The Formation of Polyaromatic Hydrocarbons and Dioxins During Pyrolysis:

A Review of the Literature with Descriptions of Biomass Composition, Fast Pyrolysis Technologies and Thermochemical Reactions

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Abstract

This review on the formation of polyaromatic hydrocarbons (PAH) and dioxins during biomass fast pyrolysis was funded by the Washington State Department of Ecology. It includes a world-wide literature review of what is known and not known about this timely area. Areas needing further research and development work are identified and, as such, serve as a base for further work. For example, the need for lignin research is identified on page 31. While it was not possible to find any references to the presence of leachable polyaromatic hydrocarbons or dioxins in chars produced from the fast pyrolysis of woody biomass, small amounts of PAHs have been reported in bio-oils produced from this process.

In general, fast pyrolysis oils typically tend to contain under 10 parts per million (ppm) of PAHs, which is lower than the values obtained in slow pyrolysis oils (exceeding 100 ppm). These small amounts of PAHs seem to be generated from a very poorly known mechanism involving poly-condensation reactions of all biomass organic components, which occurs in certain char structures. The mechanism leading to the formation of these unstable structures in chars has to be further investigated.

Fast pyrolysis bio-oil is less damaging to air and water quality than slow pyrolysis derived tars. In comparison to traditional petroleum derived fuels, bio-oil biodegrades faster, and is considerably less toxic. Fast pyrolysis oils do not need special precautions in terms of explosive concerns or toxic or ecotoxic emissions but these oils are corrosive and irritating to skin due to the presence of carboxylic acids. PAH production levels are significantly reduced at lower temperatures (below 700°C, page 19). In addition, dioxin production is significantly reduced when chlorine and metals are missing (page 13).

It was considered convenient to add several sections to this review devoted to describing biomass composition, fast pyrolysis technologies and thermo-chemical reactions in order to create a self-contained document that could offer a more complete overview of the complex phenomena associated with the formation of these undesirable compounds.

The review starts with a brief introduction describing some basic elements of biomass composition and existing pyrolysis technologies, and goes on to focus on known pathways for the formation of polyaromatic hydrocarbons (PAHs) and dioxins, their toxicity, and ways to control their production during pyrolysis. The possible relationships between the composition of the biomass, the reaction conditions and the presence of PAHs and dioxins in bio-oils and chars are also discussed.

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Chapter 1. Biomass Composition

The reactions occurring in fast pyrolysis reactors only involve the partial decomposition of biomass molecules; consequently the properties and composition of resulting bio-oil and char are feedstock dependent. Understanding the feedstock composition is critical to predicting the outcome of thermochemical reactions. This information is also relevant to developing strategies favoring the formation of desirable compounds while limiting the reactions leading to the formation of PAHs and dioxins in thermo-chemical processes.

The biomass (trees) can be classified botanically as angiospermae (arborescent angiosperms) or gymnospermae. The term softwood is applied to coniferous trees of the order coniferae which bear needles and produce seeds in cones (gymnosperms) and are usually evergreen.

The structure of wood can be described at different levels (Fengel and Wegener 1989, Zickler et al. 2007). On the *micrometer or cell level* wood is a porous solid, formed by hollow tube-shaped cells with *diameters of several micrometers* and *lengths in the order of millimeters*. These cells are called tracheids. Among wood wall layers, the secondary cell wall layer S_2 is by far the thickest one (Fengel et al. 1989, Zickler et al. 2007). On the *nanometer scale*, the cellulose microfibrils are alignated parallel to each other, surrounded by hemicelluloses and lignin (Frengel et al. 1989, Zickler et al. 2007, Saren et al. 2006).

Wood biomass is composed of c*ellulose, hemicelluloses, lignin, extractives, and mineral materials* also called ash (Campbell 1983, Klass 1998). The cellulose, hemicelluloses and lignin form the polymeric structure of the biomass cell walls.

1.1. Cellulose

Cellulose is the most abundant organic substance on earth; a mass in the order of $2x10^{15}$ kg exists at any one time. This has an equivalent energy content nearly two orders of magnitude greater than man's total annual energy consumption (Campbell 1983).

Cellulose is a linear polysaccharide which is composed of between 10,000 to 15,000 glucose units linked by ether bonds (Glycosidic bonds) (see Figure 1) (Klass 1998). Cellulose cross-linked molecular chains in long segments help to create strong associative forces by hydrogen bonds reinforcing the flat, linear configuration of the chain. The cellulose can be found in amorphous or crystalline phases.

Native metastable Cellulose I is generally found as a mixture of (1) triclinic cellulose Iα and (2) monoclinic cellulose Iβ.

While the Iα component is dominant in the cellulose produced by primitive organisms, that produced by plants has the Iβ form as dominant (Zickler et al. 2007, O'Sullivan 1997, Zhao et al. 2006, Mazeau and Heax 2003). The way in which sheets of chains are stacked along the microfibril differs between the Iα and Iβ forms. The central chain of the monoclinic phase is slightly rotated with respect to the corner chain. The Iβ phase has a larger number of intermolecular hydrogen bonds than the Iα phase. In fact, the Iβ phase is stabilized alternatively

by recurrent (O_2-O_6) and (O_3-O_6) hydrogen bonds, whereas the Iα phase displays a looser network of intermolecular hydrogen bonds, which are less relevant for the stabilization of the crystalline structure (Mazeau and Heux 2003).

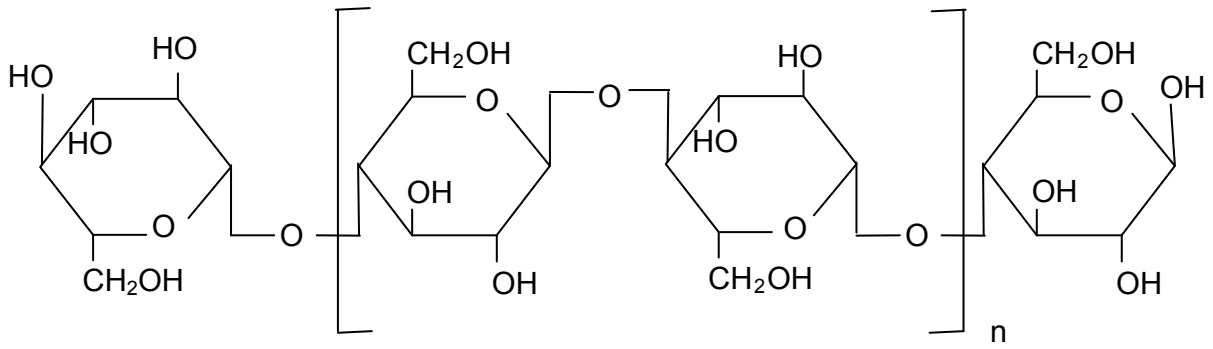


Figure 1. Cellulose Structure

Cellulose I can be recrystalyzed to become the thermodynamically more stable cellulose II, which has an anti-parallel arrangement of the strands and some inter-sheet hydrogen bonding. Cellulose II contains two different types of anhydroglucose (A and B) with different bond structures, the chain consisting of A-A or B-B repeated units.

While the amorphous parts of cellulose are readily accessible by water and reactants, access to these molecules is greatly limited by the crystal structure and hydrogen bonding of crystalline cellulose.

1.2. Hemicellulose

Hemicellulose is composed of linear polysaccharides formed of D-glucose, D-galactose, D-mannose, L-arabinose, D-xylose and acid 4-O-methyl D-glucopyranoic, all of which are highly substituted with acetic acid. It is a mixture of mainly pentoses (chiefly xylose), with lesser amounts of arabinose, glucose, mannose and galactose, so there is a hexose component as well (Campbell 1983). The structure of the hemicelluloses is very complex and less thermally resistant as a result of the diversity of sugars. The molecular chains are not linear and contain many secondary branches. Hemicellulose is amorphous because of its branched nature. In Figure 2 is presented a simplified hemicellulose structure consisting only in D-xylan units linked in the 1- and 4- positions. The carbohydrates (cellulose and hemicelluloses) are also known as hollocellulose fraction.

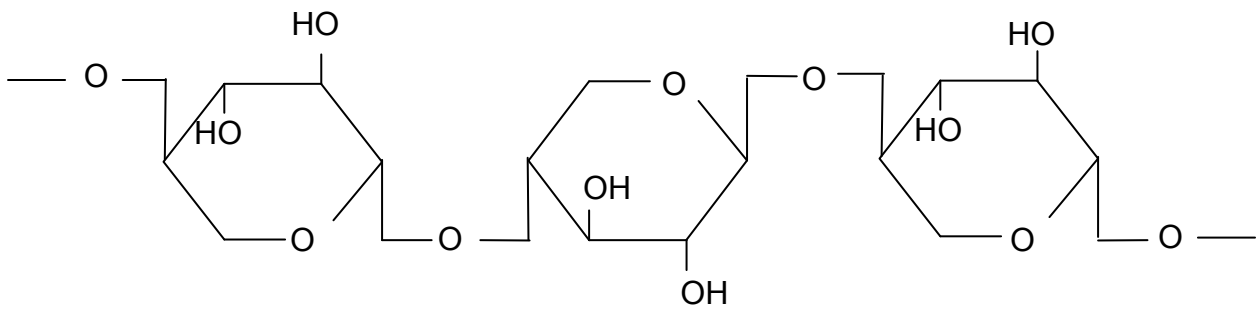
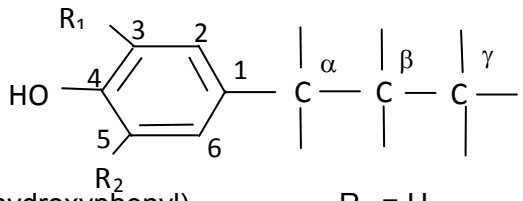


Figure 2. Hemicellulose Structure

1.3. Lignin

The lignin is chemically associated to the cellulose and hemicelluloses. It is heterogeneous polymers consisting of phenylpropane units linked through various ether and C-C linkages. The function of lignin in wood is that of a cement that interpenetrates the fibrous cellulose and hemicellulose. Lignin binds them into three-dimensional structures and protects their linkages from chemical and microbial attack. The lignins are described as polymeric natural products arising from enzyme-initiated and chemically driven dehydrogenative polymerization of primary precursors possessing a p-hydroxycinnamyl alcohol structure. Figure 3 summarizes the structure of common phenylpropane monomers forming the lignin.



For: Hydroxyphenyl (4-hydroxyphenyl) R_1 = H R_2 = H

For: Guaiacyl (3-methoxy-4-hydroxyphenyl) R_1 = H R_2= OCH_3

For: Syringyl (3, 5-dimethoxy-4-hydroxyphenyl) R_1 = OCH_3 R_2= OCH_3

Figure 3. Structure of the Carbon Skeleton of the Lignin Monomeric Units

The general complexity of the chemical structure of lignin in terms of inter-monomeric linkages can be explained by the random reactions of the phenoxy radicals. A general scheme representing the molecular structure of softwood lignin is presented in Figure 4.

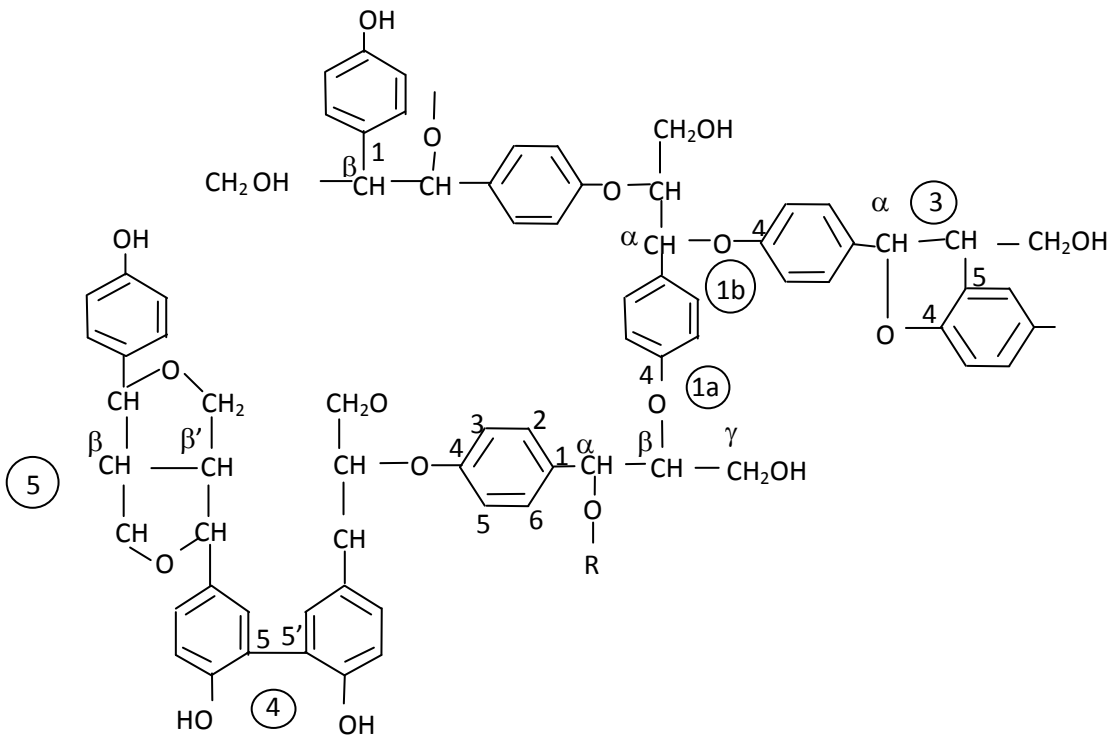


Figure 4. Lignin Structure (Dey et al. 1989)

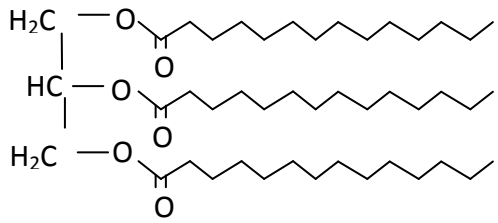
Clear differences between hardwood and softwood are observed in the frequency of 5-5' and in 4-o-5' linkages (Dey et al. 1989). This can be explained by the additional methoxy group found at carbon 5 of syringyl monomers (the syringyl groups are only observed in hardwood-derived oils). In guaiacyl lignin of conifers, there are about 20-25% of very stable carbon-carbon linkages at C-5 of the guaiacyl unit, while this value is only 10% in the case of the syringyl-guauacyl lignin in hardwood. The most common links observed are β-O-4 ether bonds (C-O-C) (approximately 60 mass % in hardwood and 50 mass % in softwood) (Murwanashyaka 2000, Radlein 1999). Lignin can occur linked to hemicelluloses sugars, such as xylose, arabinose, mannose and glucose or to phenolic acids by ether linkages. Further associations between lignins and other cell wall polymers such as glycoproteins and tannins are also possible (Dey et al. 1989).

1.4. Extractives

The extraneous compounds that do not form part of the biomass polymeric walls are called extractives. Extractives are organic products that can be extracted by hot water or with the aid of organic solvents. The extractives are products that confer odor, colors and durability to the wood. These compounds are a way to protect the trees against predators. Bark contains 4-5 times more extractives than bark-free wood.

