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DEPARTMENT OF ENERGY

Preface

This report was prepared with the support of Fossil Fuel Extraction / Department of Energy. It represents work performed under the *Chemicals for Enhanced Oil Recovery* program at Oak Ridge National Laboratory. Dr. Fred W. Burtch, of the Bartlesville Energy Technology Center, is the contract monitor for this research. The projects under Dr. Burtch's direction are directed toward production of increased oil from existing oil wells.

Enhanced Oil Recovery Chemicals from Renewable Wood Wastes

W. N. Grune, A. L. Compere, W. L. Griffith, and J. M. Crenshaw

Abstract

Using advanced petroleum recovery techniques, it may be possible to produce half as much oil from existing U.S. wells as has been previously produced. Even limited use of tertiary oil recovery methods could substantially add to U.S. domestic oil production and decrease U.S. dependence on foreign energy imports. Micellar flooding, a promising technique for enhanced oil recovery, uses chemicals to free oil from formations depleted by conventional techniques. Using micellar flooding techniques to produce additional petroleum equivalent to 1% of U.S. current consumption could require approximately 75 million lb of high viscosity polymer, 750 million lb of surfactant, and 400 million lb of 3 to 5 carbon alcohols annually. The availability of better, cheaper chemical materials for this process could decrease the overall process cost and thereby increase its use. Synthesis of micellar flood chemicals from waste materials could meet the requirements of low cost chemicals without large scale market dislocations.

With the exception of petroleum, wood is the largest single U.S. commodity. Because this industry is experienced in chemical recovery and has major landholdings, it is a good potential source for micellar flood chemicals.

Most of the wood pulp used to produce the quarter ton of paper consumed per capita per year in the U.S. is produced by cooking, or digesting, wood chips in a chemical solution. These pulping processes have effluent streams which contain substantial amounts of dissolved lignins, lignin breakdown products, and carbohydrates. There is a substantial economic incentive to use these materials as feedstocks for the production of high-valued micellar flood chemicals.

The pulp and paper industries have practiced chemical recovery for almost a century. The largest chemical recycle processes are the internal recycle of inorganic salts for reuse in pulping. This is coupled with the use of waste organic compounds in the liquor as a fuel for directly-fired evaporation processes. Diversion of effluent and low valued streams for chemical recovery using fermentation, purification, or synthesis methods appears technically feasible in several cases. The use of new recovery processes could yield a variety of different wood-effluent based products. Some of the sugar acids in pulping liquors might be used as sequestering agents in reservoirs where there are large amounts of multivalent cations in flood brines. Fermentation production of high viscosity polymers, sequestering agents, and coagent alcohols appears worth further investigation. Tall oil acids and their derivatives can be used as surfactants in some reservoirs. Some waste constituents may adsorb preferentially on formations and thereby reduce loss of surfactants and other higher-valued chemicals. The development of processes for the production of chemicals, including those chemicals used in micellar floods, from pulp and paper industry waste and low-valued process streams could provide economic benefit to the industry and to the nation.

Contents

1. Introduction

Using advanced petroleum recovery techniques, it may be possible to produce half as much oil from existing U.S. wells as has been previously produced. Even limited use of these methods across the near term could substantially increase U.S. domestic oil production. If advanced oil recovery methods are employed, they could decrease U.S. dependence upon foreign energy imports and improve the U.S. balance of trade.

A variety of methods for accomplishing tertiary petroleum recovery have been developed. Some of the methods, such as *in-situ* combustion or steam injection, are primarily physical in nature and decrease petroleum viscosity. Other methods, such as surfactant and surfactant-polymer flooding, are chemical in nature. A major part of the cost of the chemical techniques is the cost of materials which are injected into the reservoir. *Chemical and Engineering News* recently listed a middle estimate of requirements for a barrel of incremental oil produced using surfactant-polymer flooding as 17.5 lb of surfactants at \$0.43/lb; 5.25 lb of alcohols at \$0.21/lb; and 1 lb of high-viscosity polymer for mobility control at \$2.10/lb (January, 1977). Thus, \$10.68 of materials are required for recovery of an extra barrel of oil. This figure does not include the cost of preparation and injection of these materials, or interest cost for the invested capital for the recovery period. These costs make it difficult for chemically based enhanced oil recovery to be cost effective when petroleum is selling for less than 20 to 25 dollars per barrel.

The appearance of *The Nation's Energy Future* (Ray 1973) stimulated considerable federally sponsored research interest in enhanced oil recovery. The increased interest in the production of more oil from U.S. domestic reservoirs resulted in several large studies covering the economics and application of different oil recovery procedures. Two major reports, one by the National Petroleum Council for the Department of the Interior and the other, by Lewin and Associates (1976a,b) for the Energy Research and Development Administration appeared in late 1976. Both of these reports stressed the need for basic research into the behavior of micellar flood systems in reservoirs. A major concern of both reports was the problem of micellar flooding economic practicability, which was strongly dependent upon the cost of flood chemicals. In the search for feasible methods of micellar flooding, the need for better, cheaper chemicals was a major concern.

