Chapter 12

CHEMICALS FROM BIOMASS

Chapter 12.-CHEMICALS FROM BIOMASS

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CHEMICALS FROM BIOMASS

Introduction

Biomass is used as a source of several industrial chemicals, including dimethyl sulphoxide, rayons, vanillin, tall oil, paint solvents, tannins, and specialty chemicals such as alkaloids and essential oils. Biomass is also the source of furfural which is used to produce resins and adhesives and can be used in the production of nylon.[1] Aside from paper production, biomass currently is the source of cellulose acetates and nitrates and other cellulose derivatives (4 billion lb annually). Other chemicals include tall oil resin and fat acid, lignosulfonate chemicals, Kraft lignin, bark chemicals, various seed oils, and many more. Every petroleum-derived chemical currently being used could be produced from biomass and nonpetroleum minerals, but some (e. g., carbon disulphide) would require rather circuitous synthesis routes.

In the future biomass-derived chemicals could play an increasing role in the petrochemical industries. The economic decisions to use or not to use biomass will be based on an assessment of the overall process from feedstock to end product and it will probably involve consideration of various alternative synthesis routes in most cases. At present, however, too little information is available about the relative merits of biomass-versus coal-derived chemicals to expect widespread, new industrial commitments to biomass chemicals in the near future. This uncertainty depends as much on uncertainties surrounding the costs and possibilities of coal syntheses as on those surrounding biomass chemicals. Continued research into both options is needed to resolve the problem and it is likely (as has been the case in the past) that a mix of feedstocks will result.

Biomass-derived chemicals can be divided into two major areas: 1) those in which the plant has performed a major part of the synthesis and 2) those in which chemical industry feedstocks are derived by chemical synthesis from the more abundant biomass resources such as wood, grasses, and crop residues. Some examples of each type are given below. The possibilities are so enormous, only an incomplete sampling can be given here. A thorough analysis of the options for chemicals from biomass is beyond the scope of this study.

Chemicals Synthesized by Plants

Several plant species produce relatively large quantities of chemicals that can be used to produce plastics, plasticizers, lubricants, coating products (e. g., paints), and various chemicals that can serve as intermediates in the syntheses used for numerous industrial products.[2]

The biologically synthesized chemicals that are most easily used in the chemical industries are those that are either: 1) identical to existing feedstock or intermediate chemicals, or 2) have properly placed chemical groups which are susceptible to chemical attack so that they can be readily converted to the needed industrial chemicals. There is also the *possibility of* using biologically derived chemicals to produce products (such as plastics) which would be expected to have similar properties to the products currently produced. For example, nylon could be made from acids and amines other than the six carbon acids and amines currently used for nylon synthesis.

Some plant species producing various classes of chemicals are shown in tables 69

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[1] I S Goldstein, "Potential for Converting Wood Into Plastics," *Science*, vol 189, p 847, 1975

[2] L H Princen, "Potential Wealth In New Crops. Research and Development," (*Crop Resources* (New York Academic Press, 1977)

through 72. (Note that these lists are incomplete and used only to illustrate some **possibilities.) Included are the following types:**

- long-chain fatty acids which might be used for the production of polymers, lubricants, and plasticizers;
- hydroxy fatty acids which could displace the imported castor oil currently used as a supply of these fatty acids;
- epoxy fatty acids which may be useful in plastics and coating materials; and

Table 69.–Species With Long-Chain Fatty Acids in Seed Oil

Common name	Species	Component in triglyceride oil
Crambe.	Crambe abyssinica	60% C_{22}
Money plant	Lunaria annua	40% C_{22}, 20% C_{24}
Meadowfoam.	Limnanthes alba	95% C_{22} + C_{20}
Selenia	Selenia grandis	58% C_{22}
—	Leavenworthia alabamica	50 % C_{22}
Marshallia.	Marshallia caespitosa	44% C_{22}

SOURCE : L. H. Prlncen, "Potenllal Wealth in New Crops Research and Development, Crop Re*sources (New* York Academic Press, Inc.), 1977