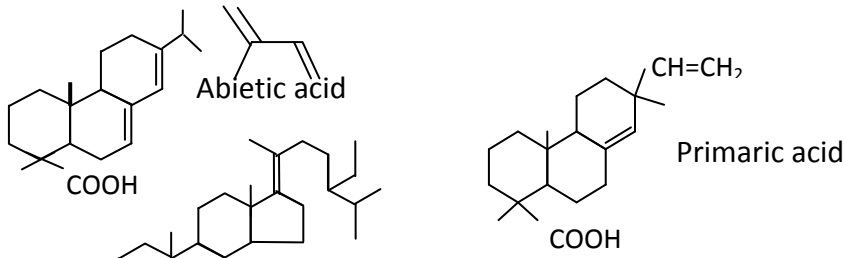
Fatty acids:	$CH_3\text{-}(CH_2)_n\text{-}CO_2H$	n= 10-30
ω-Hydroxy fatty acids:	$HOCH_2\text{-}(CH_2)_n\text{-}CO_2H$	n= 10-28
Dicarboxylic acids:	$HO_2C\text{-}(CH_2)_n\text{-}CO_2H$	n= 14-26
Fatty alcohols:	$CH_3\text{-}(CH_2)_n\text{-}CH_2OH$	n= 14-28
n- Alkanes:	$H_3C\text{-}(CH_2)_n\text{-}CH_3$	n=12-38
Ketones:	$CH_3\text{-}(CH_2)_{n1}\text{-}CO\text{-}(CH_2)_{n2}\text{-}CH_3$	
Aldehydes	$CH_3\text{-}(CH_2)_n\text{-}CHO$	

Triglycerols:

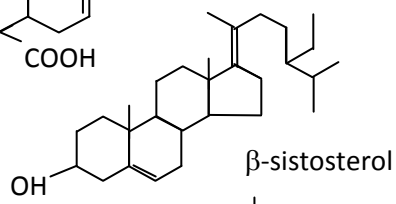


Terpenes: (Isoprene C_5H_8)

Resin acids:



Sterols:



Triterpenoids:

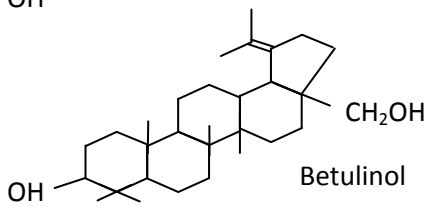


Figure 5. Some Chemical Families Found in Extractives.

Major differences between bark and bark-free wood are in the high molar mass polyphenols and hydroxyl-acid complexes (the most common of which is suberine). The extractive content of needles is 7-8 times higher than in bark-free wood. The resenes (terpenes) represent a class of hydrocarbon extractives synthesized from the molecules of isoprenes or 2-methylbutadiene that are very common in coniferous wood (softwood). Just as “six” may be considered as a “magic number” for the carbohydrate products of plants, with hexose building blocks containing six carbon atoms, so “five” may be regarded as a “magic number” for many of the hydrocarbon products found in plants. Most of these hydrocarbons are unsaturated and are built up of isoprene molecules (C_5H_8). Monoterpenes (two isoprene units) ($C_{10}H_{16}$) predominate among the volatile terpenes in softwood bark. Monoterpenes may be acyclic (as in myrcene), cyclic (as in limonene) or bicyclic (as in α-pinene) (Campbell 1983). Hardwood contains mainly

sesquiterpenes ($C_{15}H_{24}$). These compounds are in the range of Diesel molar mass (C_{12}-C_{18}). The terpenes are unstable compounds which readily undergo condensation and rearrangement. The terpenoids are terpenes with substituted groups on the basic structural units. Figure 5 represents some of the main families that can be found in the extractives.

1.5. Ash

The mineral materials (ash) are composed mainly of carbonates, sulfates and phosphates of silica and metals from the first and second group of the Periodic Table (Ca, Mg, Na and K).

Chapter 2. Pyrolysis Technologies and Their Environmental Impact

2.1. Fast Pyrolysis Technologies

The use of plant biomass to satisfy our energy needs is as old as human history. In the 1800s biomass provided 99% of the world's primary energy mix. The decline in the use of biomass started almost at the same time as construction of the first petroleum refinery in Baku in 1861. The petroleum industry produced a cheap liquid that fuelled the industrialization and increased the standard of living of the richest fraction of the world's population (Huber et al. 2006). Today biomass only accounts for 14% of the world's energy consumption, and its use is concentrated either in very poor under-developed nations, in Brazil, or in a few very advanced Scandinavian countries.

The United States consumes 7 x 10^9 barrels of oil every year. An important part of this oil could be replaced by 1.3 x 10^9 metric tons of dry biomass (almost 3.8 x 10^9 of barrels of oil energy equivalent) that could be produced sustainably every year (Huber et al. 2006, Energy Information Administration Annual Energy Outlook 2007 With Projections to 2030 (http://www.eia.doe.gov/oiaf/archive/aeo07/index.html).

A gradual shift to a biomass-based economy to replace at least 20% of transportation fuel and 25% of chemicals has been predicted by 2030 (Huber et al. 2006, Biomass Research and Development Technical Advisory Committee Roadmap for Biomass Technologies in the United States, 2007 (http://www.eere.energy.gov/biomass/pdfs/obp_roadmapv2_web.pdf)).

Biomass fast pyrolysis can certainly have a role in achieving this goal. Fast pyrolysis can directly convert up to 75% of the biomass into a liquid which can be readily stored or transported (Bridgwater et al. 1999). The oils could be generated in distributed pyrolysis units close to biomass resources and then transported to centralized bio-refineries where second-generation transportation fuels and high-value chemicals could be produced taking advantage of the economies of scale. These features open important opportunities to develop a new model of biomass economy formed by distributed pyrolysis units and centralized bio-refineries.

The pioneering work in the 1980s at the University of Waterloo and at the National Renewable Energy Laboratory established the fundamentals for the modern fast pyrolysis technologies. Although the principles of fast pyrolysis are similar to those in the traditional charcoal industry, this technology is an advanced concept carefully controlling the reaction conditions to maximize the yields of oils (Bridgwater et al. 1999). This process is usually performed at around 500°C (932°F), in the absence of oxygen with high heating rates and ensuring short vapor residence times inside of the reactors (Bridgwater et al. 1999). To convert from degree Celsius (°C) to degree Fahrenheit (°F) please use the following conversion equation: $^{o}F = (1.8 \times {}^{o}C) + 32$

Although four technologies are currently available for commercialization: (1) fluidized beds (2) vacuum pyrolysis (3) ablative pyrolysis and (4) circulating fluid beds, none of these concepts fully satisfies all the requirements to develop pyrolysis units with reasonably trouble-free operation, proven scale-up technology, and economically competitive performance (Scott et al. 1999). The more popular configurations use fluidized bed technology (see Figure 6) (Huber et

al. 2006, Vanasse et al. 1988). An exhaustive analysis of the present status of biomass pyrolysis technologies is not possible within the scope of this review. Excellent reviews on biomass fast pyrolysis technologies can be found elsewhere (Mohan et al. 2006, Meier et al. 1999, Kersten et al. 2005, Czernik et al. 2004, Bridgwater and Peacocke 2000).

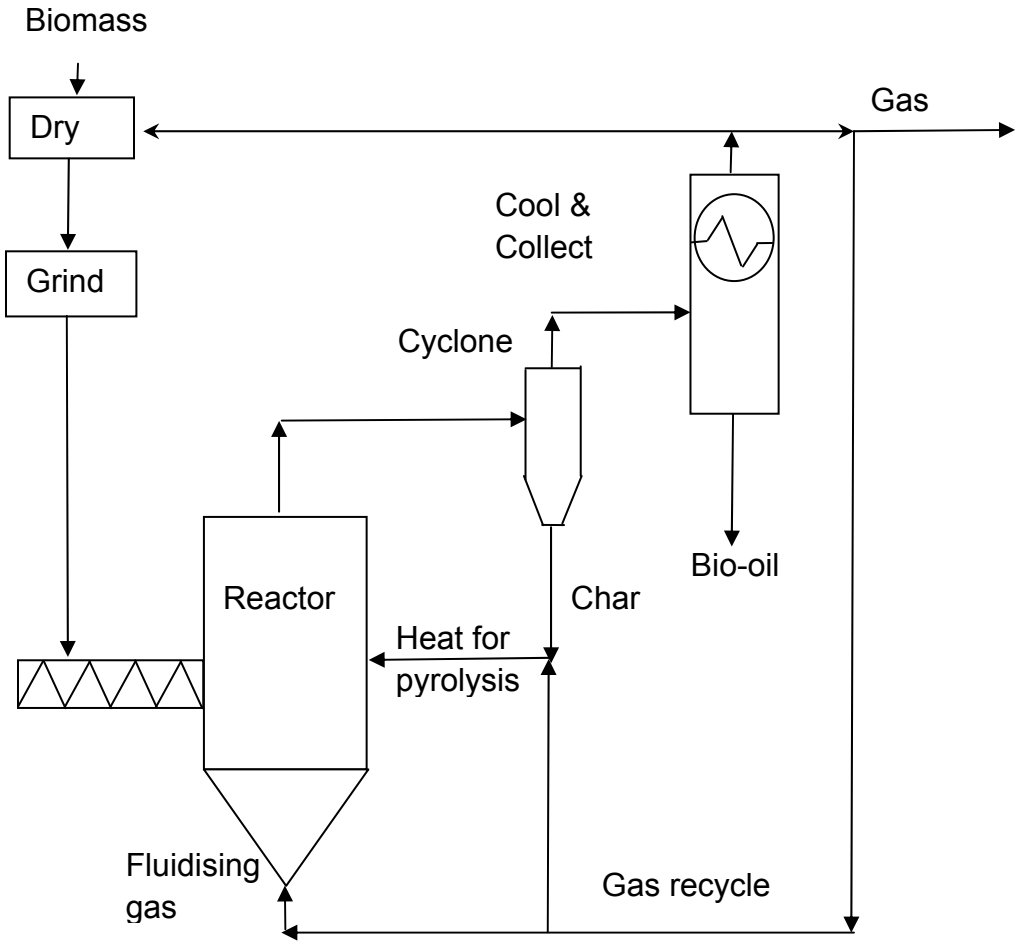


Figure 6. Conceptual Fluid Bed Fast Pyrolysis Process

Better temperature control, efficient heat transfer, and short residence times for vapors are the main advantages of fluidized beds. Existing fast pyrolysis units based in fluidized bed technologies and using large volumes of carrier gas and particles in sizes of less than 2-3 mm are not well suited to operating as mobile units. The high gas-to-biomass fed ratio results in a lowering of the thermal efficiency which is typically in the order of between 60 and 70% (Huber 2006).

The decomposition of biomass bio-polymers results in vapors, aerosols, gases and some charcoal. Cyclones and condensers are installed downstream of the pyrolysis reactors. A dark brown liquid called bio-oil with heating value of almost half that of petroleum-derived fuels is collected in these condensers. Bio-oils are miscible mixtures of between 75 and 80 mass % of polar organics and between 20 and 25 mass % of water (Bridgwater et al. 1999).

2.2. Environmental Impact of Pyrolysis Technologies

Although it was not possible to find any study fully devoted to study of the environmental impact of modern fast pyrolysis technologies, several reports on the impact of traditional charcoal kilns can be found in the literature.

The effect on forest soils of smoke emissions from Polish charcoal kilns has been documented by Uvarov (2000), Fischer (1999) and Focht (1999) have documented the effect on forest soils of smoke emissions from Polish charcoal kilns. Higher carbon content, higher carbon to nitrogen ratios, and more acidity were found in the soils exposed to smoke. These soils also exhibited higher density of soil nematodes and a larger density and diversity of collembolans and oribatid mites. Most of the data collected from soils exposed to smoke show a markedly higher level of soil biological activity. Differences in the ammonification, nitrification and mineralization process of soils exposed to smoke were also reported. The degradation potential and soil carbon mineralization of biomass gasification tars have been studied by Aldas et al. (2007). The biodegradation of tars was relatively low, indicating recalcitrance.

Researchers from the University of Waterloo (Radlein et al. 1997) have used smoke condensed fractions for the production of slow release fertilizers. In fact, concentrations up to 10 mass % of nitrogen can be incorporated by direct reaction with bio-oil functional groups. The carbonyl functional groups in smoke react with ammonia and urea. The formation of natural slow release fertilizers in soils exposed to smoke is a hypothesis that cannot be ruled out.

Very interesting research on the characterization of waste tar associated with abandoned wood pyrolysis plants from last century at the Allegheny High Plateau in Northwest Pennsylvania was performed by Edenborn and Severson (2007). More than 70 pyrolysis plants were operated in this region between 1800 and 1930. These plants operated by salvaging the small unwanted hardwood trees left behind by the lumber mills. The main products were charcoal, calcium acetate and methanol. The vapors obtained in slow pyrolysis reactors were condensed to form “pyroligneous acid” which is a complex chemical mixture that primarily contains water, methanol, acetic acid and phenols as well as insoluble and soluble tars. These tars had little commercial value at the time and were typically discharged. A hard crust, poor in volatiles and with higher softening point, is observed after exposing the tars to air. Water soluble compounds in the tar follow a dilution pattern similar to that described for other dense non-aqueous phase liquids which have an initial quasi-instantaneous release attributed to a surface washing phenomenon. Additional release is limited by the transfer from the solidified tar to the surface. The compounds released are mainly phenols and some PAHs which are toxics to some micro-organisms. The half life of phenols in natural waters is relatively short due to microbial degradation and photolysis (Edenborn and Severson 2007). Thus, specific threats to aquatic species are limited to those organisms exposed to elevated concentrations of these species near point sources. Overtime these tars erode to form a powdered soil colonized by lichens and mosses.

An excellent study of bio-oil toxicity has been produced by researchers from CIRAD (http://www.pyne.co.uk/docs/BIOTOX%20Final%20Publishable%20report.pdf). Nineteen samples were collected from several producers using fast pyrolysis oils produced in: ablative, fluidized, and circulating beds reactors. Furthermore, two samples resulting from two slow pyrolysis processes were also characterized. Very similar results in terms of toxicity, eco-toxicity and bio-degradability were obtained in spite of the important variation in the composition of studied oils. Fast pyrolysis oils seem to be more benign than slow pyrolysis derived tars

although these oils take longer to bio-degrade. Bio-oil degrades faster and is less toxic than traditional petroleum fuels. The material safety data sheet and the rules for transportation, storage and handling of biomass derived fast pyrolysis liquids can be found elsewhere (http://www.pyne.co.uk/?_id=29).

Researchers around the world are now working to identify the origins of a highly fertile human made soil known as *Terra Preta* found in regions close to the Amazonian basin in Brazil (Glaser et al. 1998, 2001a, b). Terra Preta soils are known for their thick (40-80 cm) black horizons together with the presence of ceramic, charcoal and carbon black particles. Their distribution stretches mainly along waterways from eastern Amazonia to the central Amazonia basin with sizes ranging from less than 1 ha to more than 100 ha (Glaser et al. 1998, 2001a, b). Lehmann et al. (2002, 2003) found that Terra Preta soils have significantly higher P, Ca, Mn and Zn availability and lower nutrient leaching than the surrounding soils which helps increase the yields of cowpeas and rice by 38-45 % without fertilization. Low leaching is responsible for a high nutrient availability ensuring a sustainable agriculture (Lehmann et al. 2002, 2003). ^{14}C studies conducted by Glaser (2001) age the period of formation of these soils between 500 and 2500 years ago. The organic matter in this soil could reach up to 150 g/kg, 35% of which is carbon black.

The high content of carbon black in Terra Preta soils is a good indication of an origin associated with thermo-chemical events with poor oxygen supply, similar to those found in earth pits still used for charcoal making in most developing nations. The use by natives of underground incineration methods to dispose of domestic wastes rich in proteins could be at the origin of these unique soils.

Most of the studies so far conducted to elucidate the increase in fertility of Terra Preta soils were designed to investigate the impact of char (Lehmann et al. 2002, 2003, Kishimoto et al. 1985, Shido et al. 2004). It has been found that the addition of charcoal increases plant growth and nutrition while the leaching of applied N, Ca, and Mg is significantly reduced (Lehmann 2003).

There are very few studies on how charcoal physico-chemical properties influence ecological processes. Gundale and DeLuca (2006) studied how several ecological properties of charcoal vary as a function of formation temperature and the source of woody material from which it is formed in pondersosa pine/Douglas-fir (Pinus ponderosa/Psuedotsuga menziessi) ecosystems. These authors generated charcoal in the laboratory at two temperatures (350 and 800°C) from four source materials (bark and wood from mature Douglas-fir and ponderosa pine trees). Higher net ammonification levels relative to the no-charcoal control in all charcoal types (except 800°C) ponderosa pine bark) were observed. High temperature charcoals also demonstrated higher extractable NO_3^-, pH, electrical conductivity, and total C content.