The Gulf Universities Research Consortium (1977) considered the economic effects of producing chemicals for surfactant polymer flooding, or microemulsion flooding. They indicated that the use of this chemical technique for enhanced oil recovery could make a significant contribution to the national supply of petroleum. With dwindling petroleum supplies, they thought that the importance of the technology could be enormous. However, the technology is in its infancy, and has not yet become applied to large-scale enhanced petroleum recovery projects. Microemulsion flooding involves risking an investment in chemicals and field preparation and injection costs. Thus, process use will be strongly affected by the cost of chemicals, the judgement of risk, and the cost of capital. Decreases in base costs and increases in certainty are important in establishing the technology. Both research and political efforts were required in successful early applications of this technology.

Although changes in the type of reservoir in which the microemulsion flooding technique is used could result in changes in the types of chemicals which would be used, the Gulf Universities Research Consortium made some estimates on cost and supplies of the necessary chemicals. These estimates were based on a survey of the industry using a modified Delphi approach together with appropriate literature research. Base assumptions for the microemulsion flooding included the use of 10 lb of sulfonates, 3 lb of alcohols, and 1 lb of viscosity control polymer per barrel of recovered oil. The earliest date for large-scale process application was assumed to be 1979, with the first resulting oil production in 1983. This is a project size referred to as M-1, which is the smallest commercially feasible size. In order to provide an increase of 1% of U.S. current consumption, 25 M-1 size projects would be required (Gogarty 1978). Because the costing was performed using constant 1975 dollars, the figures should be adjusted for changes in the present worth cost of materials. Three base cases were considered in forecasting the amounts of material required for microemulsion flooding. Tables 1.1 to 1.4 show the amounts of oil produced and the amounts of chemicals required for each of the different scenarios considered. The most reasonable and probable case, A, lead to an increase in microemulsion-produced-oil oil of 200,000 standard barrels per day in 1986. The upper boundary case, B, lead to an increase in microemulsion produced oil of 500,000 standard barrels per day in 1986. The minimal case, C, which is accepted as "assured", covers the applications of microemulsion recovery methods to only highly favorable situations. Current indications (Gogarty 1978, Guthrie 1978) are that 1985 incremental oil production using micellar flooding will fall between cases C

Table 1.1. Oil production by microemulsion flooding.

Year	Case A, 10^6 bbl/yr	Case B, 10^6 bbl/yr	Case C, 10^6 bbl/yr
1983	14.6	36.5	
1984	29.2	80.3	10.0
1985	51.1	131	29.2
1986	73	183	50.0
1987	102	219	50.0
1988	140	248	50.0
1989	172	272	50.0

Source Gulf Universities Research Consortium 1977

Table 1.2. Sulfonate demands for enhanced oil recovery.

Year	Case A, 10^9 lb/yr	Case B, 10^9 lb/yr
1979	0.146	0.365
1980	0.292	0.803
1981	0.511	1.31
1982	0.730	1.83
1983	1.02	2.19
1984	1.40	2.48
1985	1.72	2.72

Source Gulf Universities Research Consortium 1977

Table 1.3. Alcohol demands for enhanced oil recovery.

Year	Case A, 10^6 lb/yr	Case B, 10^6 lb/yr
1979	43.8	109.5
1980	87.6	241
1981	153.4	394
1982	219	549
1983	307	658
1984	416	745
1985	482	795

Source Gulf Universities Research Consortium 1977.

and A. For example, the chemical demand involved in scenario A are considerable. By 1986, annual demand could be 1.72 billion pounds of sulfonates, 482 million pounds of three to five carbon alcohols, and 139 million pounds of high viscosity polymers. These do not include the specialty chemicals required. Major escalations in the production of higher alcohols, sulfonates, and polymers will be required to meet these needs.

Table 1.4. Polymer demands for enhanced oil recovery.

Year	Case A, 10^6 lb/yr	Case B, 10^6 lb/yr
1979	2.9	7.3
1980	5.8	16.0
1981	21.9	55.5
1982	38.0	100.1
1983	61.3	148.4
1984	86.1	195.6
1985	109.5	224.8
1986	138.7	248.2

Source Gulf Universities Research Consortium 1977

Fig. 1.1 shows the enhanced oil recovery using both chemical and physical methods projected by two different studies. These projections vary considerably, both with author and with the price of petroleum. One of the greater incentives for the production of tertiary petroleum is a high price per barrel. In the case of chemical recovery methods, the provision of chemical intermediates having lower costs than those projected could decrease the cost of oil at which chemical recovery becomes attractive. This could provide greater amounts of oil at lower price rates.