Table 70.–Species With Hydroxy and Keto Fatty Acids

Common name	Species	Component in triglyceride oil
Bladderpod .	Lesquerella gracilis	14-OH-C_{20}(70%)
Consessi Holarrhena.	Holarrhena antidysenterica	9-OH-$C_{,8}$(70%)
Bittercress .,	Cardamine impatiens	Dihydroxy C_{22} and C_{24} (23%)
Thistle	Chamaepeuce afra	Trihydroxy C_{18}(35%)
Bladderpod	Lesquerella densipila	12-OH-C_{18}diene (50%)
Blueeyed Capemarigold. .	Dimorphotheca sinuata	9-OH-C_{18}conj. diene (67%)
Myrtle Coriaria. . .	Coriaria myrtifolia	13-OH-C_{18}conj. diene (65%)
—	Cuspedaria pterocarpa	Keto acids (25%)

SOURCE L H Princen, "Polenhal Wealth in New Crops Research and Development," *Crop Resources (New* York Academic Press, Inc), 1977

Table 71 .–Potential Sources of Epoxy Fatty Acids

Common name	Species	Epoxy acid content,%
Kinkaoil ironweed. . . .	Vernonia anthelmintica	68-75%
Euphorbia	Euphorbia lagascae	60-70
Stokesia	Stokesia laevis	75
—	Cephalocroton pueschellii	67
—	Erlangea tomentosa	50
Hartleaf Christmasbush	Alchornea cordifolia	50 (c_{20})
—	Schlectendalia luzulaefolia	45

SOURCE L H Princen, "Potenllal Wealth in New Crops Research and Development, *Crop Resources (New* York Academic Press, Inc), 1977

Table 72.–Sources of Conjugated Unsaturates

Common name	Species	Type of saturation
Common valeriana.	Valeriana officinalis	40% 9,11,13
Potmarigold colendula . . .	Calendula officinalis	55% 8,10,12
Spurvalerian centrathus. .	Centranthus macrosiphon	65% 9,11,13
Snapweed	Impatiens edgeworthii	60% 9,11,13,15
Blueeyed Capemarigold .	Dimorphotheca sinuata	60% 10,12 (+ hydroxy)
Myrtle Coriaria	Coriaria myrtifolia	65% 9,11 (+ hydroxy)

SOURCE L H Princen, "Potential Wealth in New Crops" Research and Development, *Crop I?esources (New* York Academic Press, Inc), 1977

- conjugated unsaturates potentially useful as intermediates in the synthesis of various industrial products. (These can also be obtained from structural modification of soybean and linseed fatty acids.[3]).

Other possible new sources of chemicals and materials include natural rubber from guayule *(Parthenium argentaturn),*[4] and possibly jojoba (Sirnmondia chinensis) and paper pulp from kenaf ***(Hibiscus cannabinus).***[5] Some of these plants have also received considerable attention because it may be possible to grow them on marginal lands or land where the irrigation water is insufficient to support conventional crops (see ch. 4). **It** is risky, however, to extrapolate unambiguous conclusions about their economic viability from incomplete data on the cultivation. In many cases they would also compete with food production for the available farmland. Nevertheless, continued screening of plant species together with cultivation tests should provide numerous additional options for the cultivation of crops yielding chemicals for industrial use.

Another type of chemical synthesis involves the use of specific bacteria, molds, or yeasts to synthesize the desired chemicals or substance. Commercial production of alcohol beverages by fermentation is one example. Mutant bacteria designed to produce insulin or other

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[3] W J De Jarlais, L E Cast, and J C Cowan, *I Am. Oil Chem. Soc.*, vol 50, p 18, 1973

[4] K E Foster, "A Sociotechnical Survey of Buyule Rubber Commercializat Ion," report to the National Science Foundation, Division of Policy Research and Analysis, grant No PRA 78-11632, April 1979

[5] M O Bagby, "Kenaf A Practical Fiber Resource, " *TAPPI Press Report Non-Wood Plant Fiber Pulping Process Report, No 8,* p *175,* Atlanta, Ga , 1977

drugs is another.'[7] Furthermore, other basic **biochemical processes** such as the reduction of nitrates to ammonia may also be used eventually.[8]

Further study into the details of photosynthesis, the biochemistry of plants, and molecular genetics could lead to the development of other plants or micro-organisms that could synthesize specific, predetermined chemicals. The options seem enormous at this stage of development, but considerable additional R&D is needed before the full potential of this approach can be evaluated.

