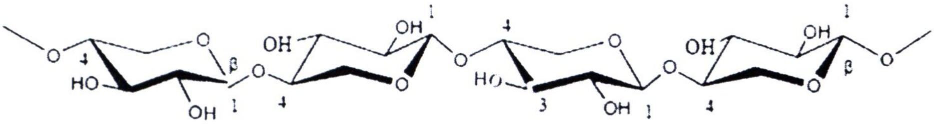


Figure 2.6 The structure of hemicellulose

Lignin is a natural polymer that is present in large quantities in the cell walls of terrestrial plants and is the main binding agent for fibrous plant components, typically comprising from 16 to 33% of plant biomass. Lignin is composed of several types of aromatic compounds such as guaiacyl lignin, syringyl lignin and p-hydroxyphenyl lignin [3], and has a three-dimensional structure containing a number of functional groups such as phenolic, hydroxyl, carboxyl, benzyl alcohol, methoxyl. Furthermore, aldehyde groups of lignin can be used as an adsorbent for removal of heavy metals from water [16].

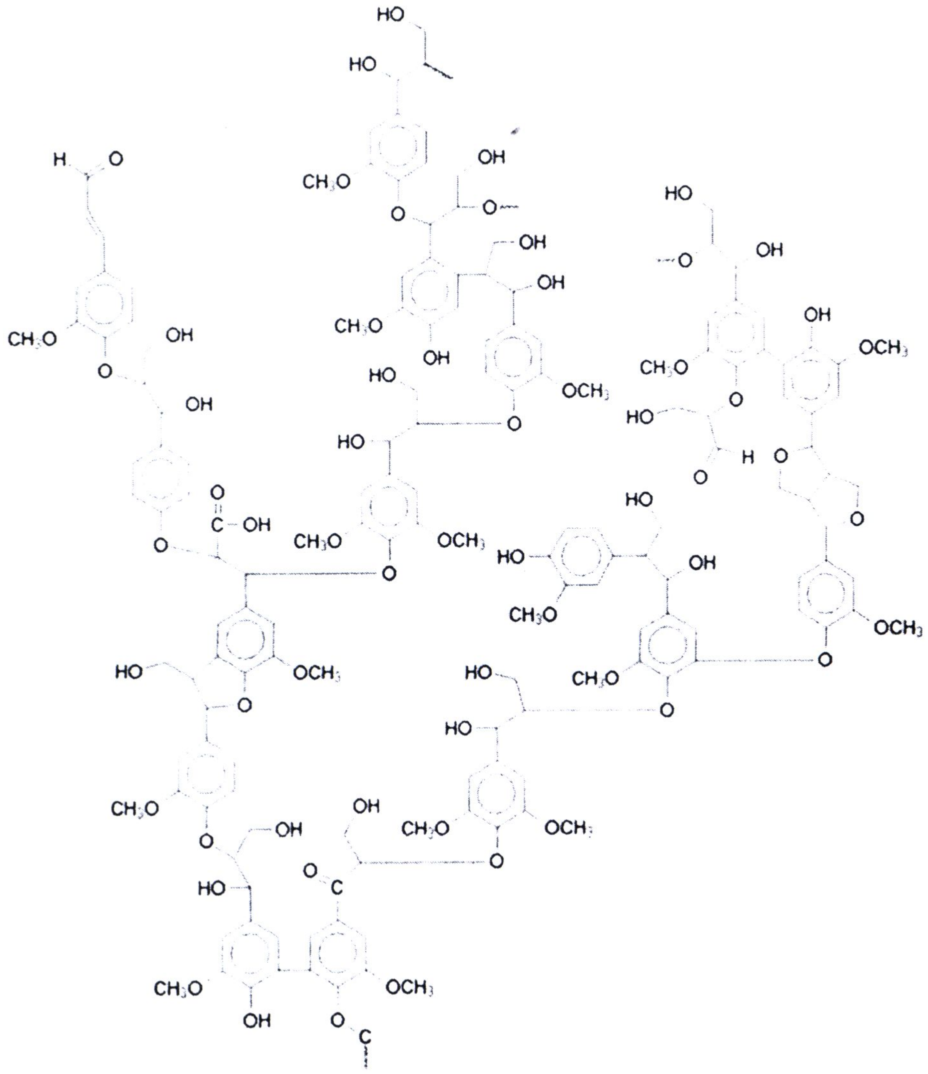


Figure 2.7 The structure of lignin

The combination of cellulose, hemicelluloses, and lignin is called lignocellulose. The corn cob composition is given in Table 2.3. The corn cob is rich in cellulose and hemicellulose, which consists about 80% of the dry matter.

Table 2.3 Composition of corn cob [17]

Component	**Amount (g/100 g dry wt. basis)**
Cellulose	38.4
Hemicellulose	40.7
Lignin	9.8
Others	11.8

2.4 Principle of Adsorption

Adsorption occurs when a gas or liquid solute forms a molecular or atomic film on the surface of a solid or a liquid. The substance accumulates on the surface is called adsorbate and the adsorbing phase is called adsorbent. The removal of an adsorbed substance from the surface on which it is adsorbed is called desorption.

Adsorption is a consequence of surface energy. In a bulk material, all the bonding requirements for ionic or covalent of the constituent atoms of the material are filled. But atoms on the clean surface experience a bond deficiency, because they are not surrounded by other atoms. Thus it is energetically favorable for the atoms to bond. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption.