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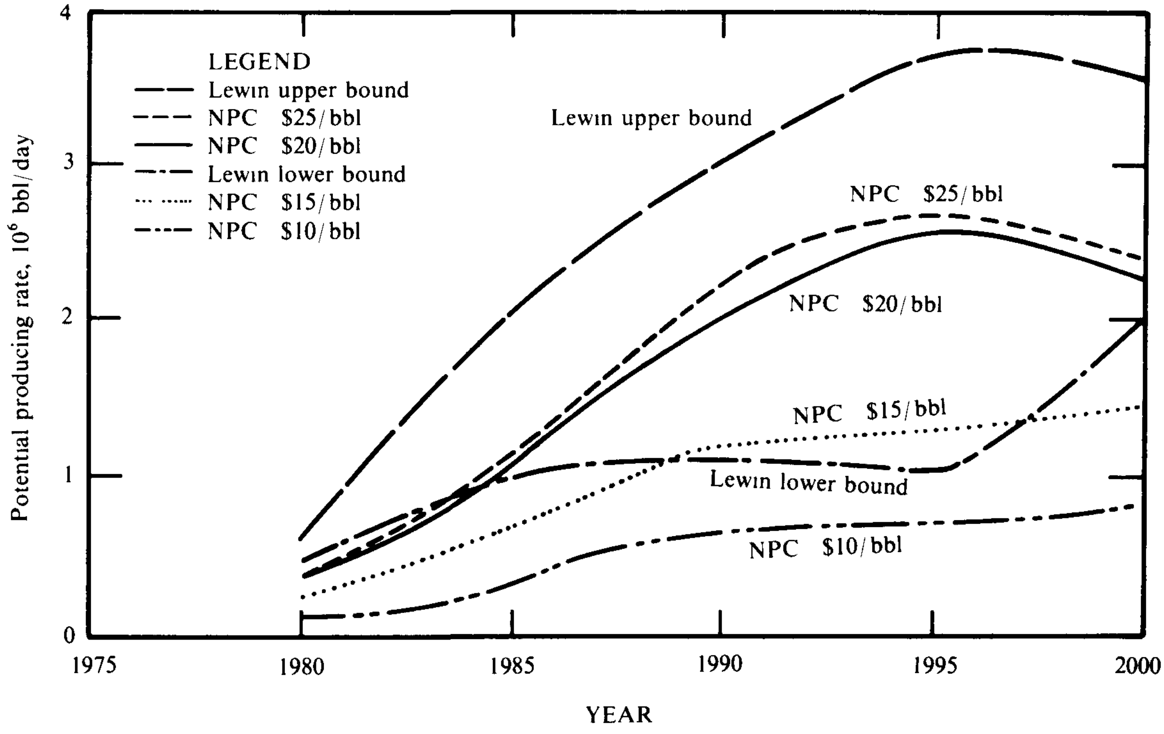

Note all curves are based on a discounted cash flow rate of return (DCFROR) requirement of 8% except Lewin lower bound which is based on a minimum DCFROR requirement of 20%

Fig. 1.1. Estimated tertiary oil production.

The wood and pulp industry could represent a good base source for many of the materials which are used in tertiary oil recovery. On a national basis, this has several advantages: the materials used would be derived from the wastes and by-products of renewable resource processing. Even if this method of oil recovery were not successful, the pulp and paper industry would be deriving economic benefit from the production of chemicals and from the recovery of the resources in their waste materials. Table 1.5 presents a 1964 estimate of the organic by-products formed in pulping processes (Hoyt and Goheen 1971).

The production of some of the chemical materials required for micellar flooding from waste steams using either chemical or fermentation routes for use in the surfactant-polymer flooding process is attractive in that it decreases the requirement for chemical intermediates and can provide potential environmental benefits. Four major types of chemicals can be potentially produced from waste streams: surfactants; alcohols, including isopropyl and butyl alcohol; high viscosity polymers; sequestering agents, such as citric acid cycle intermediates; and competitive adsorbates. It is possible to produce surfactants from wood waste streams using chemical synthesis and recovery methods. Alcohols can be produced from some of the materials in wood waste streams by fermentation and recovered using distillation methods or solvent extraction. High viscosity polymers and sequestering agents can be produced by fermentation or by chemical synthesis and recovery methods.

Table 1.5. Organic by-products formed in U.S. pulping processes in 1964.

Material	Amount, 10^3 tons
Kraft	
Thiolignin	8,800
Fatty and resin acids	405
Formic acid	600
Acetic acid	840
Sugar acids	4,900
Other organics	650
Sulfite pulping	
Lignin sulfonic acid	1,920
Hexoses	550
Pentoses	87
Acetic acid	140
Other organics	18

Source: Hoyt and Goheen 1971.

This report will explore some of the waste and low-valued streams which might be useful for the synthesis of chemicals necessary for miceller flooding. We concentrated on conventional paper processes and on chemical and microbiological synthesis methods in that these would be the most likely to find near-term use. However, if there is a major economic interest in the use of the vast resource represented by the pulp and paper industry waste streams, it is to be expected that novel processes will be developed for use. We hope that this report will be a step in opening a dialogue between the pulp and paper industry and the tertiary oil recovery industry which will profit both.

2. Why Wood?

With the exception of petroleum, wood is the largest single U.S. commodity. Chemical methods of wood processing, which are used to produce most U.S. paper, generally provide yields on the order of one-half of the dry weight wood processed. The materials removed from wood during its conversion to paper are currently recycled to provide process heat and mineral recovery in most plants. A small number of chemical by-products are recovered by pulp and paper mills for external sale. It may be possible to produce materials for use in tertiary oil recovery from this rich and varied source. Institutional conditions within the paper industry itself are favorable for by-product production, due to rapid implementation of process changes, pollution abatement, and potential for oil production from paper company land holdings.