Chemical Synthesis From Lignocellulose

The second major area of chemicals from biomass involves using the abundant biomass resources of wood, grasses, and crop residues (lignocellulosic material) to synthesize large-volume chemical feedstocks, which are converted in the chemical industry to a wide variety of more complex chemicals and materials. The large (polymer) molecules in lignocellulosic materials are converted to the desired chemical feedstocks either: 1) by chemical means or 2) with heat or microwaves. The distinction between these two approaches, however, is not always clear cut.

The chemical means include treatment with acids, alkaline chemicals, and various bacterial processes. Pretreatments also often involve some heating and mechanical grinding (see ch. 8). The three basic polymers– lignin, cellulose, and hemicellulose — are reduced to sugars and various benzene-based (so called aromatic) chemicals, which can be used to synthesize the chemical feedstocks by rather direct and efficient chemical synthesis or fermentation (see figure 38). Some of the major petrochemical feedstocks that can be produced in this way are shown in table 73, together with the quantities of these chemicals (derived mostly from petroleum) which were used by the chemical industries in 1974.

The quantities of wood that would be required to satisfy the 1974 U.S. demand for plastics, synthetic fibers, and synthetic rubber from the above chemical feedstocks are shown in table 74 for the various types of products. These estimates were derived by Goldstein[9] using optimistic assumptions about the yields of the sugars- and benzene-based chemicals from wood. Obtaining these sugars- and benzene-based compounds from wood is currently the subject of considerable R&D. (See ch. 8.) The yields for the other chemical reactions were based on established experimental and industrial data.

About 95 percent of these synthetic polymers (plastics, synthetic fibers, and synthetic rubbers) can be derived from wood or other lignocellulosic materials, although the circuitous synthesis route required for some of them might make such processes uneconomic at this time. In al 1, Slightly less than 60 million dry tons (about 1 Quad) of wood per year could supply 95 percent of these synthetic polymer needs; and the ratio of cellulose to lignin required **(2:1)** would be about the same as their natural abundance in wood. This quantity of wood is relatively modest in comparison to OTA estimates of the quantities that can be made available, and in all cases it serves as a direct substitute for chemicals derived from fossil fuels (mostly oil and natural gas). About three to five times as much wood would be needed to supply all petrochemical needs using more or less established chemical synthesis routes,[10] and again there appears to be no technical barrier to supplying these quantities of wood. In both cases, however, addi-

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[6] Pearce Wright, Time **for Bug Valley, " New** *Scientist,* p 27, July 5, 1979