Ahmed et al. (1989) characterized the solid residues resulting from the vacuum pyrolysis of Populus tremuloides. Chars are polyaromatic macro-molecules with aromatic rings bonded to the solid matrix. This attachment to the char matrix contributes to a reduced leachability of these compounds in water or other organic solvents. Although the char is material formed by large systems of PAHs, it was not possible to find any study on the leacheability of these compounds from char.

Chapter 3. Polyaromatic Hydrocarbons (PAHs) and Dioxins in Pyrolysis Products

3.1. Polyaromatic Hydrocarbons

Polyaromatic hydrocarbons (PAHs) are recognized as important environmental pollutants resulting from both natural and anthropogenic sources (Pakdel and Roy 1991). The inherent carcinogenicy and mutagenesis of some PAHs makes their emission into the environment a serious public concern. Natural sources include forest fires, volcanoes and in situ synthesis from degradation of biological materials (White and Lee 1980, Pakdel and Roy 1991, Bartle et al. 1981). Major anthropogenic sources include, among others, the burning of coal refuse banks, coke production, automobiles, commercial boilers and incinerators, wood stoves, and wood gasifiers. The literature devoted to study the formation of PAHs during thermo-chemical processes is very large and includes studies of gasification, combustion and pyrolysis. Excellent reviews on the formation of these compounds during gasification and combustion can be found elsewhere (Mastral and Callean 2000, Baek et al. 1991, Richter and Howard 2000).

It is well known that PAHs are formed in large quantities as the result of secondary thermo-chemical reactions at temperatures over 700°C (1292°F) (Ledesma et al. 2002). There are some evidences suggesting that very small amounts of these compounds can also be formed in the range of temperatures used in pyrolysis reactors (350 - 600°C) (662°F -1112°F). Thus, there is a need to examine the mechanisms and kinetics involved in the creation of these compounds as a way to limit their synthesis during pyrolysis.

Researchers from CIRAD (Centre de Cooperation International en Recherche Agronomique pour le Developpement (http://www.biomatnet.org/publications/1733fin.pdf) found that typical concentrations for total PAH in fast pyrolysis oils are below 10 ppm. The slow pyrolysis oil samples exhibit much higher values for PAH, with one of the two samples studied slightly exceeding 100 ppm. Bio-oils produced at temperatures exceeding 550°C (1022°F) had the highest PAH values for fast pyrolysis samples, ranging as high as 23 ppm at 600°C (1112°F). The lowest PAH concentration was found in a sample produced at 425°C (797°F).

Pakdel and Roy (1991) studied the content of polyaromatic hydrocarbons oils produced by vacuum pyrolysis from debarked Populus deltoids at temperatures under 500°C and of a gasification tar obtained at temperatures over 800°C (Pakdel and Roy 1991). While the content of polyaromatic hydrocarbons in the pyrolysis oils was in the range between 0.3-0.4 mass % (Pakdel and Roy 1991, Elliott et al. 1983), the tars from biomass gasification obtained at temperatures over 700°C (1292°F) showed concentrations of these compounds as high as 85 mass %. Concentrations of naphthalene of around 200 ppm in bio-oils obtained from the Auger Pyrolysis of bark were also reported by Ingram (2008).

Pakdel and Roy (1991) noted that the composition of the hydrocarbons obtained at temperatures around 500°C (932°F) are highly branched in nature (see Table 1). Branched PAHs are known to have lower environmental and toxicological impact compared with the tars obtained at high temperature, which tend to be less oxygenated in structure. Hydrocarbons produced at higher temperatures (over 700°C (1292°F)) typical of gasification processes are

highly condensed polyaromatic hydrocarbons with a high level of mutagenic activity (see Table 2) (Elliott and Baker 1986a, 1986 b). Table 2 shows the quantification of the content of polyaromatic hydrocarbons in gasification oils as reported by Pakdel and Roy (1991).

Table 1. Content of Polyaromatic Hydrocarbons in Vacuum Pyrolysis Oils at 500˚C (932°F) (Pakdel and Roy 1991)

Compound	Amount on total pyrolysis oil (ppm)	Compound	Amount on total pyrolysis oil (ppm)
1-Pentylbnzene to Nonadecylbenzene	11.8	Anthracene	0.5
2-Pentylbenzene to Nonadecylbenzene	13.0	Fluroanthrene	1.5
Naphthalene	4.9	Pyrene	2.5
Acenaphthylene	1.0	Benz(a)antracene	1.1
Acenaphthene	0.5	Chrysene	2.5
Fluorine	3.8	Benzo(a)pyrene	0.2
Phenanthrene	3.3	Benzo(k)flouranthene	0.8

Table 2. Content of PAHs in Wood Gasification Tars at 700°C (1292°F) (Pakdel and Roy 1991)

Compound	Amount on total tar (mass %)	Compound	Amount on total tar (mass %)
Ethylbenzene	0.68	Ethenylanthracene	0.27
Dimethylbenzene	1.62	Methylanthracene	1.76
1,3,5,7-cyclooctatetraene	0.68	4H-cyclopenta(def)phenanthrene	1.76
Propynylbenzene	4.07	Methylphenanthrene	0.41
7-methylbenzofuran	0.14	Fluoranthene	3.93
1-methyl-4-(1-propynyl)benzene	0.14	Pyrene	4.2
1-butynylbenzene	0.14	11H-benzo(b)fluorine	0.27
Naphthalene	15.58	Methylpyrene	2.17
Methylnaphthalene	3.12	Benz(a)anthracene	2.71
Ethenylnaphthalene	2.17	Chysene	2.71
Dimethylnaphthalene	0.27	7H-benz(de)anthacene-7-one	nd
Acenaphthylene	7.72	Methylchrysene	0.41
Acenaphthene	0.54	Benzo(a)pyrene	1.36
4-methylbiphenyl	0.14	Benzo(k)fluoranthene	2.17
Dibenzofuran	1.63	Benzo(b)fluoranthene	1.63
1 H-phenalene	0.27	Indeno(1,2,3-cd)pyrene	1.22
Fluorine	3.93	Dibenzanthracene	0.41
Methylfluorene	0.41	Dibenzanthracene	0.41
Phenanthrene	9.76	Dibenzo(ghi)perylene	nd
Anthracene	2.85	Total	84.99

Although the char resulting from biomass fast pyrolysis is a material formed by systems of PAHs, it was not possible to find any study on the leachability of small PAHs compounds.

3.2. Dioxins and Furans

Although there is abundant literature (Kulkarni et al. 2008, Lavric et al. 2005, Mukerjee 1998, Focant et al. 2004, Fletcher and McKay 1993, McKay 2002, Freeman and Olexsey 1986) dealing with the presence of PCDD/Fs in products from other thermo-chemical reactors (gasification and combustion), it was not possible to find any study on the content of dioxins in

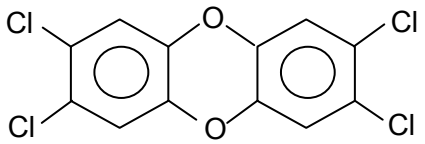
biomass fast pyrolysis products (bio-oils and chars). The paragraphs that follow are devoted to describe some studies in other thermo-chemical systems (especially incinerators).

Although incineration is an efficient way of disposing wastes, it is also a major source of toxic polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) that are released to the environment. The terms PCDD/Fs and dioxins carry the same meaning and are used indistinctly in the literature. All dioxins are solid under standard atmospheric conditions, and present very low vapor pressure and limited solubility in water (Environment Australia 1999).

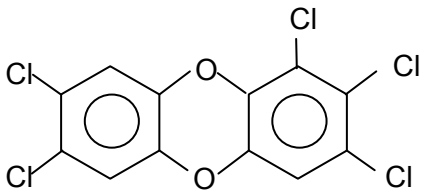
The combustion of organic matter in the presence of chlorine and metals is widely recognized as a triggering factor for the formation of these compounds. Dioxins circulate through the environment once they are generated and are cause of public concern because of their high toxicity (Tuppurainen et al. 1998, 2000).

The PCDD/Fs are chlorinated, planar, aromatic compounds containing two benzene rings. While two oxygen atoms bond a dioxin molecule, a single atom links the furans. Figure 7 shows the structure of the most toxic forms of dioxins and furans commonly tested. The position and number of chlorine atoms attached to the two benzene rings varies. The 75 different forms of dioxins and 135 forms of furans known are called congeners (see Table 2). Dioxins and furans with the same number of chlorine atoms constitute a homologue group of isomers. There are 16 homologues groups, 8 for PCDD and 8 for PCDF. For example there are 22 different isomers of dioxins and 38 of furans belonging to the same tetra-chlorinated homologue groups (Environment Australia, 1999 (http://www.environment.gov.au/settlements/publications/chemicals/dioxins/incineration-review.html).

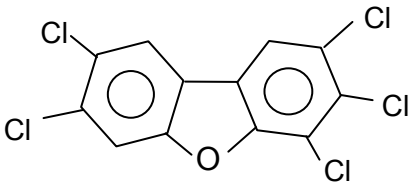
Only the homologues with four or more chlorinated atoms are considered toxic and are called: (TCDD, TCDF or “D4, F4”), penta (PCDD, PCDF or “D5, F5”), hexa (HxCDD, HxCDF, or “D6, F6”), hepta (HpCDD, HpCDF, or “D7, F7”) and octa (OCDD, OCDF, or “D8, F8”). Among these compounds the most toxic compounds are considered the PCDD/Fs that have four chlorinated atoms substituted in positions 2, 3, 7 and 8. The location and the number of chlorine atoms attached to the benzene rings determine the toxicity.



2,3,7,8, - TCDD



1,2,3,7,8,-pentaCDD



2,3,4,7,8-pentaCDF

Figure 7. Toxic Dioxins and Furans (Environment Australia 1999)

The plotting of the relative concentration of homologues and cogeners in a histogram is called "dioxin signature" and can be used to identify the sources of these compounds.

Table 3. Number of Various Isomers of Dioxins (Rappe 1996, Environment Australia 1999)

Number of chlorinated atoms	Number of PCDD isomers	Number of PCDF isomers
1	2	4
2	10	16
3	14	28
4	22	38
5	14	28
6	10	16
7	2	4
8	1	1
Total	75	135

The principal contributors to the creation of PCDD/Fs are medical waste incineration followed by municipal solid wastes (MSW) incinerators and landfill fires (Tuppurainen et al. 1998). The production of dioxin in large incinerators is influenced by the furnace type, the operational conditions, and the type and efficiency of air pollution control systems. Systems ensuring high temperatures and long vapor residence times in the furnace as well as fast cooling of combustion products are likely to achieve low emissions of PCDD/F even while using

feedstocks with large contents of chlorine. Fluidized-bed combustion technologies produce ash with low PCDD/F concentration while grate furnaces are likely to show substantially higher concentration of dioxin in fly ash (Environment Australia 1999 (http://www.environment.gov.au/settlements/publications/chemicals/dioxins/incineration-review.html).

Joung et al. (2007) studied the distribution of dioxins, furans and dioxin-like PCBs in solid products generated by pyrolysis and melting of automobile shredder residues. Low chlorinated congeners represent the major part of dioxins identified. The concentration of PCDD/Fs in char was 0.542 mg/kg. The slow-cooled slag showed a higher concentration of dioxins, which could be due to the regeneration of dioxin occurring in the wide temperature range of 250-400°C. The concentration of PCDDS/Fs in the char decreased by a factor of about 47 when the slag was produced from fast cooling.

The emissions of PCDD/F, PCB and HCB from combustion of firewood and pellets in residential stoves and boilers have been studied by Hedman et al. (2006). The authors assessed the potential emissions of polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated biphenyl (PCBS) and hexachlorobenzene (HCB) from residential combustion of biofuels. Two of the wood combustion experiments included paper and plastic waste fuels. Chlorine-containing plastic waste gave rise to high emissions.

Everaert and Baeyens (2002) assessed extensive data of PCDD/F measurements on flue gas emissions from thermal processes (including municipal solid waste incinerators, combustors of wood and industrial waste, coal fired powerplants and boilers, ferro and non-ferro processes) and pointed out that de novo synthesis is the dominant mechanism in several of these processes where conditions that favor the precursor formation are not experienced. The analysis of PCDD/F profiles from large scale thermal processes in general, and municipal solid waste incinerators (MSWIs) in particular, supports the dominant role of the de novo synthesis, irrespective of the type of thermal process considered. The lack of experimental studies measuring the content of PAHs and dioxins in pyrolysis products is a major hurdle to evaluate the environmental impact of this technology. However, the fundamental studies of biomass thermo-chemical reactions in the range of temperatures between 350 and 600°C could very helpful to identify the existence of a thermo-chemical mechanism that could lead to the formation of these undesirable compounds.

Chapter 4. Biomass Thermo-Chemical Reactions – Moderate Temperatures (350-600°C) (662-1112°F)

This chapter is devoted to describing the thermo-chemical reactions happening at moderate temperatures (350-600°C) (typical of fast pyrolysis reactors) in an attempt to identify links between known thermo-chemical reactions and the formation of PAHs and dioxins.

4.1. Introduction to Biomass Thermo-Chemical Reactions

When the biomass is heated, thermal scission of cellulose, hemicelluloses, lignin and extractives chemical bonds occurs (Boroson et al. 1989a,b, Evans 1987a,b). These reactions are called *primary thermal decomposition (pyrolysis) reactions*. In thermogravimetric analyses of lignocellulosic materials, two or three peaks appear. These peaks can be assigned to each of the biomass macro-components (extractives, cellulose, hemicelluloses and lignin) indicating that their basic identity is maintained (Koufopanos et al. 1991, Varhegyi et al. 1997, Orfao et al. 1999, Caballero et al. 1997). The inorganic ashes (1 mass % in softwood but 15 mass % in herbaceous biomass), especially potassium and calcium, catalyze biomass thermal decomposition reactions. The species formed in this initial depolymerization or fragmentation reactions may not be volatile enough and might undergo additional bond-breaking reactions (secondary thermal decomposition reactions) to form volatile products or they may undergo condensation/polymerization reactions to form high molar mass products like char. There are at least two competitive mechanisms for the formation of char: one initiated and catalyzed by the ash and the other due to the non-catalytic condensation reactions of pyrolysis products (Agblevor et al. 1994).

As the temperature of the biomass particle rises, the pyrolysis decomposition reactions start to take place on a cylindrical reaction front which, progresses toward the core of the particle (see Figure 8). The volatile species released may undergo further reactions within the pores of the particles (*intra-particle secondary reactions*) either homogeneously in the gas phase or heterogeneously by reaction with the partially converted solid biomass or with the char. These intra-particle secondary reactions can be influenced by the rates of volatile mass transfer of the primary pyrolysis products in the cell walls and the diffusion throughout the hollow section of the fiber (Hastaoglu and Berruti 1989).

The pyrolysis vapors are generated on the cell wall and have to diffuse through a very thin layer of char formed on the wall cells into the hollow section of the fiber, and then transfer out of the particle to the bulk of the gas (Hastaoglu and Berruti 1989) (see Figure 8).

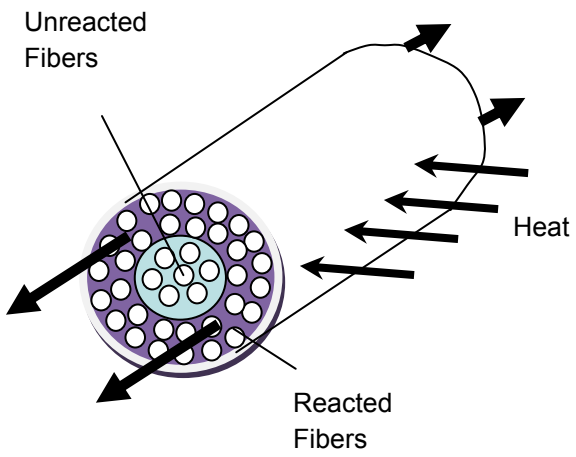


Figure 8. Representation of a Wood Pellet Made Up of Hollow Cylindrical Fibres (Hastaoglu and Berruti 1989)

A series of optical and mass spectrometric studies conducted by Brackmann et al. (2003) on the pyrolysis of wood cylinders with the fibers oriented along the cylinder symmetry axis shows that the strongest signals related to the concentration of pyrolysis products are obtained in circular end of the cylinder. The signal visible at the other cylinder surface was approximately 15 times weaker indicating that pyrolysis vapors tend to diffuse in the direction of the fiber structure. The permeability of wood for different directions relative to the wood fibers was investigated by Comstock (1970). It was found that the permeability in the direction along the wood fibers was many times higher compared to perpendicular to the fibers.