Jones (1973) indicated that the paper industry ranked 13th in U.S. sales and 11th in the number of employees in 1969. In 1970 sales were reported at $20.6 billion, about 2.2% of the GNP from this industry alone. Return on investment has been 7 to 8%. In 1970 there were 383 companies operating 842 mills at some 750 different locations. The breakdown of these 842 mills comprised 542 paper mills, 22 pulp mills, and 278 integrated paper mills. The U.S. paper industry has doubled its production every 15 to 17 years. Per capita consumption has jumped from 385 lb of paper and paper board in 1954 to 581 lb in 1969 and 604 lb in 1970. In 1969 the industry produced almost 54 million tons of paper and paperboard; production in 1970 was approximately 52.4 million tons. By 1976 the total production increased to 60.3 million tons.

The trend is toward larger mills. On the average, mills producing less than 250 tons/day are considered small, 300 to 1,000 tons/day are considered medium, and 1,000 tons/day or larger mills, large. Currently, plants with capacities up to 2,000 tons/day are being planned or under construction.

Table 2.1 shows the number of existing mills and total mill capacities for each of the five chemical pulping processes in 214 pulp mills as of December 31, 1968. All capacities are based on air-dried tons of pulp (ADT); annual capacities are based on operating at rated capacity for 350 days/year, allowing for normal maintenance and scheduled shutdowns. It must be emphasized that the data in Table 2.1 represent production capability without portraying current production figures. The U.S. is the largest pulp and paper manufacturing nation. Wood pulp production for the ten leading pulp producing nations of the world during 1968 is shown in Table 2.2.

The U.S. and Canada produced 52% of the world's wood pulp in 1968. Another 60 pulp producing nations individually pro-

Table 2.1. Chemical pulp mill capacities.

Process	Number of Mills	Capacity[a] ADT/day	Annual Capacity[a] ADT	1968 Production tons
Kraft	116	87,808	30,733,000	24,300,000
Sulfite	43	10,875	3,799,500	2,500,000
NSSC	43	10,675	3,736,500	3,500,000
Dissolving	8	4,565	1,600,000	1,500,000
Soda	4	570	200,000	200,000
Totals	214	114,493	40,069,000	32,000,000

[a] ADT stands for air-dried tons of unbleached pulp per day, air-dried pulp contains 10% moisture

Table 2.2. Ten leading pulp producing nations in 1968.

Nation	Short tons, 10^6
United States	37.89
Canada	16.40
Sweden	7.76
Japan	7.76
USSR	6.78
Finland	6.56
Mainland China	2.30
Norway	2.18
France	1.77
West Germany	1.73

Source. Hendrickson, Roberson, and Koogler 1970

duced less than one million tons of pulp and collectively produced 13.4 million tons of pulp in 1968 (Jones 1973).

Various forecasts of the future demand for wood pulp (all grades) in the U.S. are available. These forecasts (Jones 1973) range from a low of 61 million tons to a high of 89 million tons per year in 1985.

A middle of the road forecast has been made for the American Paper Institute by H. W. Meakin of the J. E. Sirrine Company. He has projected chemical pulp production through 1985. These projections indicated that the production of soda and dissolving pulps will remain reasonably constant through 1985; a slight decrease in sulfite pulp is expected.

By 1985, the kraft and NSSC processes are expected to dominate chemical pulping in the U.S. (Hendrickson, *et al* 1970). By that time, kraft pulping is projected to account for about 70% of all pulp and NSSC for about another 9%. The total production of chemical pulp is expected to slightly more than double to approximately 70 million tons. Hendrickson *et al* estimated announced and estimated expansion and phasing out operations through 1985, as shown in Tables 2.3 and 2.4. In addition to current and planned construction, there are at least twelve proposed or tentative mills in the talking stage of development. These twelve mills would, if brought to production, supply in excess of an additional 3,000 tons/day of pulp. Information to show the regional distribution of the industry in 1968 and projected for 1975 and 1980 is shown in Table 2.5.

Table 2.3. Announced new plant construction.

Type	Kraft ADT/day	Sulfite ADT/day	NSSC ADT/day
New	5,866(12)	830(2)	750(3)
Expansion	2,135(5)	0(0)	568(2)
Total	8,001(17)	830(2)	1,318(5)

Source Hendrickson, Roberson, and Koogler 1970.

Table 2.4. Announced operations phase out[a].

Time Period	Kraft ADT/day	Sulfite ADT/day	NSSC ADT/day	Soda ADT/day
In 1968[b]		835(5)		60(1)
In 1969-1970	205(1)	503(3)	235(1)	
In 1970-1980	85(1)	1,562(17)		140(2)
Total	290(2)	2,900(25)	235(1)	200(3)

[a] Figures in ( ) indicate number of mills

[b] Capacity figures for 1968 were not included in Table 2.3

Source. Hendrickson, Roberson, and Koogler 1970.

The consensus of industry representatives on the Pulp Industry Liaison Committee is that the regional distribution of pulp production through 1985 will remain essentially the same (Jones 1973). This is of some concern to forestry management in that a tightening of the wood supply in the South could occur in the late 1970's, possibly creating a shift of production to the West and North. However, by more intensified management of the better forest lands and improved silviculture, considera-

Table 2.5. Projected U. S. regional pulp production.