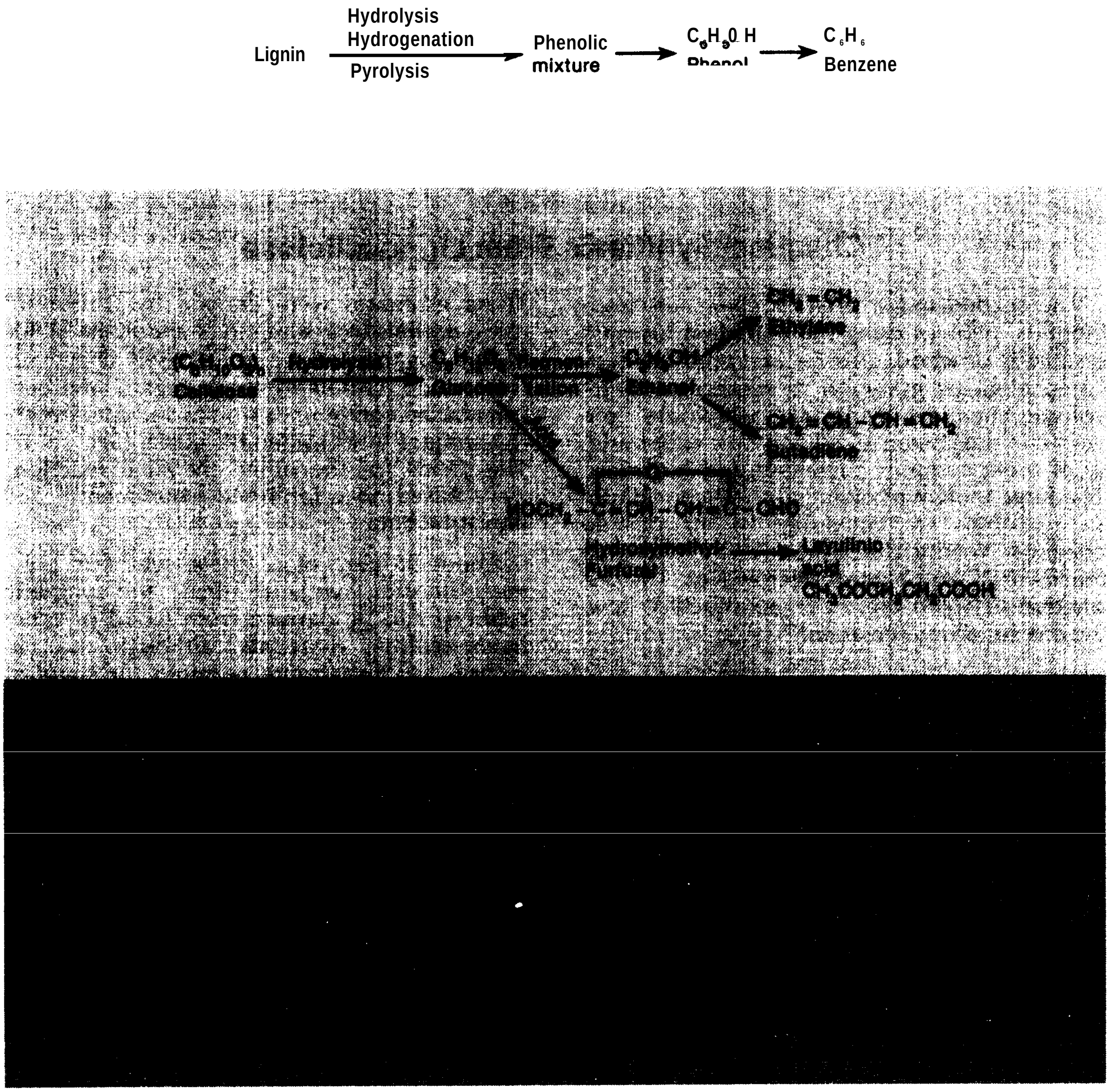
[7] "Where Genetic Engineering Will **Change Industry, "** *Business Week,* p **160, Oct 22, 1979**

[8] P **Candan, C** Manzano, **and M** Losada, "Bioconversion **of** Light **Into** Chemical Energy **Through Reduction With Water of** Nitrate **to Ammonia, "** *Nature,* vol **262, p 715, 1976**

[9] Goldstein, op cit

[10] S Goldstein, **Department** of Wood and Paper Science, North Carolina State University, Raleigh, N C , private communication, 1980

Figure 38.—Synthesis Routes for Converting Lignocellulose Into Select Chemical Feedstocks



SOURCE: 1. S. Goldstein, "Chemicals From Lignocellulose," *Biotechnol. and Bioen. Symp. No.* 6, (New York: John Wiley and Sons, Inc., 1976), p. 293.

Table 73.–Major Petrochemicals That Can Be Synthesized From Lignocellulose

	1974 U.S. production (in billions of pounds)
Total lignocellulose	
Ammonia	31.4
Methanol	6.9
Hemicellulose	
Ethanol.	2.0
cellulose	
Ethanol,	2.0
Ethylene	23,5
Butadiene	3.7
Lignin	
Phenol	2.3
Benzene	11.1

SOURCE: From I. S. Goldstein Chemicals From Lignocellulose in *Biotechnology and Bioenergy Symposium No* 6(John Wiley&Sons Inc. p 293 1976)

Table 74.–1974 Production of Plastics, Synthetic Fibers, and Rubber, and Estimated Lignocellulose Raw Material Base Required