The volatile materials may still undergo additional homogeneous or heterogeneous secondary reactions after escaping the particle (extra-particle secondary reactions). Depending on the reaction conditions, intra and/or extra-particle secondary reactions may exert either a modest or, to the contrary, dramatic controlling influence on product yields and properties. No volatile species have been observed that appear to be formed during secondary reactions from the chemical interaction of cellulose, hemicellulose, lignin and extractives derived components (Evans and Milne1987a, b). Thus, the primary and secondary reactions in vapor phase seem to be dominated by cracking and poly-condensation reactions.

A simplified scheme organizing the pyrolysis complex reaction pathways according to the phase (solid, liquid or gas) and by the range of temperature in which the thermochemical reactions proceed has been proposed by Evans and Milne (1987a, b). The reactions can be classified into pyrolysis, gasification and combustion or as part of three groups: primary, secondary and tertiary regimes (see Figure 9) (Huber et al. 2006).

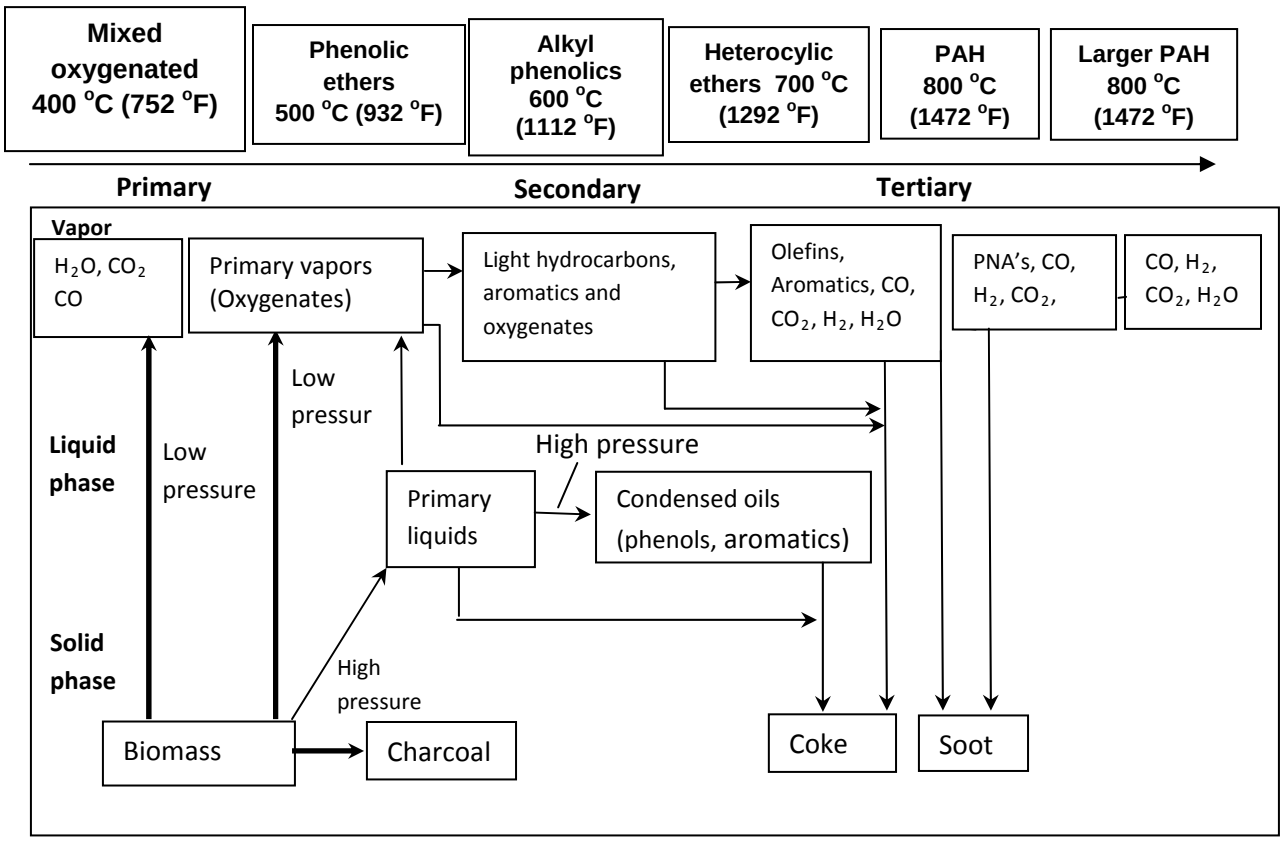


Figure 9. Pyrolysis Pathways (Evans and Milne 1987, Milne et al. 1998)

Figure 9 shows that the formation of polyaromatic hydrocarbons results from tertiary reactions at high temperatures (over 700°C) typical of gasification processes.

The primary oxygenated vapors and liquid resulting from the primary reactions include cellulose-derived molecules (such as levoglucosan and hydroxy-acetaldehyde), their analogous hemicelluloses-derived products, and lignin-derived methoxy-phenols (Milne et al. 1998). During secondary reactions, the primary vapors and liquids form gaseous olefins, aromatics, CO, CO_2, H_2, H_2O, and secondary condensed oils such as phenols and aromatics. The primary vapors undergo cracking and poly-condensation (secondary reactions regimes) when heated above 700°C. The secondary reaction temperature regime is from 700 to 850°C. Additional heating to temperatures between 850 and 1000°C results in tertiary reactions from secondary products forming CO, CO_2, H_2, H_2O, and polyaromatic hydrocarbon (PAHs) compounds including methyl derivatives of aromatics such as methyl acenaphthylene, methyl naphthalene, toluene, and indene. Some tertiary products (chiefly benzene, naphthalene, acenaphthylene, anthracene/phenanthrene, and pyrene) condense to form a liquid tertiary phase (tar). Soot and coke are formed during these secondary and tertiary processes. Coke forms from the thermolysis of liquids of organic vapors. The homogeneous nucleation of high temperature decomposition products of hydrocarbon in the gas-phase produces soot (Evans and Milne 1987).

According to Hajaligol et al. (2001) there are two mechanisms for the formation of polyaromatic hydrocarbons during biomass thermochemical reactions. The high temperature (over 700°C) secondary cracking of pyrolysis products in the gas phase as shown in Figure 9 is considered to be the major pathway for producing aliphatic and aromatic hydrocarbons (Scott et al. 1988, Boroson et al. 1989 a,b, Radlein et al. 1991 a, b, Donnot et al. 1991, Evans et al. 1987). This mechanism is responsible for the formation of very refractive tars rich in PAHs during biomass *gasification*. A second, but less studied, route for aromatics formation that takes place at a moderate temperature (300-600°C) is believed to be the evolution of aromatics from the solid char as it is formed and carbonized during the pyrolysis process. This mechanism is very poorly known so it is not commonly represented in schemes like the one shown in Figure 9.

4.2. Primary Thermo-Chemical Reactions (Reactions in Solid Phase)

Understanding the primary reactions happening in the solid phase is very important to control product selectivity (Kawamoto et al. 2007). This knowledge is also helpful to develop new strategies to reduce the content of undesirable compounds like PAH and dioxins in thermo-chemical processes. The review has been divided by biomass components but stresses cellulose due to the abundance of information on this bio-polymer. The formation of PAHs and dioxins is known to be dependent on the outcome of these primary reactions.

4.2.1. Cellulose

The main condensable molecules resulting from the thermal degradation of cellulose are: levoglucosan, 5-hydroxymethyl furfural, hydroxy-acetaldehyde, acetol, formaldehyde, and oligosugars.

Most of the discussion in this review is devoted to describing the thermal degradation of crystalline cellulose since there are very few studies dealing with the thermal behavior of amorphous cellulose.

Although the thermal degradation of crystalline cellulose has been the focus of passionate discussions for many years, there is still considerable debate over the mechanism and kinetics of these reactions (Piskorz et al. 2000). Several models have been proposed to explain the complex cellulose thermal decomposition pathways. The pioneering model of Broido-Shafizadeh shown in Figure 10 is considered as an important reference since it introduced for the first time the concept of active cellulose to explain the behavior of cellulose pyrolysis. This concept was developed as a consequence of experimental evidences showing the formation of cellulose of lower degree of polymerization at low pyrolysis temperartures (Golova 1975, Pacault and Sauret 1958, Chatterjee and Conrad 1966). Broido et al. (1973) found that crystalline cellulose undergoes a large change in degree of polymerization before weight loss occurs. Bradbury et al. (1979) noted that at low heating temperatures (259-312°C), an initiation period occurs that accelerates with heating time.

Thus, the model of Broido-Shafizadeh (Figure 10) postulates that the cellulose is converted into a more active form and that this is a rate-limiting step followed by the formation of either char, gases, or tar.

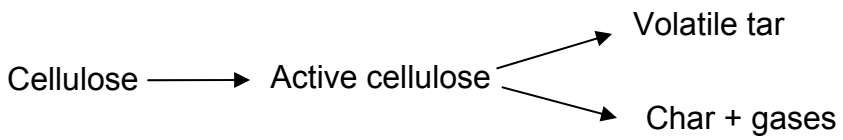


Figure 10. The Broido-Shafizadeh Model (Wooten et al. 2004, Broido and Nelson 1975)

The Broido-Shafizadeh model remains as an important reference for new researchers and as a basis for mathematical models simulating the impact of pyrolysis conditions on the yield of liquids, gases and char. However, this model cannot be used as a tool to develop strategies to control the composition of individual compounds in bio-oils and cannot explain the formation of small amounts of PAHs during some pyrolysis processes.

Several experimental results published in the literature agree that the chemical decomposition of biomass in fast pyrolysis conditions can be represented by two competing reactions: the first a dehydration of cellulose to yield an anhydrocellulose, and the second a depolymerization of cellulose to yield primary leviglucosan as well as other anhydromonosaccharides. The first of these reactions (dehydration) is important at low temperatures and heating rates, but the second becomes the major decomposition pathway at higher temperatures (Piskorz et al. 1986). A number of other earlier researchers had also reported levoglucosan as a significant intermediary product of the decomposition of cellulose (Piskorz et al. 1986).

Figure 11 shows a condensed scheme of the information collected in our literature review on cellulose thermochemical reactions in solid phase. This model could be eventually used to explain the distribution of major products obtained during pyrolysis and for the first time shows the formation of PAHs (Reaction 6) from the char resulting from thermochemical reactions in solid phase. This scheme is used as a guide for discussion in the sections that follow.

Cellulose thermo-chemical degradation reactions in solid phase have been divided into: (1) Low temperature dehydration and de-polymerization reactions, which are relevant to slow pyrolysis processes and torrefaction, (2) De-polymerization reactions at high heating rates, which are relevant to fast pyrolysis processes, (3) Fragmentation or open ring reactions catalyzed by inorganic salts, (4) Acid catalysed dehydration reactions, (5) Polymerization of anhydrosugars, (6) Crosslinking reactions of fragmentation products, and (7) Evolution of polyaromatics from char.

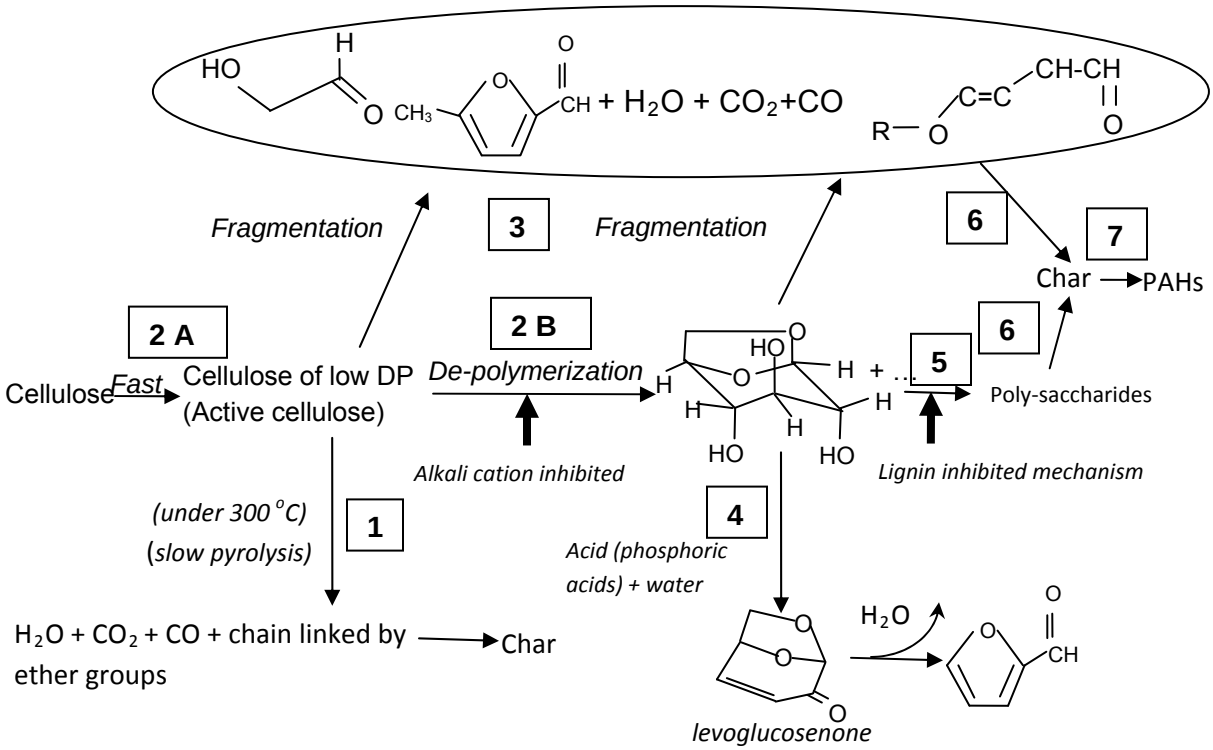


Figure 11. Cellulose Thermo-Chemical Degradation Reactions

LOW TEMPERATURE REACTIONS *(Reaction 1 Figure 11)*

Heat treatment of wood at temperatures under 250°C contributes to thermal degradation of its constituents and changes in crystallinity. Although some attention has been paid to the relationship between thermal treatment and changes of structure (O'Sullivan 1997, Zickler et al. 2007, Bhuiyan et al. 2000, 2001), very little is known of how these changes affect the structure of the char formed and consequently the outcome of thermochemical reactions responsible for the formation of small amounts of PAHs during pyrolysis.

The reduction in the degree of polymerization when heating the cellulose for several hours (Bhuiyan et al. 2000, 2001) can be associated with the generation of free radicals, elimination of water, formation of carbonyl, carboxyl and hydroperoxide groups, and the evolution of carbon dioxide. These reactions result in a charred residue formed by cross-linking reactions after long heating periods and in the liberation of water (see Figure 12).

The data obtained by Kilzer and Broido (1965) indicate that the exothermic cross-linking reactions take place at temperatures over 220°C with evolution of water. The addition of water to the media could limit these reactions and contribute to the increase in cellulose crystallinity. The products resulting from the low temperature reactions of cellulose do not seem to be of much value.

