



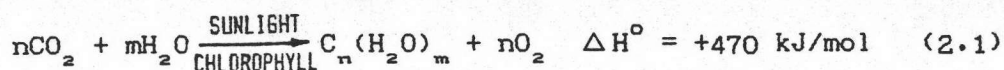
CHAPTER 2

LITERATURE REVIEW

2.1 Biomass Resources

Biomass is any material that is directly or indirectly derived from plant life and that is renewable in time periods of less than about 100 years (Probstein, 1982). Typical biomass resources are energy crops, farm and agricultural wastes, and municipal wastes. Animal wastes are also biomass materials in that they are derived, either directly or via the food chain, from plants which have been consumed as food.

As with conventional fuels, the energy in biomass is the chemical energy associated with the carbon and hydrogen atoms contained in oxidizable organic molecules. The source of the carbon and hydrogen is carbon dioxide and water. The conversion by plants of carbon dioxide and water to combustible organic form occurs by photosynthesis. Two essential ingredients for the conversion process are solar energy and chlorophyll. The chlorophyll, present in the cells of green plants, absorbs solar energy and makes it available for the photosynthesis, which may be represented by the overall chemical reaction.



$C_n(H_2O)_m$ is used here to represent the class of organic compounds called "carbohydrates", several of which are synthesized in the course of the reaction.

About one-quarter of the carbohydrates formed by photosynthesis are later oxidized in the reverse process of respiration to provide energy for plant growth. The excess carbohydrate is stored. Thus biomass consists of high hydrogen to carbon ratios and low sulfur and nitrogen concentrations.

2.1.1 Chemical Composition of Biomass

Biomass consists of two kinds of materials, one is organic matter that is produced by photosynthesis and the other is inorganic matter obtained from soils. These organic matter are carbohydrates (cellulose, starch and hemicellulose) and lignin. Their structures are composed of sugars and polymers of sugars. The base sugars and polymers that are of interest are listed in Table 2.1 which determine the properties of the plant matter of relevance to biomass energy utilization.

Table 2.1 Selected Saccharide Carbohydrates and Lignin

	Chemical Formula	Molar Mass
Monosaccharides		
Xylose*	$C_5H_{10}O_5$	150
D-glucose† (corn/grape sugar)	$C_6H_{12}O_6$	180
Fructose (fruit sugar)	$C_6H_{12}O_6$	180
Mannose*	$C_6H_{12}O_6$	180
Disaccharides		
Sucrose (cane/beet sugar)	$C_{12}H_{22}O_{11}$	342
Maltose (malt sugar)	$C_{12}H_{22}O_{11}$	342
Lactose (milk sugar)	$C_{12}H_{22}O_{11}$	342

Table 2.1 Selected Saccharide Carbohydrates and Lignin (cont.)

	Approximate Representation	Monomer Building Block	Molar Mass
Polysaccharides			
Cellulose	$(-C_6H_{10}O_5-)_n$	D-glucose	>100 000
Starch	$(-C_6H_{10}O_5-)_n$	D-glucose	35 000-90 000
Hemicellulose	—	Various sugars*	10 000-35 000
Wood	$C_{31}H_{41}O_{23}$	Lignocellulose	—
Lignin	—	Hydroxyphenylpropane‡ ($C_7H_7 \cdot C_6H_4 \cdot OH$)	5 000-10 000

* Xylose and mannose are the principal sugar constituents of wood hemicellulose.

† Also called dextrose.

‡ A compound related to phenol, C_6H_5OH .

2.1.1.1 Cellulose

Cellulose is a fibrous polysaccharide that is the main constituent of the cell walls of land plants. It is the most abundant naturally occurring organic substance. Cotton fiber is virtually pure cellulose, and cellulose is a major constituent in wood, hemp, and straw. Over a century of research has shown cellulose to be a linear polysaccharide composed of anhydroglucose units connected to each other by 1→4-glucosidic linkage. The cellulose structure is shown in Figure 2.1.

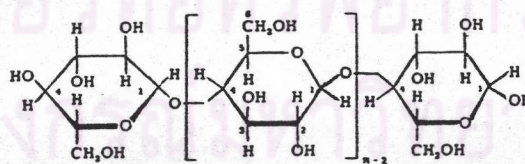


Figure 2.1 Cellulose Structure

2.1.1.2 Starch

Starch is a granular polysaccharide

which accumulates in the storage organs of plants such as seeds, tubers, roots and stem pith. It is an important constituent of corn, potato, rice and tapioca. Starch consists of 10 to 20 % α -amylose, which is water soluble, and 80 to 90 % amylopectin, which is insoluble. Both the constituents of starch are polymers of D-glucose, with amylose linked in chain structures, while amylopectin is a highly branched structure.

2.1.1.3 Hemicellulose

Hemicellulose are polysaccharides that occur in association with cellulose. They are chemically different from cellulose, are amorphous, and have much lower molar masses (Table 2.1). While cellulose is built from the single sugar

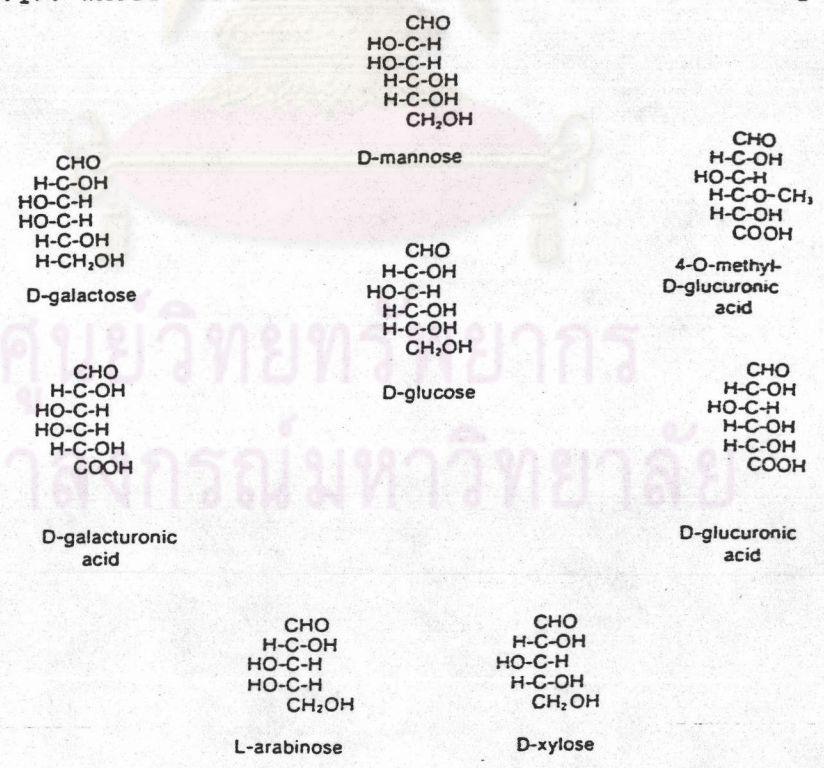


Figure 2.2 Structural Interrelationship of Commonly Occurring Hemicellulose Component Sugars

D-glucose, most hemicellulose contain two to four (and occasionally five to six) different sugars as building blocks. D-glucose is a component of some hemicellulose, although xylose is a dominant sugar in hardwood hemicellulose, and mannose is important in softwood hemicellulose. The structure is similar to that of cellulose except that the hemicellulose polymers generally contain 50 to 200 units and exhibit a branched rather than a linear structure.