Region	1968 Production, tons/day	Fraction of total	1975 Production, tons/day	1980 Production, tons/day
		Kraft		
Northeast	3,617	0 052	5,582	6,981
Northcentral	2,319	0 033	3,579	4,476
Southeast	36,249	0 522	55,939	69,962
Southcentral	15,850	0 228	24,460	30,592
Northwest	11,393	0 164	17,582	21,989
Total	69,428	1 000	107,142	134,000
		Sulfite		
Northeast	1,464	0 205	1,171	1,171
Northcentral	1,354	0 190	1,083	1,083
Southeast	471	0 066	377	377
Southcentral	0	0 000	0	0
Northwest	3,854	0 540	3,083	3,083
Total	7,143	1 000	5,714	5,714
		Neutral Sulfite Semi-Chemical		
Northeast	1,731	0 173	2,324	2,714
Northcentral	3,330	0 333	4,472	5,233
Southeast	2,926	0 293	3,929	4,598
Southcentral	1,283	0 128	1,723	2,016
Northwest	730	0 073	980	1,147
Total	10,000	1 000	13,428	15,714

Source Hendrickson, Roberson, and Koogler 1970

bly more wood can be grown to satisfy the wood pulping industry demand. Thus, it has been predicted that the distribution of chemical pulp production on a regional basis will remain substantially the same as now exists.

Because of the large amounts of land required to support the U.S. paper industry on a continuous tree production basis, the paper industry is the major North American landholder. Table 2.6 shows the landholdings of the major U.S. paper production companies. Together, these holdings amount to 68.2 million acres held, leased, or assigned in the U.S., and 44.6 million acres held, leased, or assigned abroad. Together, this acreage amounts to 112.8 million acres, 1/20 of the size of the continental U.S., including Alaska. This is substantially more land than is owned by the federal government. Some of the pulp and paper industries are beginning to explore the potential for petroleum recovery from their lands. This provides a double incentive for production of chemicals used in tertiary oil recovery.

The pulp mill includes the fundamental processes of wood preparation, pulping, screening, washing, thickening and bleaching. The fundamental processes in the paper mill include stock preparation, paper machine operation, converting and finishing. Enormous quantities of process water are required in the paper and board making operations to process the fibers and to disperse them, prior to laying them down in a web on the paper making machine forming wire.

PROCESS POLLUTANTS

Potential pollutants from pulp and paper mills can include water effluents, particulates, gases, and solid wastes from both aqueous and solid handling operations. These materials could potentially furnish raw materials sources for the production of chemicals for micellar flooding. Because of the large quantity of materials processed, the paper industry could serve as a basis for the production of the large quantities of material that might be required for tertiary petroleum recovery operations.

Water and particulate emissions from paper plants are a major environmental problem. A wide range of water effluents, including suspended solids, dissolved organic materials, lignin-derived colors, residual pulping materials and chemicals, and, in some cases, heavy metals from pulp bleaching operations are produced.

Table 2 6 Pulp and paper industry landholdings in 1972

	U S 10^6 acres			Foreign 10^6 acres		
Company	Own	Lease or manage	Use rights	Own	Lease or manage	Use rights
American Can Company	0 08	0 50	2 50			
Boise Cascade Corporation	6 28[a,b]		0 44			
Consolidated Papers Incorporated	0 59					
Continental Can Company	1 40					
Crown Zellerbach Corporation	3 00					
Diamond International	1 33					
Fibreboard Corporation	0 17					
Georgia-Pacific Corporation	3 50		0 89	1 00	1 43	
Great Northern Nekoosa Corporation	2 20	0 50				
Hammermill Paper Company	0 24	0 07				
Hoerner Waldorf Corporation	0 22	0 07				
International Paper	6 52	0 36	5 00	1 36	15 13	
Kimberly-Clark Corporation	1 3				9 00	
Marcor, Incorporated	0 07[a]		0 70			
The Mead Corporation	2 25[a]					7 00
Owens-Illinois	1 4					
Potlatch Forests, Inc	1 37					
Riegel Paper Corporation	0 35[a]					
St Regis Paper Company	2 7	5 53				
Scott Paper Company	3 2					
Union Camp Corporation	1 67					
U S Plywood	1 69	3 31				
Westvaco Corporation	1 16					
Weyerhaeuser Company	5 6				9 70	

[a] Own or control

[b] Includes foreign property

Source The Council on Economic Priorities 1972

Air pollution problems include fly ash, char from bark burners, and particulates from chemical recovery process. Sulfurous gases are also produced. The compositions and concentrations of these materials in the process effluent streams vary, depending upon the process and the plant.

The economic climate of the paper industry is particularly favorable for the production of chemicals. Internal recycle of salts and sulfur compounds has been practiced for almost a century. By-products ranging from lignin precipitates to tall oils or vanillin have been recovered and sold for decades. Waste water treatment costs are high, and it may be possible to combine waste treatment with by-product recovery in the development of chemical process for making tertiary oil recovery chemicals. However, in many cases, concentrations can range up to several percent on a dry weight basis. Chemical manufacture could be attractive for both the paper and the oil industries.