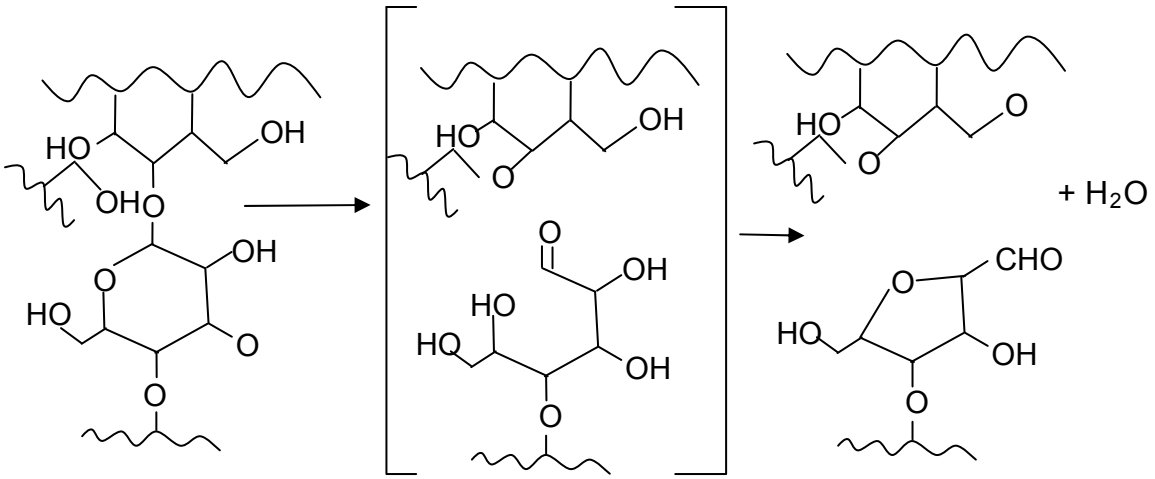


Figure 12. Broido Mechanism of Cross-Linking and Dehydration at Temperatures Under 250°C

Scheirs et al. (2001) suggested that 220°C is the minimum temperature at which chemical water elimination occurs. It is known that cellulose heated at this temperature for several hours produced considerably more char on subsequent pyrolysis at 400°C (Kilzer and Broido 1965). Scheirs et al. (2001) studied these reactions by the evolution of water and proved that a maximum is reached at temperatures between 270 and 310°C depending on the heating rate and the gases in contact with the cellulose.

A very interesting experiment was carried out by Piskorz et al. (1989). These authors pyrolyzed samples of Avicel pH-102 cellulose, which were heated at 200°C several hours in air or in vacuum but with no pretreatment. Yields of levoglucosan and other sugars reached 72% (79% on glucose equivalent basis) for both cases. The degree of polymerization had decreased from the original 227 to 40 (air sample) and to 80 (vacuum sample). This increase in the yield of sugars could be explained by an increase in cellulose crystallinity while the degree of polymerization was reduced.

DEPOLYMERIZATION REACTIONS *(Reaction 2 Figure 11)*

Pyrolysis of cellulose at temperatures in excess of 300°C opens up new reactions. Broido et al. (1973) were the first to propose that the initial depolymerization of cellulose occurs at the boundaries between the crystalline and amorphous regions by random cleavage of glycosidic linkages. Zickler et al. (2007) proposed an anisotropic degradation mechanism starting from the equatorial surfaces of the fibrils, where initial degradation occurs at the boundaries between the crystalline cellulose micro-fibrils and the surrounding hemicelluloses (Zickler et al. 2007).

Golova (1975) postulated the existence of an initial random cleavage resulting in a major reduction in chain length. However, she noted that the chain length rapidly became fairly constant at about 200 to 300 units over a degree of decomposition of the celluloses from 4 to 80%. These cellulose units are called by the Broido-Shafizadeh model as “active cellulose.” She also proposed that the thermal decomposition of the active cellulose to levoglucosan occurred by a splitting off of glucosidic units from the end of polymer chains. The thermal decomposition involved the consecutive chemical conversion of cellulose to monomeric unit, which is converted

by internal isomerization into levoglucosan. So, it is proposed that once a chain reaction is initiated, the whole chain “unzips” (Piskorz et al. 1989).

Zickler et al. (2007) and Kim et al. (2001) concluded that the decomposition preferentially proceeded along the *micro-fibril axes* and that a *crystallite size once started to decompose undergoes rapid decomposition (un-zipped mechanism) while others remain largely intact*. The mechanisms that trigger the unzipping of these units are not well known.

Piskorz et al. (2000) have shown that it is possible to depolymerize a purified cellulose to produce anhydro-oligosaccharides containing small numbers of glucosidic units if suitable reaction conditions are chosen. Carbohydrate analyses showed significant yields of anhydro-oligosaccharides from G_2 to G_7. Normally these compounds made up approximately 50% of the soluble solid fraction. The production of large amounts of oligo-sugars has been often cited as one of the weaknesses of the un-zipped mechanism. This incongruence has fueled considerable debate whether depolymerization takes place by a concerted “unzipping” process or by random breaking of the cellulose chain (Figure 13).

Radlein (1987) proved that between 5 and 13 mass % of the Avicell cellulose was converted to cellobiose (G2). The author justified the production of cellubiosan as an evidence of the existence of inherent tertiary-structural feature of active cellulose, which might encourage the production of dimmers fragments. He proposed the hypothesis that there may be two different kinds of β-1,4 connections, which alternate in the cellulose chain favoring the formation of cellubiose fragments. A similar logic could be used to justify the formation of larger oligomers since the crystalline structure of the “active cellulose” is unknown. The random breaking of the cellulose chain could be also used to explain the existing experimental results. Levoglucosan probably forms by a mechanism involving intramolecular condensation and sequential depolymerization of the glycosidic units as shown in Figure 13.

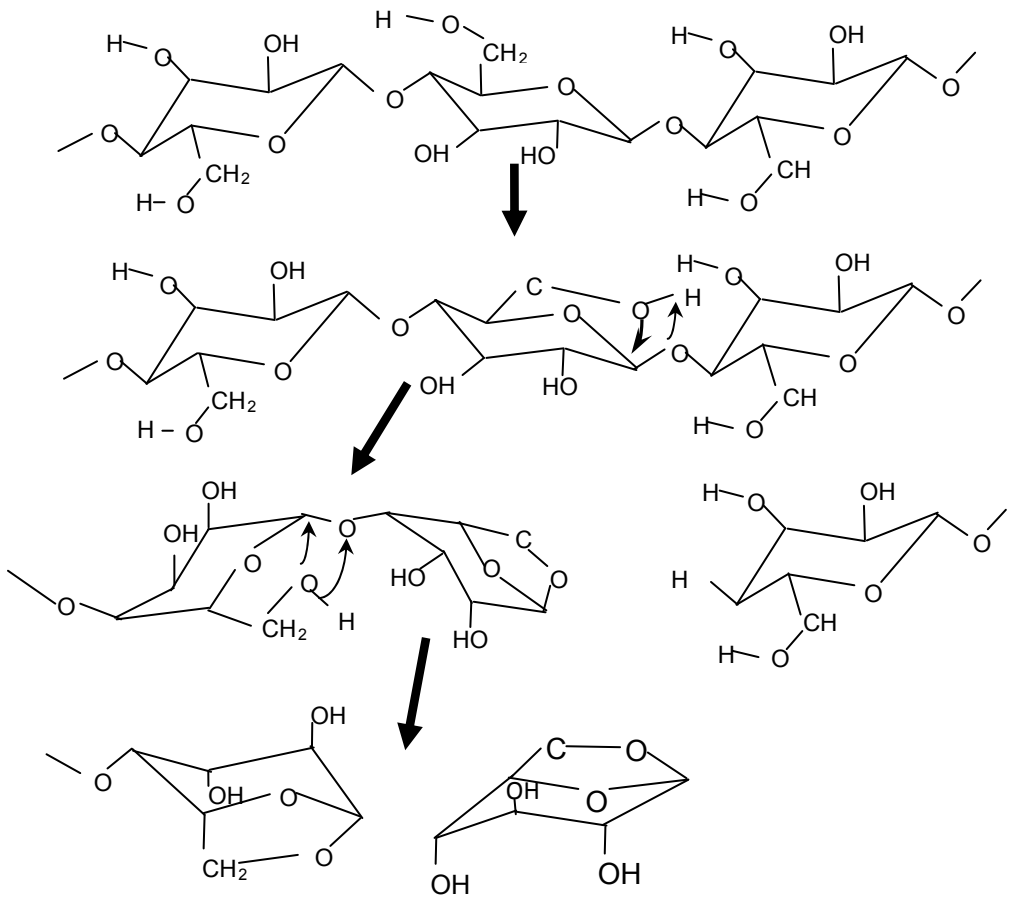


Figure 13. Mechanism for the Random Breaking of "Active" Cellulose (De-Polymerization)

FRAGMENTATION OR OPEN-RING REACTIONS *(Reaction 3 Figure 11)*

It was Broido and Kilzer (1963) who first called attention to one of the most intriguing phenomena associated with cellulose pyrolysis (Radlein et al. 1991a). They noted that very small amounts of inorganic impurities (less than 0.1 mass %) markedly alter the pyrolysis and combustion characteristics of cellulose. The presence of alkali salts has a greater influence on the reaction mechanism than temperature (Huber et al. 2006). There is a strong correlation between the content of ionic substances, the increase in the production of hydroxy-acetaldehyde and the reduction in the yield of levoglucosan during fast pyrolysis (Piskorz et al. 1986, 1988, 1989, Arisz et al. 1990, Lomax et al. 1991)). Di Blasi et al. (2007) studied the catalytic effects of diammonium phosphate on wood pyrolysis and found that the yields of char and water continuously increase at the expense mainly of organic liquid products. Julien et al. (1993) studied the influence of different anions (SO_4^{2-}, Cl^- and NO_3^-) and found that Cl^- and SO_4^{2-} have an important impact accelerating the formation of hydroxy-acetaldehyde and reducing the formation of levoglucosan. However, the effect was not as drastic as the one reported for cations. It was not possible to find any reference to the mechanism by which the

presence of akali salts could affect the structure of resulting char and consequently impact the formation of PAHs.

Piskorz et al. (1986) reported hydroxy-acetaldehyde yields of around 7.6 mass % from the dry hybrid poplar-aspen feed. The cellulose content in this woody biomass is between 39 and 43 mass %. Thus, the yield of hydroxy-acetaldehyde was between 17.4-19.2 mass % of cellulose. Assuming that only one mol of hydroxy-acetaldehyde can be formed per mol of glucose monomer by the schemes shown in Figures 14 and 15, the theoretical maximum yield of hydroxy-acetaldehyde would be 37 mass %. Approximately 50% of the theoretical yield was obtained. This is a clear confirmation that the formation of hydroxyl-acetaldehyde occurs by a very specific and selective mechanism.

Piskorz et al. (1988) proved that, in the absence of these impurities, high conversions of cellulose to levoglucosan (anhydroglucose) could be achieved by fast pyrolysis in a fluidized sand bed (Radlein 1987). Although there are considerable experimental evidences that the generation of anhydrosugars is the first step in the formation of volatile compounds during cellulose slow pyrolysis, it is not clear if this step will also occur during cellulose fast pyrolysis (Piskorz et al. 1986). Two mechanisms have been proposed to explain fast pyrolysis fragmentation reactions.

First Fragmentation Mechanism

The most common view is that the lower molecular weight products form by fragmentation of principal intermediates like levoglucosan and cellobiosan (see Figure 14) (Radlein et al. 1991a, Evans and Milne 1987a, b).

Madorsky et al. (1956) have pointed out that the C-O bonds are thermally less stable than C-C bonds. Consequently two-carbon and four carbon fragments are formed. Hydroxy-acetaldehyde is by far the main molecule with two carbon atoms resulting from fragmentation reactions. The main limitation of this mechanism is that it predicts the formation of molecules of four carbon atoms in yields two times higher than those reported for hydroxy-acetaldehyde. Such molecules at these high yields have not been identified in bio-oils.

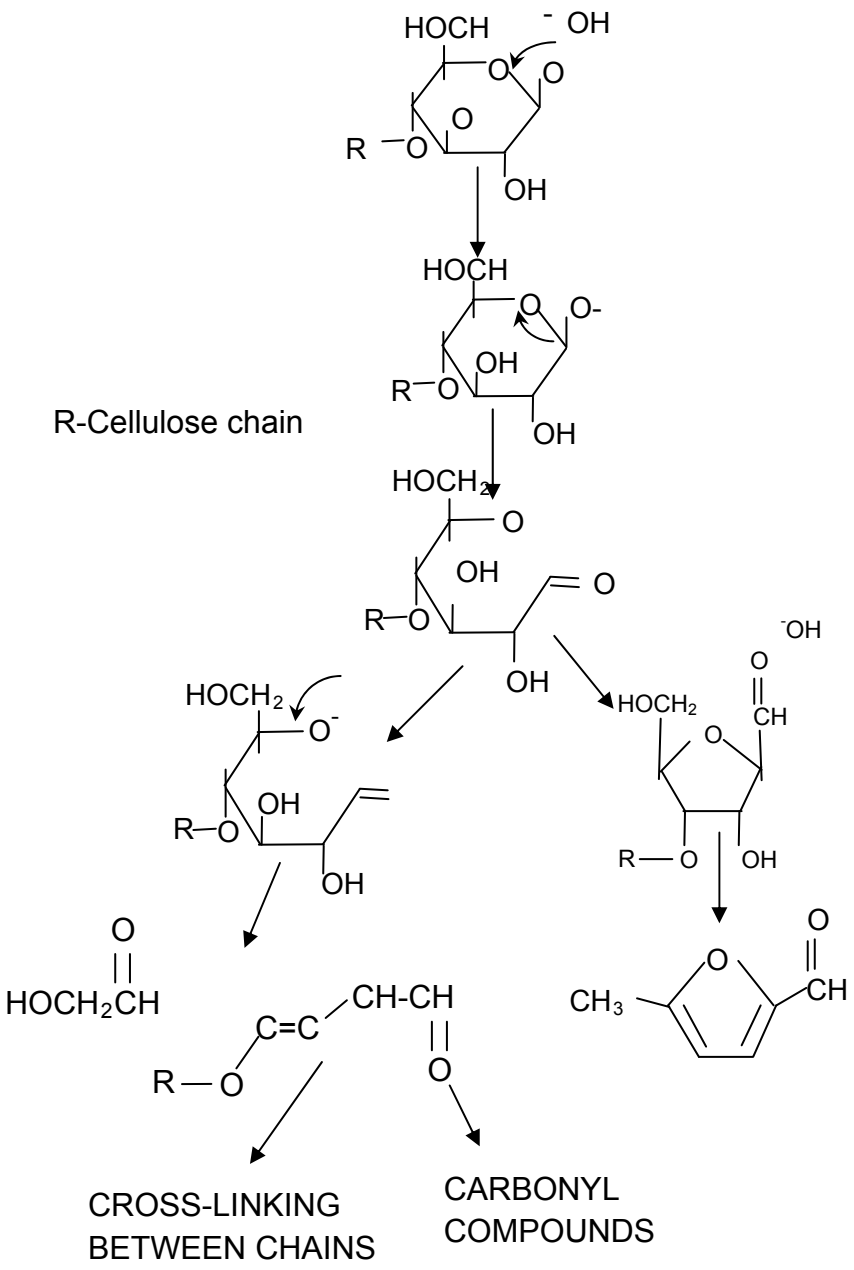


Figure 14. Alkali-Metal Catalyzed Fragmentation Reactions (Evans and Milne 1987a, b)