2.1.1.4 Lignin

Lignin is the final major constituent of plant material important to biomass processing. It is not a carbohydrate, but a polymer of single benzene rings linked with aliphatic chains. The structural formula is shown in Figure 2.3.

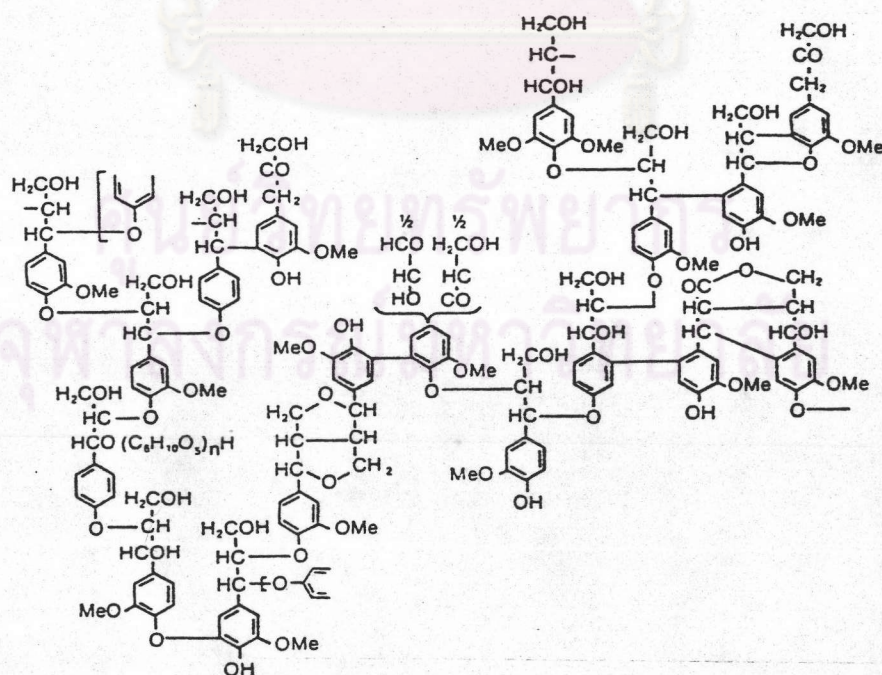


Figure 2.3 Representative Structure of Lignin

Lignin is a characteristic constituent of the walls of woody cells, and acts as a natural glue providing the plant with added mechanical strength. As can be inferred from its name, lignin is an important constituent of wood. Like hemicellulose, it is amorphous.

2.2 Biomass Conversion

In discussing the properties of specific biomass materials, it is possible that biomass can be converted to synthetic fuels. The conversion processes that turn a biomass into fuels can be either biological or thermochemical and are summarized in Figure 2.4.

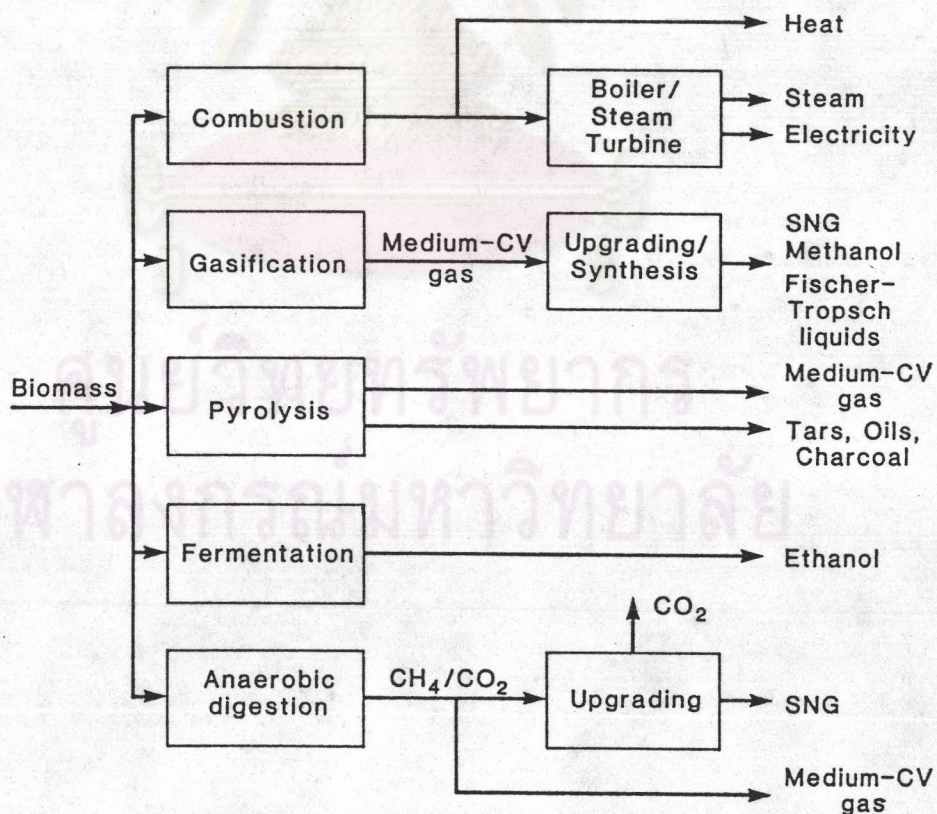


Figure 2.4 Biomass Conversion Processes

2.2.1 Thermal Conversion

Thermal conversion processes included pyrolysis, gasification, and combustion. A graphic description of these processes and their products is given in the triangular diagram of Figure 2.5.