Material	Production (10^3tons)	Lignocellulose required[a] (10^3tons)
Plastics		
Thermosetting resins		
Epoxies	125	***355*** (L)
Polyesters	455	1,220 (L)
Urea	420	—
Melamine.	80	—
Phenolic and other tar-acid resins	670	1,915 (L)
Thermoplastic resins		
Polyamide	100	285 (L)
Polyethylene		
Low density.	2,985	11,940 (c)
High density	1,420	5,680 (C)
Polypropylene and copolymers	1,125	4,500 (c)
Styrene and copolymers,	2,505	7,445 (L)
Polyvinyl chloride	2,425	4,225 (C)
Other vinyl resins	175	440 (c)
Total plastics.	12,485	
Synthetic fibers		
Cellulosic		
Rayon	410	—
Acetate	190	—
Noncellulosic		
Nylon.	1,065	3,045 (L)
Acrylic,	320	640 (C)
Polyester	1,500	4,020 (L)
Olefin	230	920 (C)
Total noncellulosic fibers,	3,115	
Synthetic rubber		
Styrene-butadiene	1,615	5,700 (c)
		1,920 (L)
Butyl.	180	1,060 (C)
Nitrile	95	190 (c)
Polybutadiene	360	2,120 (c)
Polyisoprene	100	—
Ethylene-propylene.	140	825 (C)
Neoprene and others.	280	—
Total synthetic rubber.	2,770	
Total plastics, noncellulosic fibers, and rubber.	18,370	
Obtainable from lignocellulose	17,490	58,445
Cellulose drived (C).		38,240 (C)
Lignin derived (L)		20,205 (L)

[a] Estimated from optimistic approximate yields of monomers obtainable (C) cellulose derived (L) lignin derived

SOURCE I S Goldstein. "Potential for Converting Wood Into Plastics. Science vol 189, p 847, 1975

tional energy would be needed to provide heat **for the syntheses; and, in some cases, this is** more than the energy content of the chemical feedstock.[11] **As of 1976, the petrochemical** industry consumed 1.2 Quads/yr of oil and natural gas for fuel and **2.3** Quads/yr for feedstocks.[12]

Another approach to chemicals from lignocellulose involves heat, partial combustion, or the use of microwave radiation to break the natural polymers into smaller molecules suitable for the synthesis. Biogas derived from the anaerobic digestion of biomass could also be used in some of these processes, but the yields are likely to be lower than for the more direct processes. Some possible synthetic routes are shown in figure 39.

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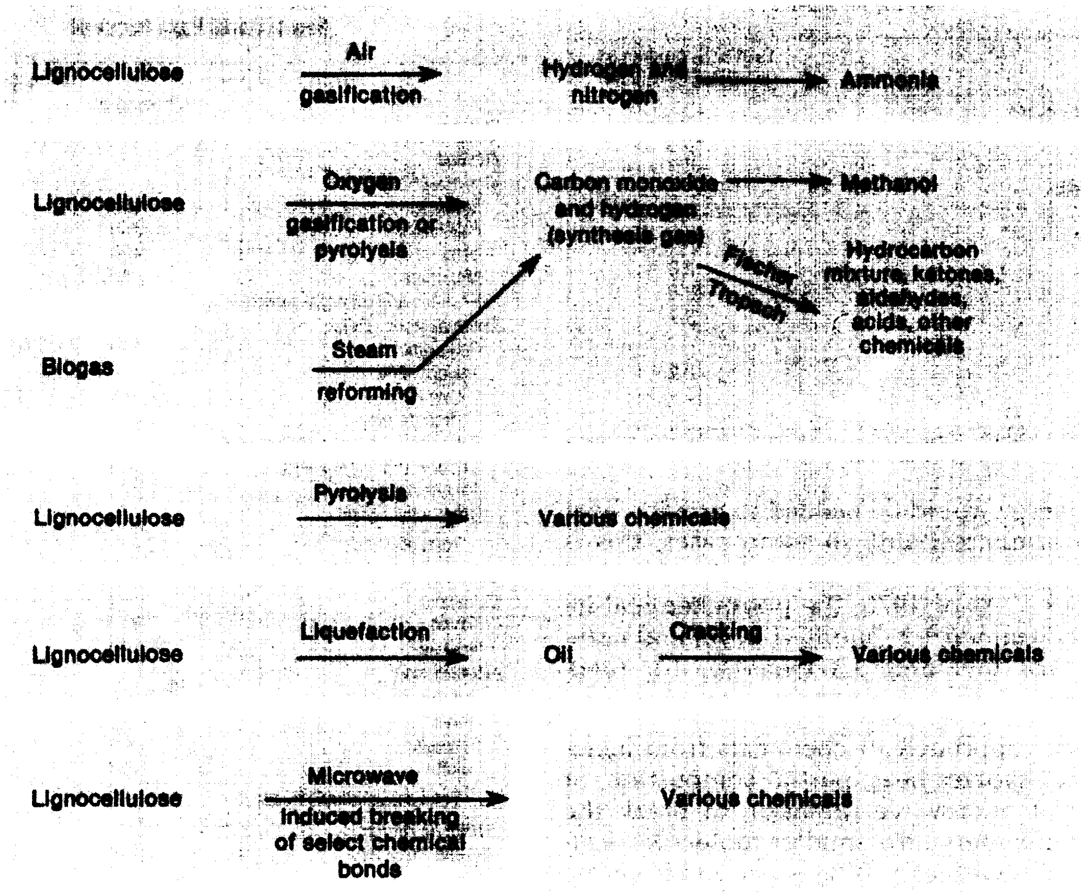
[11] "Big Future for Synthetics," *Science*, vol **208,** p **576, May 9, 1980**