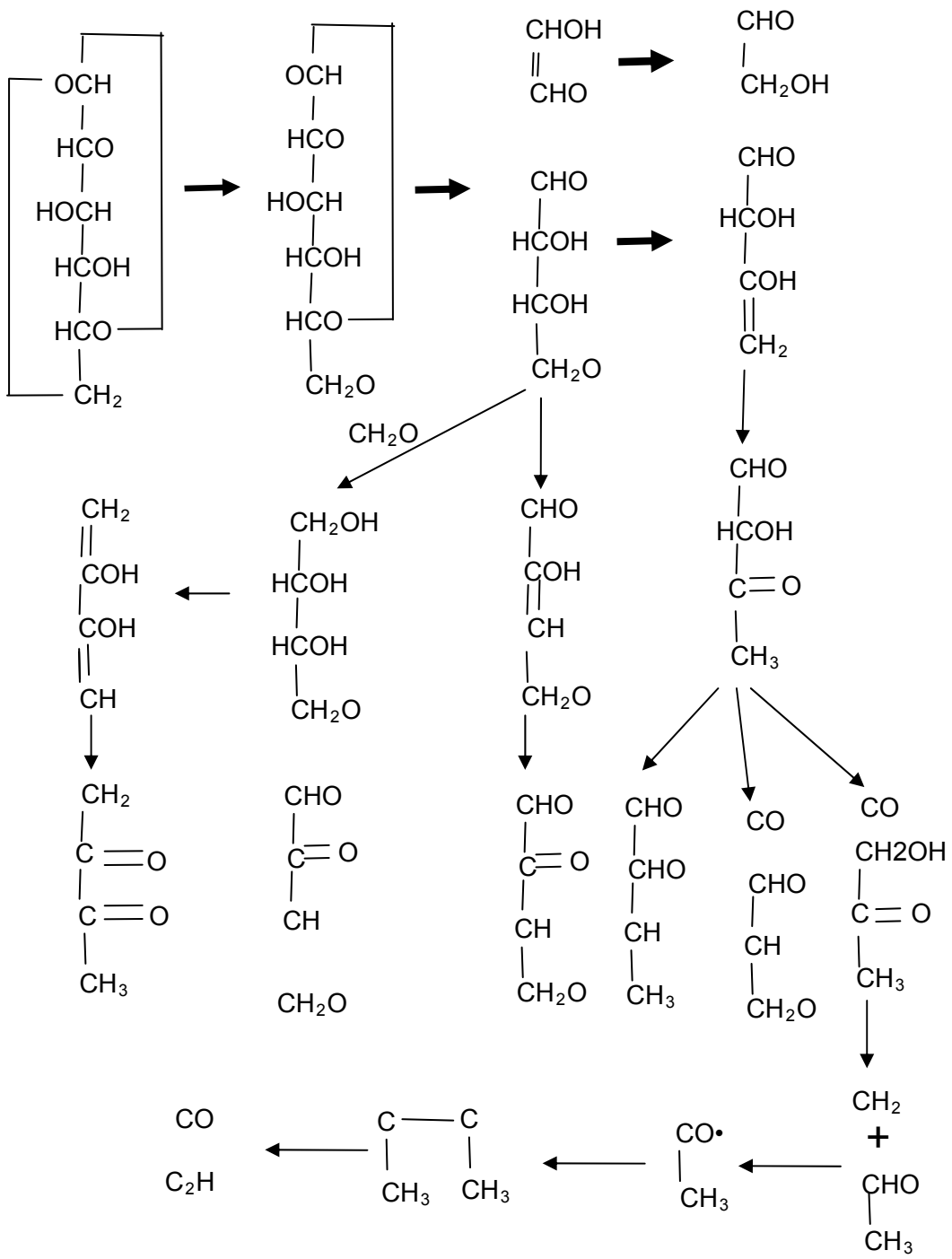


Figure 15. Detailed Fragmentation Mechanism of Cellulose (Byrne et al. 1966, Shafizadeh and Lai 1972, Piskorz et al. 1986)

According to Figure 15 the levoglucosan decomposes via dehydration, retroaldolization and decarbonylation to account for the production of various C_2, C_3 and C_4 compounds. Hydroxy-acetalkdehyde was postulated to be formed by both hydration/dehydration reactions and by retroaldolization, and hydroxypropanals by dehydration/decarbonylation reactions in a similar way illustrated in figures 14 and 15.

Although the scheme shown in Figure 15 suggests the need for the hydration of a levoglucosan unit and its later decomposition, the proposed mechanism might also proceed by direct cleavage and rearrangement of the levoglucosan structure without the initial hydration-dehydration step proposed in Figure 15.

Second Fragmentation Mechanism (Richard's Mechanism)

The second mechanism considers that the formation of levoglucosan is inhibited in the presence of salts and that in these conditions the major alternative decomposition pathway will be a ring scission yielding hydroxy-acetaldehyde as the principal product. This pathway is known as the Richard's mechanism.

Richards (1987) suggested that it is more likely that hydroxy-acetaldehyde forms directly from cellulose by a plausible mechanism involving dehydration followed by retro-Diels-Alder reaction (see Figure 16).

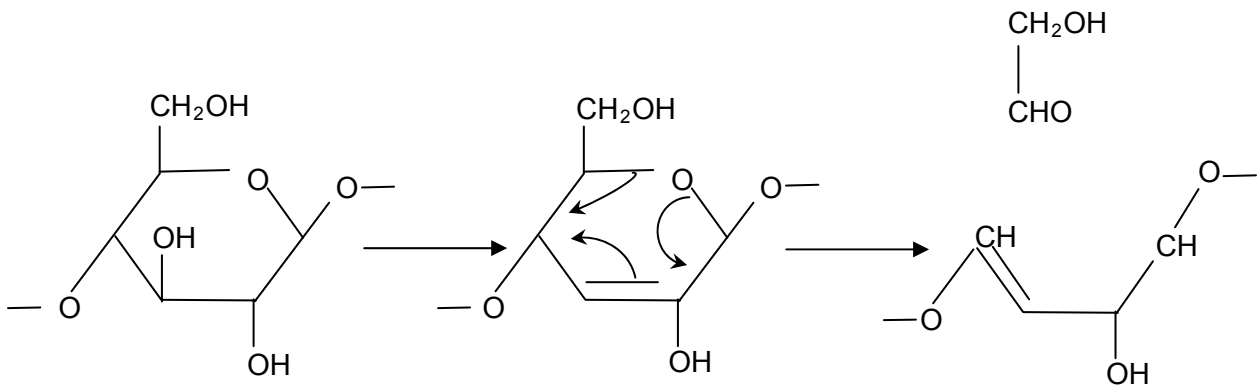


Figure 16. Fragmentation Mechanism Proposed by Richards

It is plausible that the action of an alkaline cation might inhibit the "unzipping" reaction at the terminal units of a chain (Piskorz et al. 1989). Inhibition of the "unzipping" process could explain the large effect of a small amount of ions on levoglucosan formation, especially in view of the rapidity of the pyrolysis reactions at high temperatures. Piskorz et al. (1989) noted the number of free chain ends in cellulose is more or less equivalent to an alkali cation content of 0.05 to 0.06 mass %, which is close to the critical concentration of these cations required to significantly modify the decomposition pathway. Further, in wood these cations are likely to be associated with the hemicellulose by a weak ion exchange type of bonding, which can be easily transferred to stabilize the "active" cellulose crystals. It is known that the depolymerization mechanism starts close to the amorphous zones where the hemicelluloses are abundant.

ACID CATALYSED DEHYDRATION REACTIONS *(Reaction 4 Figure 11)*

While carbonyl compounds, acid and lactones are released by alkali and neutral matrices (NaOH, $ZnCl_2$, NaCl), furans and anhydrohexoses are favored under neutral and acid conditions when using HCl and H_2SO_4 (Radlein et al. 1991b). There is still considerable controversy regarding the mechanism by which acid-catalyzed reactions proceed. Some researchers have even argued that the effect of acids can be explained by the simple removal of the catalytic ash (alkali cations).

Dobele et al. (2001, 2003) found that levoglucosenone predominates in the volatiles of acid catalysed pyrolysis. However, the relative total amount of both 1,6-anhydrosaccharides varied only in a narrow range 75-85% regardless of the impregnation and pretreatment conditions of the celluloses.

Kawamoto et al. (2007) studied the pyrolysis of cellulose in sulfone (tetramethylene sulfone) with sulfuric acid or polyphosphoric acid and found that the acid-catalyzed reactions resulted in levoglucosenone, furfural and 5-hydroxymethyl furfural (5-HMF). Experimental results suggest that the reaction: Levoglucosenone → furfural requires water. Controlling the water content in pyrolysis reactors was found to be a quite effective approach to modify product selectivity.

POLYMERIZATION OF ANHYDROSUGARS *(Reaction 5 Figure 11)*

Wooten et al. (2004) emphasized the poorly studied interactions between the intermediary thermal degradation products (active cellulose, levoglucosan, oligo-sugars) and the reaction mechanism leading to the formation of char. Two carbohydrate “like” compounds and five different non-carbohydrate structures were observed and quantified.

Kawamoto et al. (2003) and Hosoya et al. (2006) have proposed that the polymerization of anhydrosugars could result in polysaccharides (a reversible reaction), which can be precursors of char formation. Levoglucosan polymerizes into dextran. However, it has been found that thermal polymerization of levoglucosan was inhibited substantially during co-pyrolysis of cellulose with a lignin sample (Hosoya et al. 2006, 2007a, b). Significant interactions were observed in cellulose-lignin pyrolysis, when lignin inhibited the thermal polymerization of levoglucosan formed from cellulose and enhanced the formation of the low molecular weight products from cellulose with reduced yield of char fraction. The authors proposed the existence of a stabilization mechanism due to CH-π interactions to form stable levoglucosan-aromatic compound complexes.

Kawamoto et al. (2003) reported that non carbonized products are obtained in the residue when cellulose is suspended in solfone (tetramethylene sulfone). Solfone is a good solvent for levoglucosan. Kawamoto and Saka (2006) explained this result is also based in what they called “peeling reaction mechanism,” which is very similar to “un-zipped mechanism” discussed previously. The authors suggest that the levoglucosan (primary product from this mechanism) is solubilised into the solvent, inhibiting the ring-opening polymerization reaction that is proposed as key reaction for carbonization formation.

CROSSLINKING REACTIONS OF FRAGMENTATION PRODUCTS AND FORMATION OF POLYAROMATIC HYDROCARBONS FROM CHAR (Reaction 6 and 7-Figure 11)

Hajaligol et al. (2001) was the first to note the existence of a very poorly known mechanism leading to the formation of polyaromatic hydrocarbons from the char formed. Hajaligol et al. (2001) proved that it is possible to release some polyaromatics in the vapors' phase when the chars are heated at temperatures over 400°C. The structure of the char related to the release of polyaromatic hydrocarbons is not well known. These reactions can occur from the char resulting from any of the biomass components. Thus, it was decided to treat these reactions in a separate section (see 4.3. Secondary homogeneous reactions in solid phase).

4.2.2. Hemicellulose

The main products of the thermal decomposition of hemicelluloses found in the bio-oils are acetic acid, furans, and mono and oligo-pentoses.

Hemicelluloses have a much more diverse structure than cellulose and have lower thermal stability due to their lack of crystallinity. Hemicellulose thermal degradation starts at temperatures as low as 200°C. The yields of 2-furaldehyde increase when the substrate is impregnated with acid catalysts (10 mass % on xylan) (Radlein et al. 1991a, b).

Xylan degradation is subject to fragmentation effects similar to those observed for cellulose in the presence of inorganic impurities. Xylan possesses ion-exchange sites, which make it particularly susceptible to uptake of impurity cations.

4.2.3. Lignin

The thermal degradation of lignin results in the formation of monomeric phenols, guaiacols and syringols, formic acid, formaldehyde, methanol, carbon dioxide and water. De-methoxylation of lignin is the source of methanol.

Knowledge of lignin pyrolysis is very limited. Very little is known about the pyrolysis reactions responsible for the formation of lignin derived oligomes during biomass pyrolysis. In general the thermal degradation of lignin can be described by a competitive mechanism involving depolymerization and condensation/carbonization reactions as suggested by Kawamoto et al. (2007b).

Depolymerization

The β-ether linkage is the most abundant structure in lignin macromolecules, so has a controlling effect on the depolymerization and condensation reactions (Kawamoto et al. 2007b). Phenolic β-ether structure is more reactive than the non-phenolic type. Although the content of phenolic structure is low in natural lignin (Whiting and Goring 1982), chain depolymerization is expected via successive formation of the new phenolic structure through cleaving the phenolic end structure. The phenolic α and β-ester types dimmer became reactive at temperatures around 200-250°C.

Kawamoto et al. (2007a) studied the reactivity to depolymerization and found that this parameter depends on the chemical structure of the lignin and varies in the following order: α-O-4 (phenolic (ph) and non-phenolic (nonph)) and β-O-4 (ph) > β-O-4 (nonph), β-1 (ph, nonph) > biphenyl (ph, non ph). Major depolymerization pathways for β-O-4 types include: (1) Cβ-O cleavage to form cinnamyl alcohols and phenols, and Cγ elimination yielding vinyl ethers.

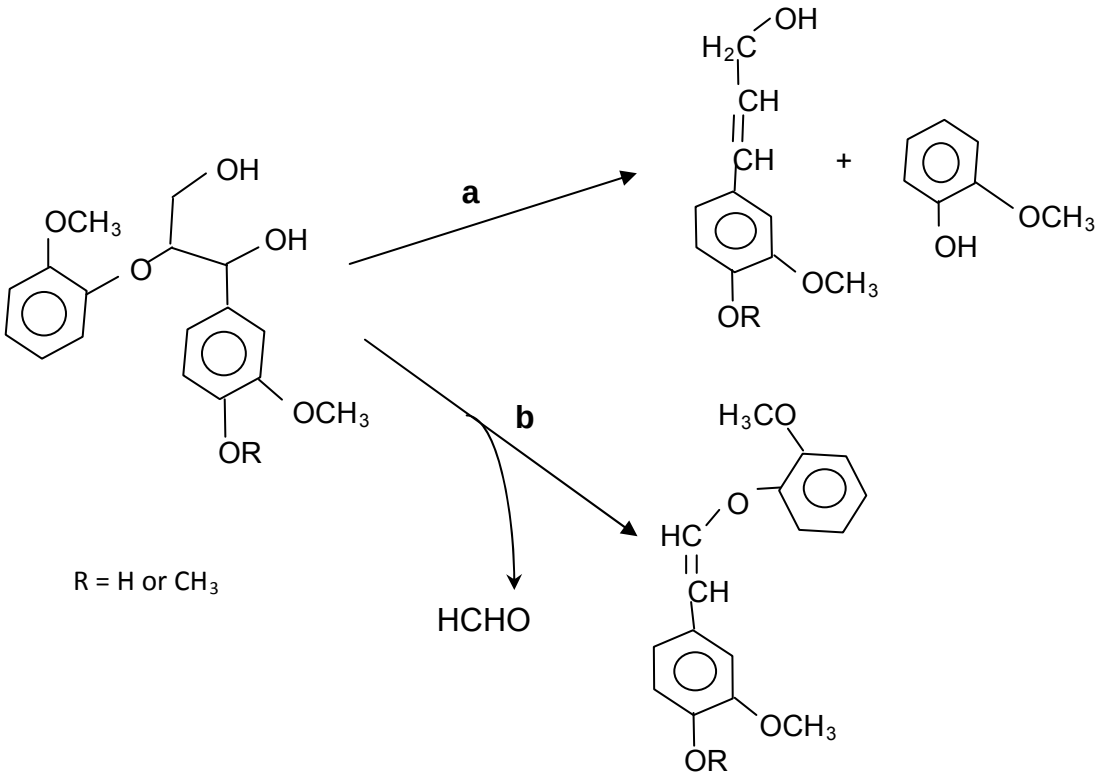


Figure 17. Depolymerization Pathways of the β-ether Lignins (Nakamura et al. 2008)

As illustrated by Figure 17, the β-ethers undergo two types of reactions: C_β-O cleavage to cinnamyl alcohol or guaiacol (pathway a) and C-γ-elimination to enol ether (pathway b) (Nakamura et al. (2008)). The authors also observed a considerable activation when using phenolic compounds. As for the linkage type, reactivity of the phenolic form is greater in the order of α-ether > β-ether > β-aryl >>aryl-aryl types (Nakamura et al. 2008). It is interesting to note that the dimmers were one of the main products resulting from the pyrolysis of lignin. Studies conducted with lignin derived from Japanese cedar (milled wood lignin samples) also show that β-ether cleavage to cinnamyl alcohol-type structure and Cg-elimination to stilbene-type structures are major primary pyrolytic reactions.

Several mechanisms including ionic (heterolytic) and homolytic mechanisms are proposed for the pyrolytic cleavage of the β-ether linkage. *Relative reactivities* for these mechanisms are quite different between phenolic and non-phenolic forms even in the same types of bonds (Kawamoto et al. 2007b).

Two ionic mechanisms (heterolytic) have been proposed. Klein and Virk (1983) used kinetic analysis of the formation behavior of styrene and phenol from phenethyl phenyl ether, which has no substituent groups, to propose the *six-centered retro-ene mechanism* (Kawamoto et al. 2007b). The *oxirane mechanisms proposed* by Kislitsyn et al. (1971) assume that the β-ether is heterolytically cleaved by the attack of Cα- or Cγ-hydroxyl group to the β-carbon.