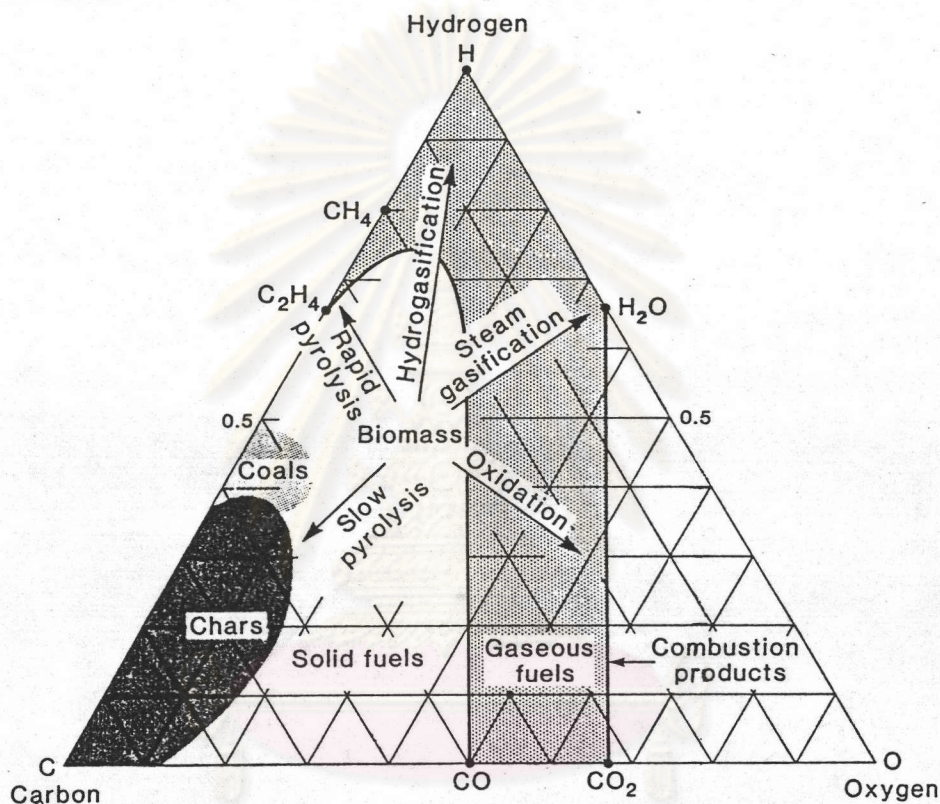


Figure 2.5 Thermal Conversion of Biomass (Probstein, 1982)

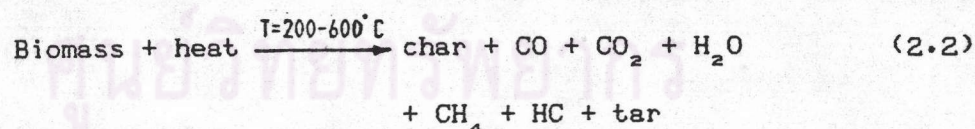
2.2.2 Biochemical Conversion

Fermentation and anaerobic digestion are the two biochemical processes of interest. Fermentation is any chemical change of organic material that is accompanied by effervescence, normally without the participation of oxygen. In case of biomass material, fermentation is the anaerobic decomposition of

carbohydrates to alcohols in the presence of enzymes that produces ethanol to be the principal product. While anaerobic digestion is the decomposition of any organic material by the metabolic action of bacteria without the participation of atmospheric oxygen. Methane and carbon dioxide are the main products of the decomposition. It is said that fermentation produces synthetic fuel as a liquid product in the presence of enzymes, while anaerobic digestion produces synthetic fuel as a gaseous product from a result of the metabolic activity of bacteria.

2.3 Pyrolysis

Pyrolysis is the decomposition of organic matter by heat in the absence of oxygen. Mostly biomass is decomposed at temperatures of 200 to 600 °C to yield a medium energy gas, a complex pyrolysis oil, and char. The breakdown of biomass is as follows :



There are two kinds of pyrolysis : slow and fast. In slow pyrolysis the reactions taking place are always in "local equilibrium", the heating time being sufficiently slow to allow equilibrium along the temperature path. For this case the ultimate yield and product distribution depends on the temperature history. In fast pyrolysis there is a negligible amount of reaction during

the heating up period and pyrolysis reactions occurring take place isothermally at the final temperature.

2.3.1 Pyrolysis Mechanisms

If the mechanism and kinetics of the pyrolytic reactions were known or could be anticipated, the pyrolysis conditions could be controlled in order to enhance the formation of the desirable products and may be helpful in the design of synthetic fuel plants. Many investigators have attempted to describe the pyrolysis mechanisms (Allan & Matilla, 1971; Shafizadeh, 1972; Antal, 1982).

2.3.1.1 Cellulose

All of the studies described the mechanism of cellulose pyrolysis based on three principal ranges of temperatures.

At low temperature (below 250 °C), the degree of polymerization (DP) of cellulose undergoes a rapid drop over from 1,000 to a steady state value of about 200 during the early stages of pyrolysis and obtains two structures. One structure is a crystalline structure which is transformed into the major source of levoglucosan. The other structure is a non-crystalline structure. In this structure dehydration occurs by cross link reactions to form char yield.

In Figure 2.6, at low temperatures and slow heating rates, the lower path predominates. Under faster heating, the upper path becomes more important.

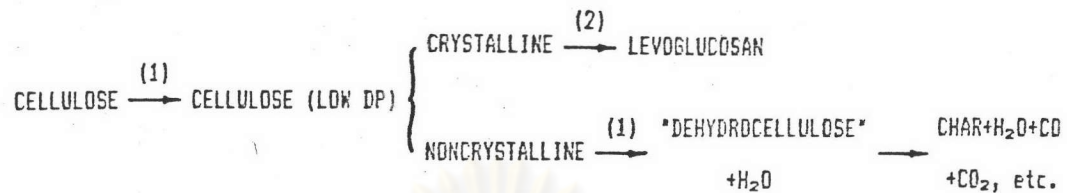


Figure 2.6 Low Temperature Pathways of Cellulose Pyrolysis

At moderate temperature (above 250 °C), thermal degradation of cellulosic material proceeds through a complex series of concurrent and consecutive chemical reactions as follows :

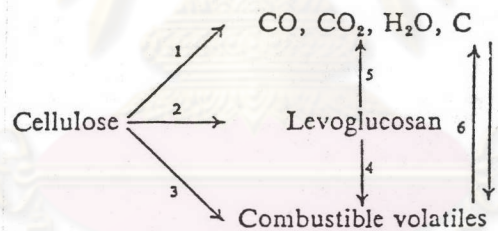


Figure 2.7 Competing Pathways for Cellulose Pyrolysis

The nature and extent of many individual reactions involved in this process are not known or insufficiently defined. However, it is known that these reactions are highly influenced by : the temperatures and periods of heating ; the ambient atmosphere, oxygen, water and other reacting or inert gases ; and the composition and physical nature of the substrate.

The general reactions can be divided into primary and secondary reactions, according to whether they directly affect the cellulosic substrate or one of the intermediate degradation products. Alternatively, two general pathways for degradation of cellulosic materials may be recognized. One involves fragmentation, and formation of combustible volatiles that could feed the flames, and the second mainly involves dehydration and the formation of carbonaceous char.

Heating at lower temperatures enhances the dehydration and charring reactions. Formation of levoglucosan, which is a principal intermediate compound, takes place at somewhat higher temperatures and leads to further decomposition reactions at elevated temperatures.