3. Pulping Processes

Many of the wood wastes from which products for use in enhanced oil recovery could be manufactured are wood pulping process streams. Pulping is the process which separates cellulosic fibers from interstitial lignin. The clean cellulose fibers are then bleached and made into paper or specialty boards. Pulping may be accomplished by physical, chemical, or combined physical-chemical methods. The process streams are a function of the process and of the individual mill which produces the pulp, since considerable process variation exists. The concentration, as well as composition, of these streams also varies considerably.

MECHANICAL PULPING

Groundwood pulping and the production of pulps from waste paper are the major types of mechanical pulping processes. Lignin is separated from cellulose fibers in these processes by physical methods. The process yields are consequently very high, since little organic material is lost during pulping. Process stream volume is very low, and process streams do not contain large amounts of soluble phenolic products from lignin breakdown.

Groundwood pulp is employed mainly in the manufacture of newsprint, toweling, tissue, wallpaper, and coated specialty papers such as that used for some illustrated magazines. Since it contains practically all the wood substance, yields generally exceed 90%. Most of it is produced by the large newsprint mills in the South from southern pines. In all, about 60 mills with an aggregate daily capacity of approximately 14,000 tons produce this type of pulp in the U.S., of which about 20 mills are large operations. This is distinct from pulps produced by other mechanical processes which are generally employed for building or molded products.

Groundwood pulp is produced from both groundwood and chips. In the older process roundwood is pressed against large rotating grindstones by hydraulic rams while water is sprayed on the stone (Rydholm 1965). On discharge from the grinder, the pulp is screened free of wood slivers and other coarse debris and thickened on deckers. The thickened pulp is then discharged to a stock chest for use in the paper mill or lapped for shipment. After clarification by sedimentation, filtration, or flotation, the filtrate from the deckers is largely returned to the process but a portion is sewered to prevent the buildup of solubles in the system with attending slime problems. The overflow rarely exceeds 10,000 gal/ton of bone-dry pulp and in some instances is as low as 2000 gal/ton (Gurnham 1963; Kleppe and Rogers 1970). A flow sheet of this process is shown in Fig. 3.1.

In some modern newsprint mills, the groundwood operation is completely closed. Any effluent appears in the paper machine effluent. In this event, the raw waste load is the sum of typical losses from both the groundwood pulping and papermaking.

In recent years a considerable amount of groundwood has been produced by passing wood chips through refiners of the disc type (Stephenson 1969). Two stages of refining are employed, a third taking place as part of the papermaking operation. The refiners contain fixed and rotating discs between which the chips pass together with a stream of water. The pulp is discharged

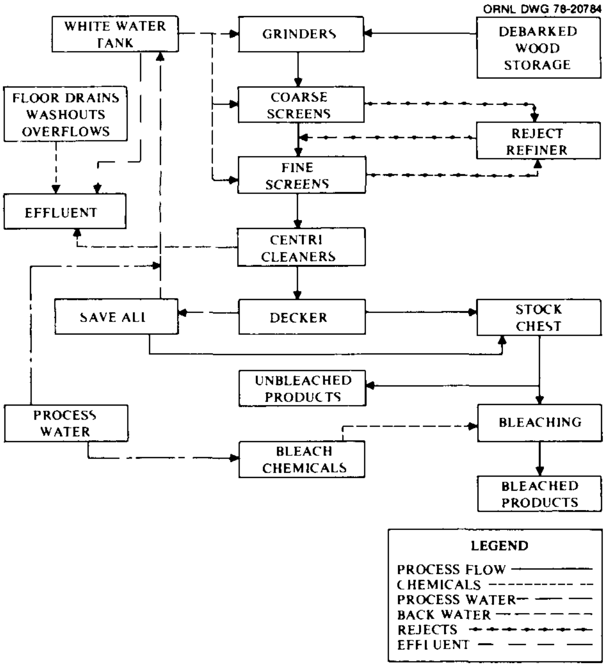

Fig. 3.1. Stone groundwood pulping process.

as a thick slurry, after which it is handled in a manner similar to stone groundwood. Generally, less water is required with refiners than with stones. Fig. 3.2 represents the process diagram of a typical refiner groundwood operation. Effluent volume, BOD_5, and suspended solids losses for all groundwood pulping are shown in Tables 3.1 and 3.2.

Table 3.1. Stone groundwood effluent characteristics.

Mill	Effluent Flow gal/ton	BOD_5 lb/ton	Total Suspended Solids, lb/ton
1	6,300	11	16
2	1,900	8	14
3	4,400	11	11
4	5,400	9	12
5	8,300	18	11
6	2,700	19	16
7	2,200	4	42
8	2,600	14	21