[12] G B Hegeman, *Report to the Petrochemical Energy Group on 1976 Petrochemical Industry Profile* (Cambridge, Mass Arthur D Little, Inc, June 28, 1977)

Figure 39.—Chemical Synthesis Involving Thermal Processes and Microwaves



SOURCE: Office of Technology Assessment.

The production of ammonia[13] and methanol from wood can be accomplished with commercial technology (see ch. 7 for further details of the methanol synthesis). The Fischer Tropsch process is commercial in South Africa (although the source of the synthesis gas is coal rather than biomss). The economics of the processes other than methanol synthesis have not been assessed by OTA for this report.

The other processes yielding various chemicals are considerably less developed. The yields of some chemicals that have been produced in laboratory experiments using rapid heating and gasification (pyrolysis) of various types of biomass are shown in table 75. Presumably by learning more about pyrolysis, the yields of select chemicals would be increased to a level where it could be economical to extract that chemical from the gas. An example might be the conceptual equation:

$$\begin{array}{ccccc} C_{10}H_{14}O_6 & \rightarrow & 3CO_2 & + & 3.5\,C_2H_4 \\ \text{Wood} & & \text{Carbon dioxide} & & \text{Ethylene} \\ \text{(solid)} & & \text{(gas)} & & \text{(gas)} \end{array}$$

where 43 weight percent of the dry wood is converted to ethylene (which is by far the largest volume petrochemical used **for chemical synthesis in** the world). If it becomes practical to achieve relatively high (e. g., **30** weight percent) yields of ethylene, then this process could be competitive with petroleum-derived

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[13] R W Rutherford and K Ruschin, "Production of Ammonia Synthesis Gas From Wood Fuel in India, " presented at a meeting of the Institute of Chemical Engineers, London, Oct 11, 1949