At high temperature (above 500 °C), the pyrolysis chemistry of biomass materials has not received much

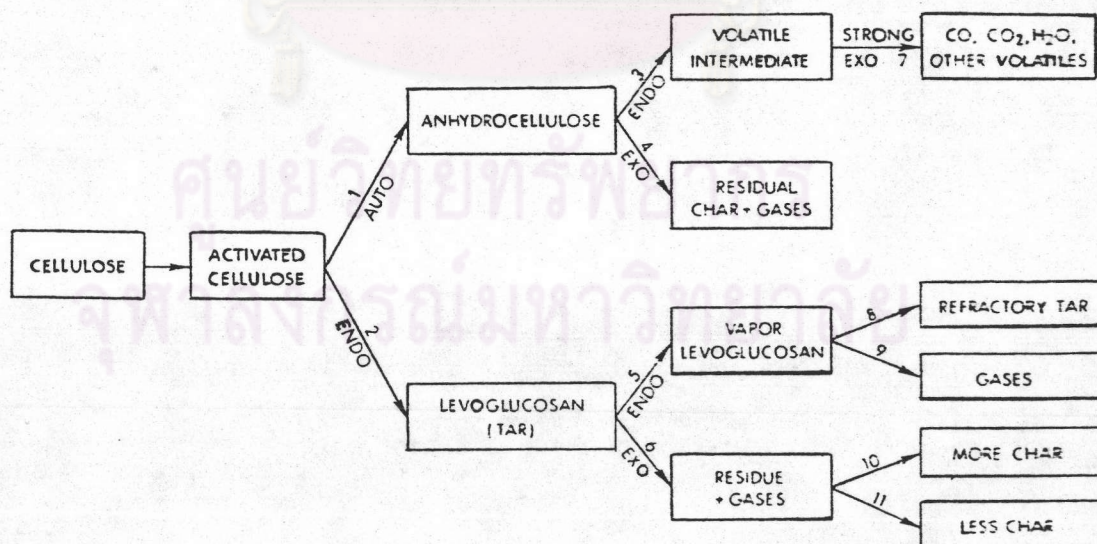


Figure 2.8 Pathways of Cellulose Pyrolysis

attention in the literature. At high temperatures, the pyrolysis mechanism is given in Figure 2.8. Increasing pressure encourages char forming pathways 4 and 6, whereas decreasing pressure encourages volatiles forming pathways 3 and 5.

2.3.1.2 Hemicellulose

On heating in the temperature range of pyrolysis, hemicellulose (polymeric sugars) evolves more gases and less tar than cellulose. Speculations as to reaction pathways for the condensable organics from hemicellulose parallel those for cellulose. Hemicellulose pyrolysis mechanism has a two step decomposition. First, depolymerization to water soluble fragments occurs, followed by decomposition to volatiles.

The early pyrolysis of hemicellulose to scission of a carbon-to-oxygen bond to a pentosan leads to formation of acetic acid and either formaldehyde or carbon monoxide and hydrogen may affect pyrolysis of cellulose and lignin.

2.3.1.3 Carbohydrate

The major pathways active during the pyrolysis of carbohydrate materials are shown in Figure 2.9. The "reaction tree" is somewhat speculative in that not all the branches have been observed to play an active role in the pyrolysis of all carbohydrate materials. Because the relative importance of

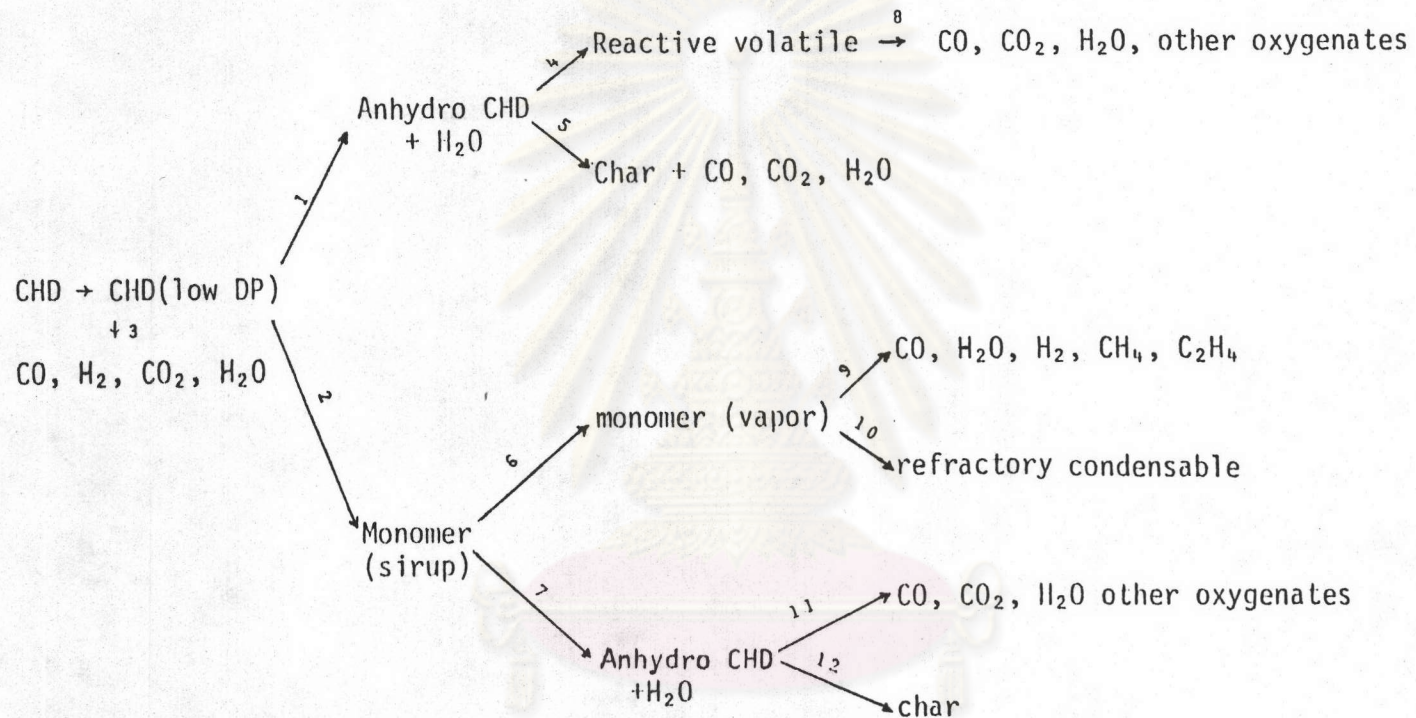


Figure 2.9 Pathways of Carbohydrate Pyrolysis Phenomena

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each pathway is influenced by the pyrolysis temperature, the molecular structure of the individual carbohydrate, the presence of additive, the pressure and chemical composition of the environment, and so forth, it is not surprising that some of the branches would be "dormant" for some materials under certain sets of pyrolysis conditions.