The homolitic mechanisms can be explained via benzyl radical (Autrey et al. 1991, Britt et al. 1995, Evans et al. 1986) or via quinone methide intermediary (Sano 1975, 1989, Kishimoto and Sano 2002, Kawamoto et al. 2004). Kawamoto et al. (2007b) have reported that the α-ether linkage in the methylated dimmer is cleaved in homolytic mechanism. Kawamoto et al. (2007b) have reported that high reactivity of the phenolic and β-ether dimmers are related to the quinine methide formation. Push and pull reaction of p-hydroxyl group and Cα-OR in quinine methide formation substantially activates the heterolytic cleavage of the α-ether bond.

Condensation/Carbonization

Kawamoto et al. (2007b) also studied the reactivities to condensation/carbonization and found that the tendency to polymerize varies in the following order: β-1 (ph, nonph) > β-O-4 (ph) >α-O-4 (ph) >β-O-4 (nonph), α-O-4 (ph), β-O-4 (nonph), biphenyl (ph, nonph), α-O-4 (nonph), β-1 (nonph).

Carbonization with the formation of char precursors (PAH-like structure in the solid) starts at 400°C and at these temperatures almost all the compounds became reactives. These results indicate that the reaction of the aromatic ring itself (including the O-CH_3 homolysis) would be important in the carbonization.

Nakamura et al. (2007) has observed that over 400°C it is possible to observe a change from a single aromatic ring system to a multiple ring system in the solid phase indicating the formation of polyaromatic hydrocarbons (PAHs), precursors of char formation. Nakamura suggests that the formation of radicals on the aromatic carbons after the hemolytic release of O-CH_3 group may be the starting step for the formation of PAH-like multiple ring system leading to the formation of char (Nakamura et al. 2007).

Although the release of PAH rings is not favored thermodynamically, some of these rings may find their way into the bio-oils under certain operational conditions. Nakamura et al. (2007) suggest that the formation of conjugated Cα=Cβ structure and the following condensation are effectively inhibited below 300°C by methylation. These results strongly indicate that the phenolic unit in the original milled wood lignin (MWL) is a key structure for relatively low temperature condensation. The phenolic unit is considered to exist as an end-group in the lignin ether chain, so condensation reaction would occur at this end group to form larger molecules.

In general it can be concluded that the mechanism by which primary thermochemical reactions impact the structure of polyaromatic hydrocarbons as part of the formation of carbonaceous materials, and the mechanism by which some of these rings are released from the macromolecular structure, are still very poorly known.

4.3. Secondary Homogeneous Reactions in Solid Phase Leading to Formation of PAHs

The solid residue, primary char that is formed at low temperature, can undergo a chemical transformation at moderate to high temperatures (above 400°C) to produce a more stable and relatively ordered carbon structure (Hajaligol et al. 2001). This step does not represent a significant weight loss of material compared with the first decomposition step, but it is very important in the formation of the primary carbon skeleton for the high temperature graphitization process. Furthermore, this second step may be an important route for the formation of volatile aromatic compounds during chemical transformation from low to high temperature char. Although this route may not be important in the formation of aromatics at high temperature, it is believed to be of significant importance during conditions of slow pyrolysis. There has been very little emphasis on the formation of aromatic hydrocarbons at low temperatures (Underwood and Graham 1989, Braun et al. 1987, Lavrov 1974, Dikun et al. 1975). This is likely due to the lower probability of forming aromatic structures from pyrolysis of heavily oxygenated species at low temperatures. The temperature range between 400 and 600°C in which this pathway becomes significant coincides with the one at which the char structure develops aliphatic and aromatic structures (Hajaligol et al. 2001). The impacts of heating rate, final temperature, and the presence of metals in the formation of polyaromatic hydrocarbons are not well known.

4.4. Secondary Heterogeneous Intra-Particle Reactions

In contrast to the large amount of literature on the primary pyrolysis of biomass (Koufopanos et al. 1991, Varhegyi et al. 1997, Orfao et al. 1999, Caballero et al. 1997a, b, Agblevor et al. 1994, Raveendran et al. 1996, Roy et al. 1990, Antal et al. 1998, Varhegyi et al. 1994), there appear to have been few studies on homogeneous vapour phase (Boroson et al. 1989 a, Diebold 1985, Liden 1985, Mottocks 1981, Serio 1984) and heterogeneous inter and extra-particle reactions (Boroson et al. 1989a, b).

The diffusion mechanism of pyrolysis vapors through the biomass particles is still very poorly known. Boronson et al. (1989 a,b) studied the char-induced conversion of newly formed wood pyrolysis tars measured for independent variations in temperature and tar char space time. Heterogeneous conversion was significant but essentially constant at 14 +/- 7 mass % of tar, for temperatures from 400 to 600°C and space time from 2.5 to 100 ms. Lignin was identified as a major source, but not the only source, of this char-reactive tar fraction. Carbon dioxide and CO are definite products of this char-induced tar conversion, and additional char (coke) is a highly probable product (Boroson et al. 1989a, b).

4.5. Secondary Homogeneous Reactions

The secondary homogeneous reaction at temperatures between 700 and 1000°C is responsible for the formation of large amounts of polyaromatic hydrocarbons during biomass gasification. The primary oxygenated oils produced during wood pyrolysis below 500°C can be changed to highly aromatic, deoxygenated tar by additional thermal treatment at 700°C or above (Pakdel and Roy 1991, Evans 1987a, b). The concurrent decrease in phenols and increase in PAHs has been demonstrated many times.

Hosoya et al. (2007a, b) has reported that while stable primary tars from wood polysachharides undergo secondary reactions including carbonization after condensation at the reactor wall with

lower temperatures than their boiling points, primary tar from lignin undergoes vapor phase carbonization reactions.

Several authors (Warnat et al. 1988, 1987, 1992, 1998, 1999, 2000, 2001; Mukherjee et al. 1994, Masonjones et al. 1996) have reported PAH from other carbonaceous molecules subjected to high temperature (over 700°C) in the absence of oxygen (Ledesma et al. 2002). There are several studies involving detailed elementary reactions of light hydrocarbon fuels such as methane, ethane, ethylene, acetylene, propane and n-butene; however, the mechanisms (Ledesma et al. 2002) are only partially applicable to the modeling of PAH formation from large-scale combustion devices, such as coal and biomass fired burners where the nature of fuel fragments is substantially different and the reaction chemistry is coupled to transport processes.

Ledesma et al. (2002) conducted experiments with catechol as a model compound representing the compounds emitted from the primary pyrolysis reactions of lignin. The formation of polyaromatic hydrocarbons was only noticeable at temperatures over 700°C (in the range of gasification reactions).

Although there is a large amount of literature devoted to describing the formation of dioxins by homogeneous and heterogeneous thermo-chemical reactions, it is not even known if these compounds can be formed in the reaction conditions employed by fast pyrolysis reactors. The next chapter is devoted to analysis of these reactions.

Chapter 5. Formation of Dioxins During Thermo-Chemical Reactions

5.1. Introduction to the Mechanisms of Dioxin Formation

The production of dibenzo-p-dioxin and dibenzofuran (PCDD/F) is a minor reaction pathway consuming a relatively small fraction of the chlorine available in the combustion environment but that results in the production of highly toxic compounds. The reactions responsible for the formation of dioxins never proceed to completion in spite of the over-abundance of chlorine and other elements (carbon, hydrogen and oxygen) in the incinerators (Environment Australia 1999, Bozzelli and Chiang 1996, Ritter and Bozzelli 1994). The formation of these compounds is kinetically limited.

Although chlorinated compounds and metal catalysts in the fuels are important factors in the formation or inhibition of PCDD/F (Ruokajarvi et al. 2001), major reductions in the content of these compounds can be achieved by optimizing the combustion parameters (e.g. water concentrations, temperature profiles and residence time). PCDD/F precursors are formed in combustion environments at temperatures above 1000°C, but the residence time of resulting products when cooled to the range of temperatures between 250 and 650°C plays a much more important role controlling PCDD/F formation (Ruokajarvi et al. 2001). The maximum formation of PCDD/F has been identified at approximately 300°C (Tuppurainen et al. 1998).

The rapid cooling of flue gases using scrubbers could certainly contribute to reducing the content of these compounds in incinerators. Ideally, no PCDD/Fs should be formed if the temperature changes instantaneously. However, post-furnace formation of PCDD/F generally can take place at detectable rates under the influence of catalysts (mainly copper) even within the short residence time of scrubbers at temperatures of around 300°C (Tuppurainen et al. 1998). Copper catalysts are known to enhance the formation of PCDDs by a factor of 3 orders of magnitude (Tuppurainen et al. 2000).

The main two mechanisms (Figure 18) proposed to explain the formation of dioxins during incineration (combustion) of municipal solid wastes are: pyrosynthesis (or precursor mechanism) and de novo synthesis. Both mechanisms occur simultaneously and/or independently and result in the formation of compounds with unique finger prints (Altarawneh et al. 2007):

(1) The pyrosynthesis (also known as precursor mechanism) supposes that the dioxins are formed by the polycondensation of precursors (e.g. polychlorophenols, polychlorobenzenes, PCBs). This mechanism occurs in the gas phase at temperatures between 300 and 600°C. The surface-catalysed formation of these species is generally believed to be a major contributor to PCDD/F from incineration processes. The resulting products have a PCDF/PCDD ratio much lower than 1 (Everaert and Boeyens 2002).

(2) The de novo synthesis involves the presence of carbon as the solid phase. O_2 is also essential for the de novo formation. This mechanism occurs at temperatures between 200 and 400°C. The PCDF/PCDD ratio is usually higher than 1 (Everaert and Boeyens 2002).

Although the real contribution of these mechanisms is still a subject of debate, it is generally accepted that the operating conditions (especially the temperature history of the combustion gases) determine the relative importance of these mechanisms. At higher processing temperatures the precursor-type reaction predominates over the novo pathway. On the other hand, at low temperatures, the de novo-type reactions become faster than the precursor route (Konduri & Altwicker 1994). It has been shown that as the temperature decreases to around 300°C, the PCDF formation rate subsides and the PCDD formation rate markedly increases.

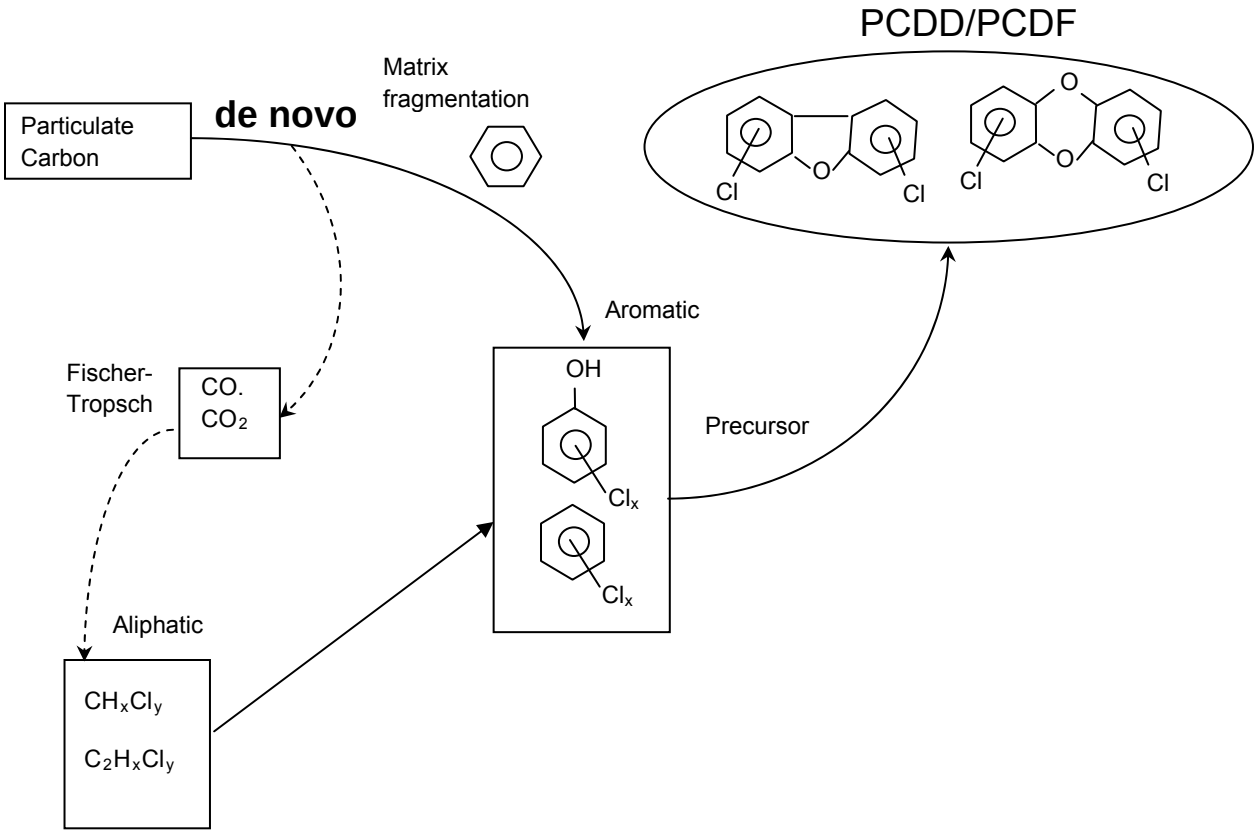


Figure 18. Schematic Representation of PCDD/F Formation Routes (Froese et al. 1996a)

Table 4 shows a list of several studies reported by Everaert and Baeyens (2002) that can be consulted for more information on the mechanisms explaining the formation of dioxins.

Table 4. List of Some Studies Reported on the Formation of PCDD/F (Everaert and Baeyens 2002)

Authors	Solid phase	Gas phase	Formation peak temp. (°C)	Indicated formation mechanism
Luijk et al. (1994)	Activated carbon	Air, H_2O, chlorophenol	300	Precursor
Luijk et al. (1994)	Activated carbon and CuCl2	Air, H_2O, HCl	300	De novo
Milligan and Altwicker (1993)	Fly ash	O_2, N_2, chlorophenol	325	Precursor
Altwicker and Milligan (1993)	Fly ash	O_2, N_2	325	De Novo
Naikwadi et al. (1993)	Fly ash	Air, chlorophenol	300	Precursor
Gullett et al. (1992)	Metal oxides	O_2, N_2, chlorophenol	400	Precursor
Gullett et al. (1992a,b)	CuO or CuSO4	O_2, N_2, HCl or Cl_2, or SO_2, phenol	400	Precursor
Dickson et al. (1992)	Silica gel, activated carbon, CuCl2	Air, chlorophenol	300	Precursor
Dickson et al. (1992)	Silica gel, activated carbon	Air	300	De novo
Karasek and Dickson (1987)	Fly ash, fire brick	N_2, chlorophenol	300	Precursor and de novo
Born et al. (1993)	Carbon-fly ash	O_2, N_2, H_2O, HCl, phenol	400	Precursor
Schoonenboom et al. (1995)	KCl, CuCl2, activated carbon, alumina	Air	350	De novo
Froese and Hutzinger (1996)	Carbon-free fly ash, metal oxides	O_2, N_2, acetylene	400	Precursor
Stieglitz and Vogg (1997)	Fly ash and various mixtures	Air, H_2O, SO_2, HCl, Cl_2	300	De Novo
Stieglitz et al. (1997)	Carbon-free fly ash, carbon	Air, H2O	350	De novo
Addink et al. (1992)	Fly ash, activated carbon	Air	350	De novo
Hagenmaier et al. (1987)	Fly ash	Air	300	De novo

5.1.1. The Pyrosynthesis (Precursor Mechanism)

Homogeneous Reactions

The organic and inorganic chlorine is released during the combustion step in the form of HCl, which reacts with products of incomplete combustion to form chlorinated phenols and benzenes. These compounds are known to be dioxin precursors and the reactions precede more effectively around 750°C (Environment Australia 1999).