75.—Product Results in Fast Pyrolysis of Biomass and Its Constituents

Reference	Type and form of of biomass	Rate of heating	temperature of pyrolysis/ gasification	Residence time at temperature	Environment	Approximate weight percent of organics											
						Char	Tar	Gases	H_2	CH_4	C_2H_4	CO	CO_2	C_2H_6	C_3H_6	H_2O	Other
Antal (1979)	Whatman filter paper (cellulose) 0.125 g	100° C/min to 500° C/min	700° C	3.5 s	Hot steam or argon	10	2	88	1.2	7.2	5.5	47.2	11.5	1.0	0.15		0.15
Berkowitz-Mattuck and Noguchi (1963)	Cotton cellulose cloth	Carbon-arc radiant at 5 cal/cm²-s 25 cal/cm²-s	NA	1 s irradition	Cold helium	~ 20 ~ 8					0 0.86	5 7.3	0				(a) (b)
Martin (1965)	α-cellulose + 2% carbon black	Carbon-arc radiant at cal/cm²-s 4.4 11.6 early 11.6 late 10²-10³	NA	0.4-8 s irradiation ~ 1 s ~ 8 s	Cold helium	20-35 4 4 0	80 55		0.02 0.5	0.02 0.9	0.02 0.9	3 13	4 10			10 15	(c) (d)
Lincoln (1965)	α-cellulose + 2% carbon black	Carbon-arc & Xenon lamp 1.5 cal/cm²-s 11.0 cal/cm²-s 3,000 cal/cm²-s	~ 300° C >600° C >600° C	10 s 4 s ½ ms	Cold helium	33 3 1	19 51 0	48 46 99	NA	NA	NA	3 13 37	9 11 4			32 16 28	Volatile organics 3 6 30
Lewellen, et al. (1976)	Cellulose filter paper 0.75 × 2.5 × 0.01 cm strip	Electrically heated mesh 400°-1,000° C/s	250°-1,000° C	0.[illegible] 400° C/s	Vacuum to 1 atm cold He	No char	No gas analysis. Weight loss versus time only										
(1976)	Douglas fir 1.5 mg samples	Pyroprobe at ~ 200° C/s	550° C	3-4 s	Cold argon or air					2.0	1.0	21	5.7	0.3	1.6	15.3	Propane 1.6 Many organics at 0.1-1% level
Prahacs (1967)	Na, Ca, Mg-base spent liquors	Atomized spray into hot reactor	600°-900° C 5-45 psig	11-100 s	Self-generated steam	Down to 3%			Up to 11%		Illuminants up to 7%						
Prahacs, et al. (1971)	Bark, slash wood, and spent liquors Bark	N.A. various reactors up to pilot scale Batch fed	600°-1,000° C 0-25 psig 810° C 0 psig	3-60 s 3.6 s	N_2 or self generated			89.5			6.2				0.6		C_2H_2 0.9 Benzene 2.1 Toluene 0.3
Rensfelt, et al. (1978)	Poplar wood	~ 1,000° C/s	400°-1,000° C	~ 1 s	Steam, H_2					5	5 (optimized)						
Brink and Massoudi (1978)	White fir particles 20-40 mesh	~ 1,000° C/s	316°-871° C 843° C	3-5 s 3.0 s	N_2	2.5	7.1	92	~ 1	~ 10	~ 5	~ 62	~ 13				
Diebold and Smith (1979)	Ecofuel II, 200 μm	10^4°-10^5° C/s	500°-900° C	50-100 ms	Steam and CO_2	19			1	4	Unsaturates 24	36	16				
Stern, et al. (1965)	Sawdust 20-30 mesh	Fast	1,000° C	Long (steel wool) (Alundum)	Self-generated	22.2 14.0	4.4 0.4	71.0 84.4	4.6 4.0	0.3 7.1	0 0.25	65.5 68.4	0.6 4.8		2.3 2.2		
Brink (1976)	Wood, MSW, and kraft black liquor	Probably fast	(475°-1,125° C) 850°C	Uncertain	6.5% moisture wood 52.5% moisture wood				1.8 3.8	11.2 7.2	7.0 4.2	73.0 47.7	13.2 35.2		45		

[a] Tar fraction, mainly levoglucosan. [b] Variety of polar organics boiling below 187° C. [c] Acetaldehyde 0.45; acrolein 0.15; acetone, furan, methanol ~ 0.7. [d] Acetaldehyde 1.3; acrolein, acetone 0.25; methanol, furan 0.15.

NOTE: References to table 75 appear on p. 234.

SOURCE: Milne, "Pyrolysis—The Thermal Behavior Below 600° C," *A Survey of Biomass Gasification* (vol. 2: Golden, Colo.: Solar Energy Research Institute, 1979).

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Berkowitz-Mattuck, J, B. and T. **Noguchi**, "Pyrolysis of Untreated and **APO-THPC** Treated Cotton Cellulose During l-See. Exposure to Radiation Flux Levels of 5-25 **cal/mc²** sec.1, *J. Applied Polymer Science, vol. 7,* p. ***709, 1963.***

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ethylene. The ethylene could be converted to ethanol, and overall processing costs (wood to ethanol) may be considerably lower than those projected for fermentation processes (see chs. 7 and 8).

The liquefaction process for producing a pyrolytic oil (see ch. 7) might also be carried further by cracking the oil in a way that is analogous to current oil refinery technology. In addition, microwave energy (or other electromagnetic radiation) could possibly be used to break specific predetermined chemical bonds in order to guide and control the decomposition of the biomass.

Rapid pyrolysis, cracking, and microwave processes are still at the research stage and considerable work is required to determine their feasibility. Efforts along these directions, might lead to significant advances in the use of biomass for chemicals and fuels.

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