On the pyrolysis of carbohydrate materials at the low ($<250^{\circ}\text{C}$), moderate ($250^{\circ}\text{C} < T < 500^{\circ}\text{C}$) and high ($>500^{\circ}\text{C}$) temperatures pathways are numbered 1, 2 and 3 respectively. The un-numbered initiation reaction, which results in a reaction in degree of polymerization of polymer, is known to play a significant role in the pyrolysis of crystalline cellulose.

Pathway 1 involves intermolecular cross linking reactions: the formation of ether links across polymer chains accompanied by the evolution of water. Pathway 1 is virtually inactive in crystalline cellulose, but plays a dominant role in product formation during the low temperature pyrolysis of all noncrystalline carbohydrates. Subsequent degradation of the anhydrocarbohydrate occurs by the two competing pathways 4 (followed by 8) and 5. Pathway 4 involves the endothermic evolution of volatile species which subsequently undergo strongly exothermic reactions in the vapor phase to produce a variety of carbonyl compounds, CO , CO_2 and water. Low pressures and long residence times favor pathways 4 and 8. Conversely, high pressure favor the exothermic condensation reaction comprising pathway 5, which ultimately results in the formation of char, H_2O , CO_2 and CO from the anhydrocarbohydrate.

At somewhat higher temperatures transglucosylation reaction (pathway 2) result in the depolymerization of carbohydrates and the formation of sugar and anhydrosugar monomers. Pathway 2 is the dominant source of products during the pyrolysis of crystalline cellulose, but plays a less important role with amorphous carbohydrates. Following their formation, the monomer may either enter the vapor phase (pathway 6) or condense to form a dextrin (pathway 7). Conditions which enhance the ease of mass transfer to the vapor phase (low pressures and small particle sizes) favor pathway 6.

If the vapor phase monomers encounter temperatures in excess of 600°C they rapidly crack to form a hydrocarbon rich synthesis gas (pathway 9), whereas lower temperature and extended residence times lead to the formation of condensable materials (tars). Mass transfer limiting conditions, or the presence of acid or alkali catalysts, favor pathway 7. Pathways 1 and 7 are similar in that they lead to the formation of an anhydrocarbohydrate (dextrin) and are favored by low temperature and acid catalysts. Pathways 11 and 12 are analogous to pathways 4 and 5 discussed earlier.

The mechanisms of the individual reactions composing the various pathways depicted in Figure 2.9 are not well understood. Evidence supporting the roles of reactions in pathways 1, 2 and 7 exist in the literature. Little or no information exists concerning the mechanisms of the remaining pathways.

2.3.1.4 Lignin

The rich structural variety in the hypothesized lignin macromolecule gives rise to many mechanistic pathways to observed condensable organic compounds. The relative importance of a given pathway in the scheme below is strongly influenced by the lignin substrate and prevalent experimental conditions. One virtue of the "reaction tree" give in Figure 2.10 is its similarity to the earlier tree describing cellulose pyrolysis.

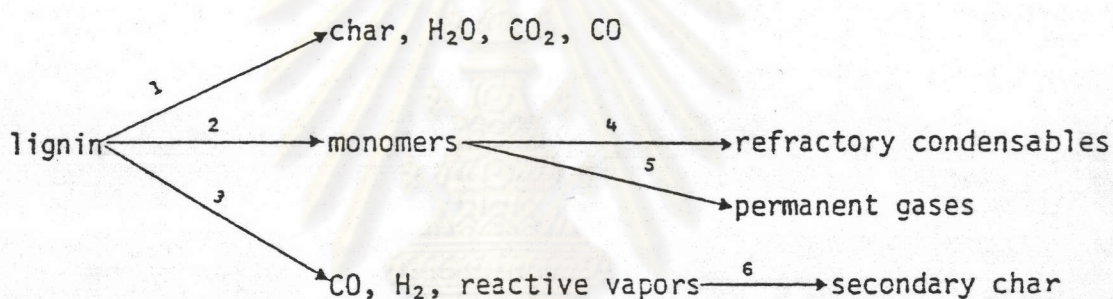


Figure 2.10 Lignin Pyrolysis Phenomena

At low temperatures (<240 °C) pathway 1 appear the role of dehydration reactions, then at higher temperatures (>240 °C), the formation of a variety of lignin monomers occurs in pathway 2. High heating rates and low pressures also effect on the formation of lignin monomers. At temperatures above 500 °C, the monomeric species evolved by pathway 2 begin to undergo degradation by vapor phase pyrolysis composing pathways 4 and 5. The lower temperature vapor phase condensation pathway 4 results in the formation of refractory, condensable materials,

whereas the higher temperature vapor phase "cracking" pathway 5 accounts for the evolution of much of the CO, CH₄ and other gaseous hydrocarbons obtained from the high temperature pyrolysis of lignin.

Char formation was observed to occur by the condensation of vapor phase species, apparently left in a supersaturated state after the rapid heating of the lignin substrate. These two pathways are designated as 3 and 6. The high temperature lignin pyrolysis pathway 3 involves fragmentation reactions and the formation of very high relative yields of CO.

2.3.2 Effect of Variables on Pyrolysis

Of most interest in the pyrolysis is the prediction of the rate and amount of volatile yield and product distribution for a given biomass and set of pyrolysis conditions. The important chemical variables are the elemental and functional compositions of the organic and inorganic matter in biomass, and among the more important basic physical variables are the final temperature, the time and rate of heating. Effect of variables on pyrolysis are discussed as follows :

2.3.2.1 Composition of Biomass

The biomass materials are generally complex and heterogeneous raw materials derived from different types of dead and living plant cells, the structure and composition

of which varies for different parts and species of the plants. Each of these compounds have different thermal properties and yield different products. At temperatures above 300 °C the polysaccharides break down at the glucosic linkage to provide tar containing lower molecular weight anhydrosugar derivatives and relatively little char, whereas the lignin is mainly condensed to a carbonaceous char and gives smaller amounts of phenolic compounds.

The heterogeneity of biomass presents a major obstacle to chemical utilization due to proportionately lower yields of individual products that can be derived from each component. It also affects the yield of charcoal or other types of fuels that could be obtained by straight pyrolysis.

2.3.2.2 Pyrolysis Temperature

The pyrolysis temperature affects both the amount and composition of the volatile yields. There are three principal stages of pyrolysis. In the first stage, above 200 °C and below 300 °C, the evolution of volatile matter is not large and what is released is principally gas composed mainly of oxides of carbon and water. In the active or second stage of decomposition, above 300 °C but below 500 °C, about three-quarters of all the volatile matter ultimately released is evolved. In the third stage (between 500 °C and 800 °C), there is a secondary degasification associated with the transformation of the char, accompanied by the release of noncondensable gases, mainly hydrogen.

2.3.2.3 Heating Rate

The effect of heating rate on the amount and composition of pyrolysis volatile yields is an important variable. Traditional laboratory and assay heating conditions have been characterized by rates of temperature increase around $20^{\circ}\text{C}/\text{sec}$ during the period of rapid evolution of the volatile matter, so slow heating is defined to correspond to gradients about equal to or smaller than this value. Rapid heating is loosely defined in the literature as being larger than 10^3 to 10^5 $^{\circ}\text{C}/\text{sec}$.