Adsorption is operative in most natural physical, biological, and chemical systems, and is widely used in industrial applications such as gas and water purification.

2.4.1 Types of Adsorption

Types of adsorption depend on the nature of attractive forces which exist between the adsorbate and adsorbent, adsorption can be classified as:

1. Physical adsorption (Physisorption) is a type of adsorption in which the adsorbate adheres to the surface only through Van der Waals (weak intermolecular) interactions. Even though the van der Waals interaction is attractive, as the adsorbed atom moves closer to the surface the wave functions of electron starts to overlap with that of the surface atoms. Further the energy of the system will increase due to the orthogonality of wave functions of the approaching atom and surface atoms.

In physical adsorption, the interaction energy is very weak. The van der Waals attractive force originates from the charge fluctuations between two correlated bonding molecules or atoms, in other words, the mutually induced dipole moments.

Since the forces of attraction are weak, the process of physisorption can be easily reversed by heating or decreasing the pressure of the adsorbate.

Enthalpy of adsorption, which is the enthalpy change for physical adsorption of one mole of an adsorbate on an adsorbent surface, is usually in the range of 20 kJ/mole to 40 kJ/mole

2. Chemical adsorption (Chemisorption) is a type of adsorption whereby a molecule adheres to a surface through the formation of a chemical bond, as opposed to the Van der Waals forces which cause physical adsorption. The forces of attraction between the adsorbate and the adsorbent are very strong. The molecules of adsorbate form chemical bonds with the molecules of the adsorbent present in the surface.

Adsorption is generally accompanied by the release of energy. Most adsorption processes are exothermic in nature. Adsorption is a spontaneous process, and, therefore, its free energy change is negative. However, the entropy change associated with adsorption is generally negative because the adsorbate molecules lose their translation freedom when they get attached to the surface of the adsorbent. Therefore, in order for free energy change to be negative, the enthalpy change must be sufficiently negative. This explanation accounts for exothermic adsorption processes.

In chemical adsorptions, the values of enthalpy change are an order of magnitude high, ranging from 200 kJ/mole to 400 kJ/mole.

The differences between physical adsorption and chemical adsorption are summarized in Table 2.4.

Table2.4 Comparison between physical adsorption and Chemical adsorption [18]

Physical adsorption	**Chemical adsorption**
Forces of attraction are vander Waals' forces	Forces of attraction are chemical bond forces
Low enthalpy of adsorption (20 - 40 kJ/mole)	High enthapy of adsorption (200 – 400 kJ/mole)
This process is observed under conditions of low temperature	This process takes place at high temperatures
It is not specific	It is highly specific
Multi-molecular layers may be formed	Generally, monomolecular layer is formed
Process is reversible	Process is irreversible

2.5 Literature review

There were a few studies on decaffeination of green tea. AmraPerva-Uzunalie and co-researchers [19] studied the extraction efficiency of catechins and caffeine from green tea leaves. It was found that maximum achieved extraction efficiency of catechins with water was obtained at 80 °C for 20 min (97%). Degradation of catechins was observed at higher extraction temperatures and with prolonged extraction times. SiripatSuteerapataranonet al. [20] found that caffeine in tea infusionswas dependent on infusion conditions such as water temperature, infusion time and leaf form (non-ground or ground). For non-ground leaf samples, the higher the water temperature and the longer the infusion time, the higher the caffeine concentrations in tea infusions. The concentration of caffeine was essentially constant after a certain period of infusion time.

There are several reports about the extraction methods of caffeine. Chang and co-researchers [21] studied about extraction and decaffeination by using supercritical carbon dioxide. This method was effective and left no solvent residues. A new method using high pressure processing to extract caffeine from green tea leaves was studied by Xi Jun [22]. It was used to extract caffeine from green tea leaves. Compared with solvent extraction methods, high pressure processing extraction has some advantagessuch as higher yield, shorter extraction time and lower levels of impurity. However,those methods need expensive equipment. Extraction caffeine from tea leaf using solvents such as chloroform or methylene chloride was used. However, because of their toxicity, these solvents are not widely accepted by consumers.

A novel approach for decaffeination by using a natural, nontoxic, and inexpensive methods have been reported.Sakanaka et al. [2] found that lignocellulose prepared from sawdust could be used to purify polyphenols in tea by decaffeination. Ye and co-workers [3] studied about using lignocelluloses prepared from woody tea stalk, pine sawdust and sugarcane bagasse as adsorbents to isolate decaffeinated catechins from tea extracts. They found tea stalk lignocellulose could be used to produce decaffeinated tea catechins.

There was also research reporting that caffeine could bind with the metal ions.It was likely that the interactions between caffeine and metal ions were through its oxygen and nitrogen atoms. Because of the blockage on N1, N3 and N7 atoms by methyl groups, caffeine probably bound to metal ions through its O2 and O6 atoms. The complex formation capacity of caffeine in tea and coffee was determined for Ca, Mg, Fe, Zn, Pb, Mn, Co and Cr metal ions by SevgiKolayli [23]. The results showed very little complex formation capacity of caffeine. ShohrehNafisi and co-workers [24] found that the weak interactions of calcium and magnesium ions with caffeine might be through O6 atom.

The past research has shown that biomass, which contained lignocellulose, had the ability to adsorb caffeine and polyphenol. Corn cob is an agricultural by-product which has several advantages. It is inexpensive and biodegradable. In addition, metal ions can also interact with caffeine. In this work, adsorption of caffeine from green tea using corn cob in Na^+ and Ca^{2+}-forms were carried out.