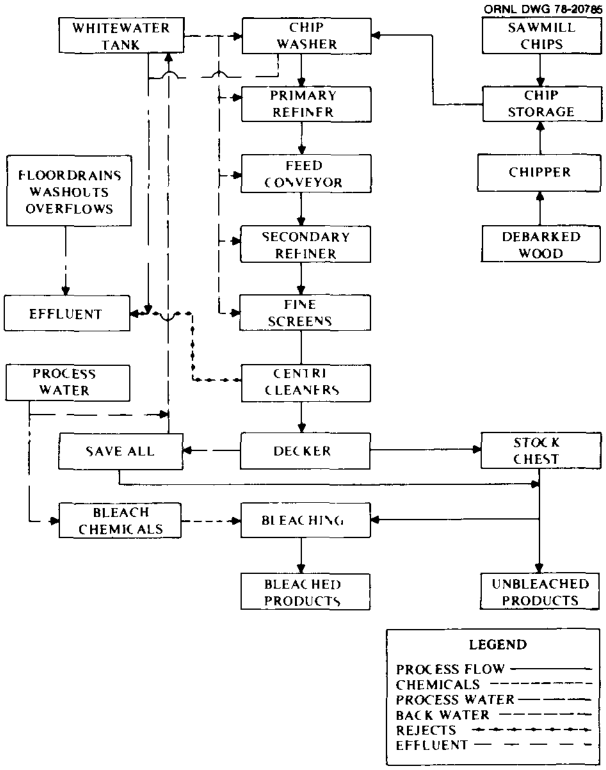

Fig. 3.2. Refiner groundwood pulping process.

Table 3.2. Refiner groundwood effluent characteristics.

Mill	Effluent Flow, gal/ton	BOD_5 lb/ton	Total Suspended Solids, lb/ton
1	2,600	26	105
2	4,300	120	100
3	5,800	15	110
4	6,700	18	59
5	4,400	15	30
6	1,700	32	35
7	5,900	30	35

Chemi-mechanical

Some groundwood-type pulps are produced by first soaking barked logs or wood chips in dilute chemical solutions which soften the wood, thus reducing the energy required for grinding. Chemical treatment results in higher BOD_5 losses than occur in ordinary groundwood operation as indicated in Table 3.3.

Groundwood pulp is generally bleached with hydrogen or sodium peroxide, sodium or zinc hydrosulfite, or sodium sulfite (Holiday and Solari 1963; Allen, *et al* 1963). Interest has recently developed in the use of peracetic acid, sodium borohydride, and amine borides for this purpose, but their use has not become established practice.

In practice, the pH is generally adjusted to between 4.5 and 7.0 depending upon the bleaching agent and sometimes complexing chemicals are added to overcome the effect of elements, such as iron and manganese, that may be present. Buffers and catalytic agents in trace quantities are also sometimes used. Since groundwood can be bleached at high consistency, it is frequently accomplished at stock chest levels without washing. Hence, the residues of bleaching appear in the white water of the paper machine system.

Since the zinc content of effluents from the zinc hydrosulfite process is generally less than 10 mg/l it does not cause a problem when diluted with other effluents and receiving waters.

Table 3.3. Cold soda and chemi-groundwood effluent characteristics.

Mill	Effluent Flow gal/ton	BOD_5 lb/ton	Total Suspended Solids, lb/ton
	Cold Soda Pulping		
1	2,000	73	15
2	3,700	92	26
3	5,500	101	32
	Chemi-Groundwood Pulping		
1	2,400	81	24
2	3,300	69	37

Wastewater Treatment

The large integrated mills, as well as paper mills alone, treat the groundwood effluent in combination with the total discharge. Thirty-eight mills which manufacture 9,750 tons daily provide treatment. Of these, 12, representing a daily production of 5,000 tons of groundwood, provide secondary treatment. Storage oxidation basins, aerated lagoons, and activated sludge are all employed.

The effluent from groundwood pulping can be clarified to a high degree by settling, particularly if other effluents containing fiber and fillers are combined with it, since 90% of the suspended solids present are settleable. However, the sludge produced is extremely hydrous, often averaging only 0.5% consistency and is difficult to dewater. It can be dewatered only on combination with other less hydrous waste slurries. Flotation is equally as effective as settling or clarification.

Groundwood mill effluent is responsive to biological treatment both alone and in combination with other pulping wastes. Lower oxidation rates have been observed for it than for chemical pulping effluents according to Bishop and Wilson (1954), but when combined with kraft pulping effluent the rate becomes normal.

Some modern newsprint mills clarify the groundwood pulping effluent and employ it for dilution on the paper machine. Hence, losses from both pulping and papermaking are contained in a single discharge which is then mixed with other pulp mill waste prior to treatment.

Chemi-mechanical effluents present no problem when combined for treatment with other mill effluents (Heustis 1961,1962) for as previously pointed out, they represent a higher BOD_5 loading than ordinary groundwood. The settling characteristics of the suspended solids contained in them are very similar to those of groundwood.

Since there is presently no case where groundwood effluent is treated separately, data for this category are not available (Gehm 1973).

Deinking Pulp

Waste papers are deinked for recovery of their fiber content primarily at ten large mills in the U.S. Seven of these deink magazine, ledger, and other various grades of raw stocks and three mills deink newsprint only. A large number of small mills deink a variety of waste papers on an small scale and frequently on an intermittent basis. Mills also reclaim pulp from trimmed, broken, and unused waste papers derived from the manufacturing process itself.