At slow heating rates or with large pieces of biomass, pyrolysis leads to a high proportion of charcoal. At the most rapid heating rates, cellulose is largely converted to a gas containing a high proportion of olefins and char production is minimal.

2.3.3 Products Evolved during Pyrolysis

During pyrolysis, biomass is decomposed to yield gases, tar and char. These products can be understood as the sum of the breakdown of its three components: cellulose, hemicellulose and lignin. The composition of products is studied in the laboratory using gas chromatography and mass spectrometry.

2.3.3.1 Cellulose

The initial decomposition product of

cellulose pyrolysis is levoglucosan, $C_6H_{10}O_5$ and anhydride of glucose. Subsequent coking and cracking reactions result in a char that contains oxygen and hydrogen in addition to the carbon. The char remaining on pyrolysis of wood contains about 80% carbon, 17% oxygen and 3% hydrogen.

Pyrolysis products of cellulose are given in Table 2.2 for several pyrolysis experiments. The nature of the products depends on the rate of heating and the temperature.

Table 2.2 Pyrolysis Products of Cellulose Reported in Two Different Studies

	Wt % of Sample		
	(Antal et al. 1979) 500 C	(Tsuchiya and Sumi 1970) 320 C	520 C
Total Accounted For	64%	89.5%	68.0%
Char	12	67.8	12.8
Tar ^a	35	10.3	28.4
Water	—	9.3	20.7
H ₂ ^b	0.4		
CO ^b	18	0.5	2.6
CO ₂ ^b	30	1.5	2.9
CH ₄ ^b	0.5		
C ₂ H ₄ ^b	0.5		
C ₃ H ₆ ^b	0.5		
C ₂ H ₆	0.5		
Other	1.3		
Hydrocarbons		—	0.3
Furan	0.03		0.04
2-Methylfuran		0.02	0.05
Furfural		0.06	0.08
5-Methylfural			
5-Hydroxymethyl Furfural		0.01	0.08
Levoglucosan ^c		3.8	18.2
1, 6-Anhydro-D-Glucofuranose		0.2	2.2
-D Glucose ^c		0.03	0.2
-D Glucose ^c		0.04	0.3
Dimers of Anhydroglucose		0.2	0.4
Unknown ^c		0.12	0.08
Unanalyzed Tar ^c		5.9	7.0

^aIncludes all tar fractions below.

^bUpper limits - mass balance only 64%.

^cTar fraction.

2.3.3.2 Hemicellulose and Holocellulose

A few studies have been made on the

gaseous and other products of holocellulose and hemicellulose pyrolysis. Holocellulose and hemicellulose tend to yield more gases and less tar than cellulose. Table 2.3 gives examples of product compositions for pyrolysis of a holocellulose and a hemicellulose.

2.3.3.3 Lignin

The thermal decomposition of lignin yields a substantial quantity of aromatic compounds and produces more charcoal than cellulose. Lignin is built of simpler molecules of aromatic compounds linked together by straight-chain compounds. The products of pyrolysis come from both aromatic and straight chain fragments of primary pyrolysis. Some of the products obtained in lignin pyrolysis are given in Table 2.4.

Table 2.3 Pyrolysis Products from a Holocellulose and a Hemicellulose (Xylan) (Shafizadeh, 1977)

	Wt % Product	
	Holocellulose (400 C)	Xylan (500 C)
Char	20.2	10
Tar	—	64
Water	37.3	7
CO ₂	11.0	8
CO	5.3	—
Low Molecular Weight Hydrocarbons	0.4	
Methanol	1.1	1.3
Acetaldehyde	0.2	2.4
Acetic Acid	1.4	1.5
Furan	0.5	Trace
Acrylaldehyde	0.07	
Diacetyl	0.2	
1-Hydroxy-2-Propanone	0.06	0.4
2-Furaldehyde	0.5	4.5
Acetone-Propionaldehyde		0.3
2-3-Butanedione		Trace
3-Hydroxy-2-Butanone		0.6

Table 2.4 Volatile Products from Lignin Pyrolysis

	Douglas Fir Lignin ^a Pyrolyzed at 400-445 C for 7.5h	Kraft Black Liquor ^b Pyrolyzed at 490 C
Char	53-54.6%	Methyl mercaptan
Aqueous distilled	15-25%	Dimethyl sulfide
Tar	~9%	Benzene
Gases	—	Toluene
Organic acids	formic, acetic propionic plus traces of others	m and/or p-Xylene Anisol Phenol
Phenols	phenol, o-cresol p-cresol, guaiacol 2, 4-xyleneol, 4-methyl and ethyl guaiacol, 4-n-propylguaiacol	o-cresol m and/or p-cresol 2, 5 and/or 2, 4 dimethyl 3, 5 dimethyl phenol
Catechols	catechol, 4-methyl and ethyl catechol, 4-n-propyl catechol	2, 3 dimethyl phenol 3, 4 dimethyl phenol

^aFletcher and Harris 1952.^bBrink et al. 1971.

2.4 Properties of Biomass Relevant to Thermochemical

Processes

Biomass is made up of three principal chemical components consist of cellulose, hemicellulose and lignin and both the structure and the pyrolysis or gasification of the infinite varieties of biomass can be understood in terms of the behavior of these chemical components. In addition, minor amounts of extractables consist of hydrocarbons, tannins, oils and resins can add to the fuel and chemicals derived from the biomass.

Because of the many forms of biomass, it is difficult to make general statements about the thermal properties of all biomass materials. An understanding of the structure and properties of biomass materials is necessary in order to evaluate their utility.

2.4.1 Bulk Chemical Properties of Biomass

The chemical properties of biomass provide information on proximate and ultimate analysis data which indicate volatility and elemental composition in biomass.

The proximate analysis classifies the biomass in terms of its moisture content (M), volatile matter (V.M.), ash and fixed carbon (by difference). Typical proximate analysis for biomass are given in Table 2.5.

The ultimate analysis is generally used to report elemental composition, in biomass conversion, for carbon, hydrogen, nitrogen, sulfur and oxygen (by difference). Table 2.6 shows the ultimate analysis for biomass.