The gas-phase route is considered one of the most important mechanisms for the formation of PCDD/Fs. The pioneering models proposed to explain the formation of dioxins assumed that only PCDD (and not PCDF) could be formed from chlorinated phenols through radical-molecule reactions. It was initially thought that the self-recombination of phenoxy radicals was not fast

enough to have a significant impact on the formation of PCDFs. Recent experimental evidences have shown that chlorinated phenoxy radicals can dimmerize to form both PCDDs and PCDFs (Altarawneh et al. 2007).

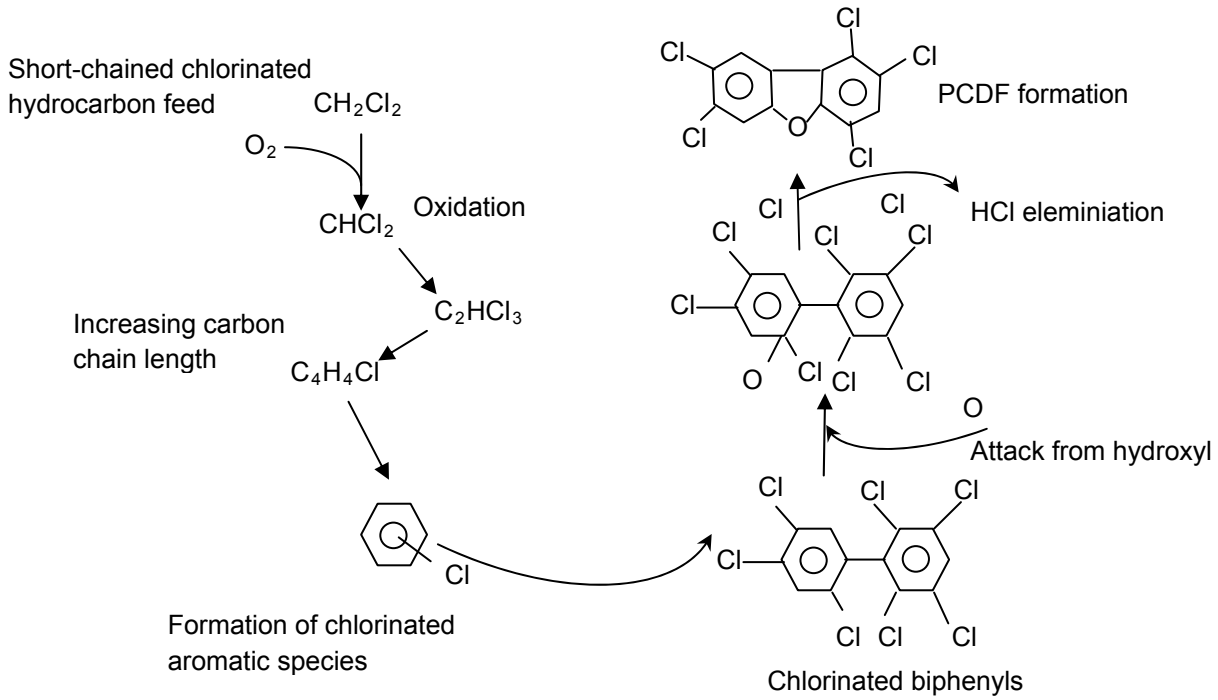


Figure 19. Homogeneous Pathway for PCDD/F Formation (Environment Australia 1999)

Ritter and Bozzelli (1994) conceptualized the conversion of precursor species to PCDD/F from short-chain chlorinated hydrocarbons in the gas phase (see Figure 19). This scheme was developed to explain mechanistically the formation of polychlorinated benzene from relatively simple short-chained chlorinated hydrocarbons, subsequently leading to the formation of PCDD/Fs.

Heterogeneous Reactions

Heterogeneous catalytic synthesis on the surface of fly ash particles is well documented (Tuppurainen et al. 1998). Four steps have been proposed to explain this mechanism: (1) creation of ashes and products of incomplete combustion (2) formation of surface-active molecules (3) complex organic (radical) reactions and (4) partial desorption of products.

Catalytic condensation and de-chlorination reactions of chlorinated phenols and benzenes occur when the gases reach the colder regions in incineration plants (200 to 450°C). Tuppurainen et al. (1998) has proposed different reaction schemes for PCDD and PCDF formation. These authors have suggested that PCDD formation proceeds via the surface-catalysed coupling of chlorinated phenolate anions, followed by oxidative ring closing.

The presence of oxygen in a stoiciometric excess at temperatures around 750°C is considered an ideal condition for the formation of products of incomplete combustion through radical mechanisms (Tuppurainen et al. 1998).

Polychlorinated benzenes may be formed by radical mechanisms or by the combination of chlorine and chlorophenyl radicals. The addition of two chlorophenyl radicals give polychlorinated biphenyls, PCB compounds. Oxidized PCBs can be possible precursors for PCDFs.

Fly ash from incinerators is one of the possible surfaces that could catalyze the formation of PCDD/Fs (Milligan & Altwicker 1996a, b) (Figure 20). The complexity of the fly ash structure has been simulated using several model materials (Al_2O_3, Al_2O_3-SiO_2, $MgSiO_2$, SiO_2, SiO_2NaOH, carbon, glasswool, and fire brick) (Tuppurainen et al. 1998). These experiments show that PCDD/Fs can be generated on the surfaces of all these materials.

Milligan & Altwicker (1996a, b) studied the influence of reaction times and temperature on the conversion of tetrachlorophenol on fly ash. The authors only detected PCDD, while PCDF levels were beyond the detection limits of this analysis.

Thus fly ash can serve as an active catalyst serving as an electron transfer oxidant, which leads to the coupling of two aromatic rings. Dioxin formation is observed following HCl and Cl elimination reactions. It has been noted that more alkaline ash effectively adsorbs PCPs on its surface, promoting the formation of PCDD (Environment Australia 1999 http://www.environment.gov.au/settlements/publications/chemicals/dioxins/incineration-review.html). Fly ash could also catalyze a reaction between oxygen and hydrogen chloride, giving molecular chlorine and chlorine radicals via the Deacon reaction. It is well known that Cu based catalysts can catalyze these reactions (Tuppurainen et al. 1998).

The role of chloro-phenols as precursors of PCDDs has been firmly established. Most of the abundant PCDD cogeners (1,3,6,8-TCDD, 1,3,7,9-TCDD, 1,2,4,7,9-PCDD, 1,2,4,6,8-PCDD, 1,2,3,7,9-PCDD, 1,2,3,4,6,8-HCDD, 1,2,3,6,8,9-HCDD, 1,2,3,6,7,9-HCDD, 1,2,3,6,7,8-HCDD and 1,2,3,7,8,9-HCDD) have been found to be products of more stable chlorophenols resulting from fly ash catalyzed reactions at temperatures around 300°C (Tuppurainen et al. 1998).

Although the dioxins can be formed in the range of pyrolysis temperatures (300-400°C) (Tuppurainen et al. 1998) as a result of fly ash catalysed reactions, the precursors (chlorinated phenols and benzenes) have to be formed at higher temperatures (usually around 750°C) (Froese & Hutzinger 1996a, b). This may explain why it was not possible to find any report on the presence of dioxins in bio-oils or chars. The temperature history in pyrolysis reactors is very different to that of incinerators. The formation of dioxins is heavily dependent on this parameter.

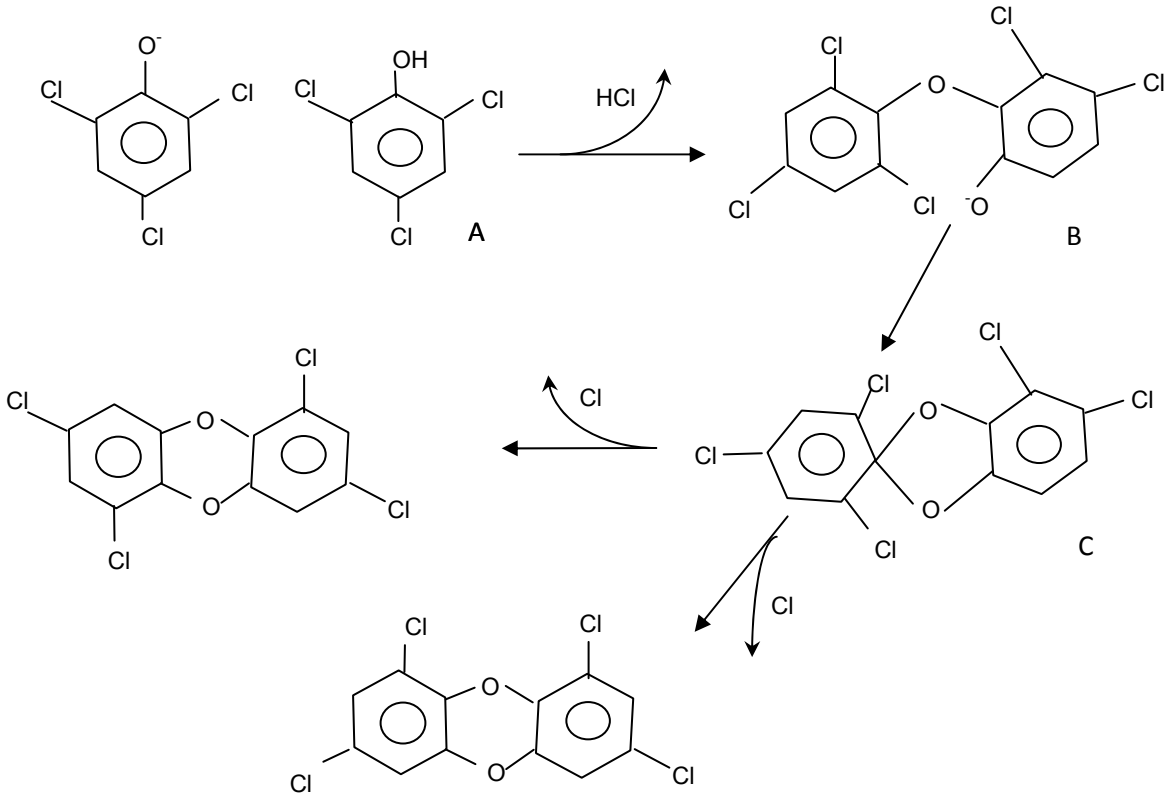


Figure 20. Formation of PCDD in the Fly Ash Catalyzed Precursor Pathway (Environment Australia 1999)

5.1.2. De Novo Mechanism

Stieglitz and Vogg (1987) were the first to observe and describe the De Novo Mechanism. It considers that the chlorine is transferred from the metal chloride ligands on the ash surface to aromatic carbon rings (see Figure 21). Yields of PCDD/F depend on the reaction temperature. It has been observed that the maximum yield displays a peak around 325°C (Milligan and Altwicker, 1995). The mechanism relies on the presence of carbon matrix imbedded in the porous structure of fly ash particles.

The presence of organic or inorganic chlorine, oxygen, and copper is a prerequisite for PCDD/F formation through the de novo mechanism. Neither CO nor CO_2 from the combustion gases contributes to the formation of PCDF by this mechanism. The rates of formation of PCDD/F depend on the activity of fly ash. Since the chlorine in the de novo synthesis comes from metal chlorides on the surface of fly ash, the concentration of chlorine in the combustion gases is not important.

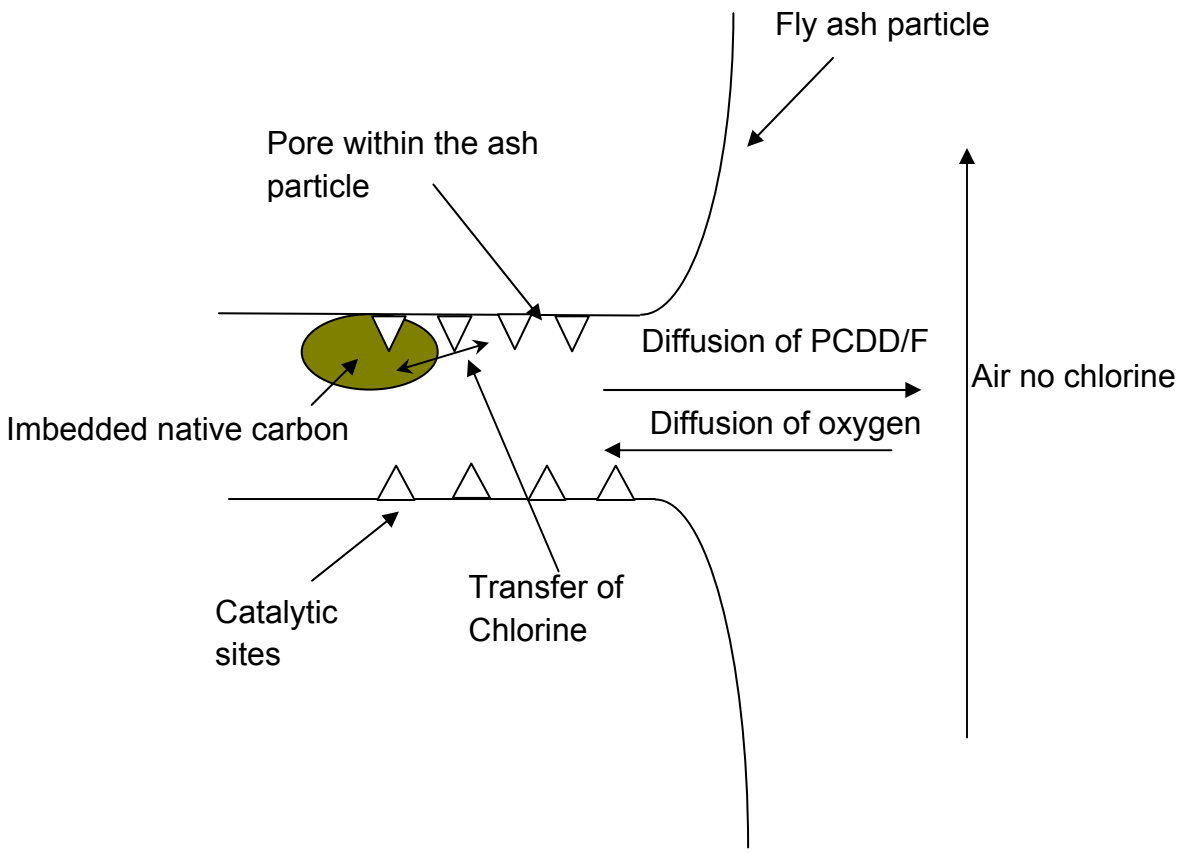


Figure 21. Mechanistic View of the De Novo Mechanism of Dioxine Formation (Environment Australia 1999)

The de novo mechanism supposes that there are some structures similar to the dibenzo-p-dioxins, dibenzofurans in the residual carbon attached to the fly ash. Hinton and Lane (1991a, b) have demonstrated that the formation of dioxins is mostly related to the catalytic activity of fly ash and not to its chlorinated content.

Milligan and Altwicker (1996a, b) have shown that external mass transfer limitations are not important during precursor/fly ash reactions under post-combustion incinerator conditions. A part of the PCDD/Fs formed diffuses to the gas phase, with the rest remaining in the fly ash. This is why fly ash often contains large amounts of PCDD/F.

One major difference between the de novo mechanism and the pyrosysthesis mechanism is that the de novo mechanism leads preferentially to the formation of PCDF. The formation of PCDD/F by the de novo route is minimized in systems burning uniform fuel at higher temperatures, at longer residence times and at low chlorinate-sulfur ratios.

The absence of oxygen in pyrolysis reactors and the low concentration of chlorinated compounds in biomass are perhaps the main reasons for the absence of chlorinated compounds in bio-oils.

Chapter 6. Conclusions

It was not possible to find any reference on the presence of leachable polyaromatic hydrocarbons and dioxins in chars produced from woody biomass fast pyrolysis. There are some reports on the presence of small amounts of PAHs in some bio-oils. These small amounts of PAHs are produced as a result of a complex set of poly-condensation reactions in solid phase leading to formation of unstable polyaromatic moieties in chars. The mechanism leading to the formation of these unstable structures has to be further investigated.

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Note: This list encompasses references used by the author, some of which (but not all) are specifically cited in the report.

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