Table 2.5 Proximate Analysis Data for Biomass Material
from Jenkin (1980) (Dry Basis, % Weight)

Fuel	Volatile matter	Ash	Fixed carbon	Total
Alfalfa seed straw	68.2	6.0	25.8	100.0
Almond shell	69.2	4.8	26.0	100.0
Barley straw (high)	64.9	10.3	24.8	100.0
Barley straw (low)	64.9	10.3	24.8	100.0
Bean straw	68.0	10.2	21.8	100.0
Corn cobs	74.2	1.5	24.2	99.9
Corn stalks	73.3	6.4	20.3	100.0
Cotton gin trash	63.6	17.6	18.8	100.0
Cotton stalks	62.9	17.2	19.9	100.0
Olive pits	75.6	3.2	21.2	100.0
Peach pits	73.9	0.9	25.2	100.0
Prune pits	78.8	0.5	25.7	100.0
RDF (refuse derived fuel)	72.0	10.4	17.6	100.0
Rice hulls	60.2-62.1	16.9-17.2	20.7-21.8	100.0
Safflower straw	68.6	6.0	25.4	100.0
Walnut shell (cracked)	79.6	1.1	19.3	100.0
Walnut shell (1/4" pellets)	70.2	5.8	24.0	100.0
Wheat straw (50/50 corn stalks)	68.4	7.4	24.2	100.0
Wood blocks	75.0	0.2	24.8	100.0
Wood chips (city tree prunings)	71.7	3.0	25.3	100.0
Wood chips (hogged)	78.0	0.3	21.7	100.0
Wood chips (Manzanita)	72.8	0.4	26.8	100.0
Wood chips (prune tree)	76.4	1.1	22.5	100.0
Wood chips (barked whole log)	76.4	0.1	23.5	100.0

Table 2.6 Ultimate Analysis Data for Biomass (Dry Basis, % Weight)

Material	C	H	N	S	O	Ash	Higher Heating Value (Btu/lb)
Pittsburgh seam coal	75.5	5.0	1.2	3.1	4.9	10.3	13,650
West Kentucky No. 11 coal	74.4	5.1	1.5	3.8	7.9	7.3	13,460
Utah coal	77.9	6.0	1.5	0.6	9.9	4.1	14,170
Wyoming Elkol coal	71.5	5.3	1.2	0.9	16.9	4.2	12,710
Lignite	64.0	4.2	0.9	1.3	19.2	10.4	10,712
Charcoal	80.3	3.1	0.2	0.0	11.3	3.4	13,370
Douglas fir	52.3	6.3	0.1	0.0	40.5	0.8	9,050
Douglas fir bark	56.2	5.9	0.0	0.0	36.7	1.2	9,500
Pine bark	52.3	5.8	0.2	0.0	38.8	2.9	8,780
Western hemlock	50.4	5.8	0.1	0.1	41.4	2.2	8,620
Redwood	53.5	5.9	0.1	0.0	40.3	0.2	9,040
Beech	51.6	6.3	0.0	0.0	41.5	0.6	8,760
Hickory	49.7	6.5	0.0	0.0	43.1	0.7	8,670
Maple	50.6	6.0	0.3	0.00	41.7	1.1	8,580
Poplar	51.6	6.3	0.0	0.0	41.5	0.6	8,920
Rice hulls	38.5	5.7	0.5	0.0	39.8	15.5	6,610
Rice straw	39.2	5.1	0.6	0.1	35.8	19.2	6,540
Sawdust pellets	47.2	6.5	0.0	0.0	45.4	1.0	8,814
Paper	43.4	5.8	0.3	0.2	44.3	6.0	7,572
Redwood wastewood	53.4	6.0	0.1	39.9	0.1	0.6	9,163
Alabama oak woodwaste	49.5	5.7	0.2	0.0	41.3	3.3	8,266
Animal waste	42.7	5.5	2.4	0.3	31.3	17.8	7,380
Municipal solid waste	47.6	6.0	1.2	0.3	32.9	12.0	8,546

2.4.2 Physical Properties

In addition to chemical properties, the other major physical data necessary for predicting the thermal response of biomass materials under pyrolysis, gasification and combustion processes are thermal conductivity, heat capacity and density.

2.4.2.1 Thermal Conductivity

Thermal conductivity is defined in general terms as a proportionality factor which relates heat flow through a material to a temperature difference across a specified distance in that material. Mathematically, thermal conductivity is defined by Fourier's Law of Heat Conduction, given here for unidimensional heat flux in the x-direction in rectangular

coordinates :

$$q_x = -k_x \frac{dT}{dX} \quad (2.3)$$

Due to thermal conductivity depends on the various materials present in a substance. Thus thermal conductivity is a function of the major constituents, including moisture content, cellulose, hemicellulose, and lignin. Table 2.7 compiles available thermal conductivity data for biomass materials that is probably effective thermal conductivities of solid powder rather than of the solid pieces.

Table 2.7 Thermal Conductivity of Selected Biomass Materials

Material	Bulk Density (lb/ft ³)	Temperature (F)	Thermal Conductivity (Btu/ft-h-F)	Reference
Ashes, wood	—	32-212	0.040	Kern 1950
Cardboard	—	—	0.037	Kern 1950
Carbon, porous, with grain				
Grade 60 48% porosity	65.5 ^a	Room Temp.	0.083	Perry and Chilton 1973
Grade 45 47% porosity	64.9 ^a	Room Temp.	0.083	Perry and Chilton 1973
Grade 25 47% porosity	64.3 ^a	Room Temp.	0.083	Perry and Chilton 1973
Carbon refractory brick 17% porosity	102.9 ^a	Room Temp.	1.33	Perry and Chilton 1973
Celotex, sheet fiber from sugar cane	13.2	—	0.028	Handbook Chem. Phys. 1966
	14.3	—	0.028	Handbook Chem. Phys. 1966
	14.4	32	0.0253	McAdams 1954
	14.4	0	0.0242	McAdams 1954
	14.4	-100	0.0208	McAdams 1954
	14.4	-200	0.0173	McAdams 1954
	14.4	-300	0.0133	McAdams 1954
Charcoal - from maple, beech, and birch				
Coarse	13.2	—	0.030	Handbook Chem. Phys. 1966
6 mesh	15.2	—	0.031	Handbook Chem. Phys. 1966
20 mesh	19.2	—	0.032	Handbook Chem. Phys. 1966
Charcoal flakes	11.9	176	0.043	McAdams 1954
	15	176	0.051	McAdams 1954
		0 to 100	0.11	Perry and Chilton 1973
Coke powder				
Cork, regranulated				
Fine particles	9.4	—	0.025	Handbook Chem. Phys. 1966
3/16-in. particles	8.1	—	0.026	Handbook Chem. Phys. 1966
Corkboard	5.4	—	0.021	Handbook Chem. Phys. 1966
	7.0	—	0.022	Handbook Chem. Phys. 1966
	10.5	—	0.025	Handbook Chem. Phys. 1966
	14.0	—	0.028	Handbook Chem. Phys. 1966
	6.9	32	0.0205	McAdams 1954
	6.9	0	0.0200	McAdams 1954
	6.9	-100	0.0133	McAdams 1954
	6.9	-200	0.0142	McAdams 1954
	6.9	-300	0.0100	McAdams 1954
Cork, pulverized	10.0	32	0.035	McAdams 1954
	10.0	100	0.039	McAdams 1954
	10.0	200	0.032	McAdams 1954
Cotton	5.0	200	0.037	McAdams 1954
	5.0	100	0.035	McAdams 1954
	5.0	32	0.0325	McAdams 1954
	5.0	-100	0.0276	McAdams 1954
	5.0	-200	0.0235	McAdams 1954
	5.0	-300	0.0198	McAdams 1954

Table 2.7 Thermal Conductivity of Selected Biomass Materials

(cont.)

Material	Bulk Density (lb/ft ³)	Temperature (°F)	Thermal Conductivity (Btu/ft-h-F)	Reference
Graphite				
2 3/4 in. diam., 3/4 in. thick				
30% porosity	98.6 ^a	—	7.33	Handbook Chem. Phys. 1966
Porous, Grade 50 52% porosity	65.5 ^a	—	4.17	Handbook Chem. Phys. 1966
Porous, Grade 45 53% porosity	64.9 ^a	—	3.75	Handbook Chem. Phys. 1966
Porous, Grade 25 53% porosity	64.3 ^{a*}	—	3.33	Handbook Chem. Phys. 1966
Paper	—	—	0.075	McAdams 1954
Paper or pulp, macerated	2.5-3.5	—	0.021	Lewis 1968
Sawdust, various	12.0	—	0.034	Handbook Chem. Phys. 1966
Redwood (and shavings)	10.9	—	0.035	Handbook Chem. Phys. 1966
Sawdust (soft pine and oak)	8-15	—	0.0375	Lewis 1968
10-40 mesh	—	-295	0.016	Chow 1948
	—	-180	0.0195	Chow 1948
	—	-105	0.0235	Chow 1948
	—	-55	0.0255	Chow 1948
	—	-20	0.0295	Chow 1948
	—	+5	0.0325	Chow 1948
	—	+30	0.0335	Chow 1948
	—	+35	0.0385	Chow 1948
	—	+62	0.040	Chow 1948
Shredded redwood bark	4.0	32	0.0290	McAdams 1954
	4.0	-100	0.0235	McAdams 1954
	4.0	-200	0.0196	McAdams 1954
	4.0	-300	0.0155	McAdams 1954
	—	-50	0.0168	Rowley et al. 1945
	—	-25	0.0190	Rowley et al. 1945
	—	+25	0.0203	Rowley et al. 1945
	—	+75	0.0226	Rowley et al. 1945
Sheet Insulite, from wood pulp	16.2	—	0.028	Handbook Chem. Phys. 1966
	16.9	—	0.028	Handbook Chem. Phys. 1966
Wood fiber, mat	1.7	-50	0.016	Rowley et al. 1945
	1.7	0	0.018	Rowley et al. 1945
	1.7	+50	0.020	Rowley et al. 1945
	1.7	+100	0.023	Rowley et al. 1945
Blanket	3.5	-50	0.016	Rowley et al. 1945
	3.5	0	0.018	Rowley et al. 1945
	3.5	50	0.020	Rowley et al. 1945
	3.5	100	0.022	Rowley et al. 1945
Excelsior	1.64	-50	0.019	Rowley et al. 1945
	1.64	0	0.022	Rowley et al. 1945
	1.64	50	0.025	Rowley et al. 1945
	1.64	100	0.024	Rowley et al. 1945
Solid woods				
Balsa	8-12	-300	0.0151	Gray et al. 1960
	8-12	-285	0.0150	Gray et al. 1960
	8-12	-260	0.0157	Gray et al. 1960
	8-12	-207	0.0183	Gray et al. 1960
	8-12	-190	0.0192	Gray et al. 1960
	8-12	-160	0.0208	Gray et al. 1960
	8-12	-130	0.0233	Gray et al. 1960
	8-12	-95	0.0232	Gray et al. 1960
Balsa, across grain	7.3	—	0.028	Handbook Chem. Phys. 1966
	8.3	—	0.032	Handbook Chem. Phys. 1966
	20	—	0.048	Handbook Chem. Phys. 1966
Cypress, across grain	29	—	0.056	Handbook Chem. Phys. 1966
Mahogany, across grain	34	—	0.075	Handbook Chem. Phys. 1966
Maple, across grain	44.7	122	0.11	McAdams 1954
Fir	26	75	0.063	Chapman 1974
Oak	30-38	86	0.096	Chapman 1974
Yellow pine	40	75	0.085	Chapman 1974
White pine	27	86	0.065	Chapman 1974
Pine, white, across grain	34	59	0.087	McAdams 1954
	32	—	0.032	Handbook Chem. Phys. 1966
Pine, Virginia, across grain	34	—	0.082	Handbook Chem. Phys. 1966
Pine board, 1 1/4-in. thick	—	-50	0.0515	Gray et al. 1960
	—	0	0.054	Gray et al. 1960
	—	+50	0.0575	Gray et al. 1960
	—	+100	0.059	Gray et al. 1960
Pine, with grain	34.4	70	0.20	McAdams 1954
Oak, across grain	51.5	59	0.12	McAdams 1954

^a Apparent density

Completely lacking in the available data are thermal conductivities at higher temperatures. If thermal conductivity values are to be used in modelling pyrolysis or gasification processes, then new data over the actual range of processing conditions must be developed, including data for densified materials.

2.4.2.2 Heat Capacity

Heat capacity as normally reported is defined in terms of the enthalpy content of a material and represents the relative ability of a material to store energy. Enthalpy is a function of temperature and pressure.

$$H = H(T, P) \quad (2.4)$$

and

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP \quad (2.5)$$

For solids and liquids $\frac{\partial H}{\partial P}$ is very small and

$$dH = \left(\frac{\partial H}{\partial T}\right)_P dT \quad (2.6)$$

By definition the temperature dependency term $\left(\frac{\partial H}{\partial T}\right)_P$ called heat capacity at constant pressure, C_p , and is reported on a per unit weight basis. The resulting equation for the enthalpy change is as follows :

$$H = \int_{T_{ref}}^T C_p dT \quad (2.7)$$

The heat capacity is a function of the composition and temperature but not the density of the material as long as compacting does not alter the chemical structure.

As with thermal conductivity, no references were readily available for heat capacity of biomass materials for the temperature range of thermal processing condition needed for pyrolysis or gasification ; new data are needed for applicable temperature ranges.

2.4.2.3 Density

The density of the material is important in considering energy contents of fuels on a volumetric basis, such as for transport, solids handling and sizing reaction vessels. There are three ways of reporting solid material density : bulk density, apparent particle density and skeletal density. These density values differ in the way in which the material volume is calculated. The bulk density volume basis includes the actual volume of the solid, the pore volume, and the void volume between solid particles. Apparent particle density includes solid volume and pore volume. Skeletal density, or true density, includes only solid volume. The three values are related as follows :

$$p_b = p_s(1 - \epsilon_p) \quad (2.8)$$

$$p = p_s(1 - \epsilon_b) \quad (2.9)$$

Thus the density of biomass depends on the nature of the material, its moisture content, and degree of densification.