The deinking process involves cooking the papers in an alkaline solution. Soda ash, caustic soda, sodium silicate, and, at times sodium peroxide, are used. Some employ dispersing agents, chemicals which saponify the ink vehicles and solubilize coating adhesives allowing the ink coatings, and fillers to be subsequently washed from the pulp (Alieri, *et al*, 1956; National Council on Air and Stream Improvement 1946; Hodge and Morgan 1947). In the case of newsprint, which consists only of fiber and ink, a detergent is used to separate the ink so that it can be washed out.

Washing is accomplished on Lancaster washers, in beaters, and on side-hill screens. With some magazine stocks as much as 40% of the bale weight of the paper is lost to the sewer in the washing operation (Stephenson 1970).

After washing, the recovered pulp is generally given a light bleach with a hypochlorite or peroxide. The pulp is washed again after bleaching on drum washers in large mills, but small ones usually wash in the beaters. Losses from bleaching are very small as compared to cooking and washing losses. Since the effluent from bleaching is generally employed for pulp washing it is included in the sewer loss from the entire washing operation.

Since the range of losses from the deinking of magazine and ledger type stocks is so wide and newsprint so constant, separate figures are presented for each in Table 3.4. The ash content of the suspended matter contained in the former is generally high and in the latter low.

The suspended solids concentration of deinking wastes from magazine and ledger stocks runs from 1,000 to 3,100 mg/l of suspended solids and the BOD_5 in the order of 300 to 500 mg/l. Combustibles present in the suspended solids range from 28 to 61% and in the total solids from 1,900 to 10,800 mg/l (Alieri, *et al*, 1956). Losses in terms of pounds per ton of product are shown in Table 3.4.

Table 3.4. Deinking mill effluent characteristics.

Mill	Effluent, gal/ton	BOD_5, lb/ton	Total suspended solids, lb/ton
	Magazine and ledger stock		
1	30,700	80	508
2	29,200	41	59
3	65,000	40	237
4	31,300	75	171
5	48,700	44	294
6	42,200	64	366
7	43,300	91	301
8	58,700	114	355
9	54,000	83	152
10	14,700	97	139
11	30,000	101	740
	Newsprint		
1	9,700	101	233

Source. Alieri 1956

Fig. 3.3 shows a deinking of waste paper process flow diagram for a modern large operation.

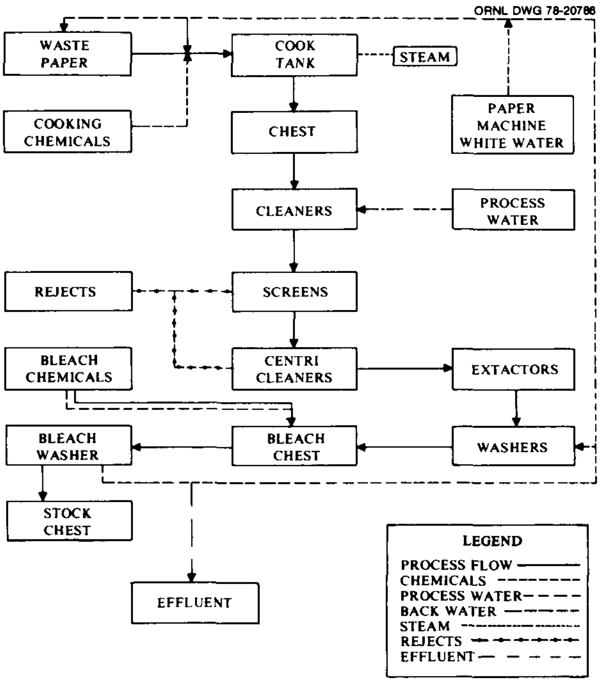

Fig. 3.3. Deinking and repulping process.

Deinking Effluent Treatment

Sedimentation results in the average removal of close to 70% of the total suspended solids from deinking waste. Removal of the settleable solids is generally accompanied by a BOD_5 reduction in excess of 40%. The sludge produced from the deinking of coated papers is readily dewatered mechanically but represents a serious disposal problem because of the large amount produced and its great wet bulk.

Sedimentation also leaves an overflow which is high in turbidity. Chemical coagulation has not proven effective. Although some chemical agents are effective sedimentation aids, cost of their application is prohibitive. The extent of sludge production can be visualized from the bale weight loss figure which can run as high as 50%. Most newsprint deinking waste is discharged at present to public sewage systems for treatment.

Six white paper mills deink old papers on a large scale and five treat their wastes for the reduction of BOD. Four have aerated stabilization basins, one being supplemented by spray disposal on the land. The fifth uses storage oxidation which is accomplished in two large basins. Treatability of this waste was first determined on a demonstration scale by Palladino (1959) using the activated sludge process. Limitations of this process led Blosser (1961) to experiment with aerated stabilization basin treatment. This in turn led to successful applications described by Laing (1969), Haynes (1969) and Quirk and Matusky (1969). Flower (1969) described land disposal following partial aerated basin treatment at the storage oxidation installation.

Table 3.5 summarizes the treatment and performance of the three biological oxidation installations for which data were

Table 3.5. Treatment of deinking wastes.

Treatment	Flow, 10^6 gal/day	Influent BOD_5 lb/ton	Effluent BOD_5 lb/ton	Influent Total suspended solids, lb/ton	Effluent total suspended solids, lb/ton
Aerated lagoon	7.5	95	21	523	23
Aerated lagoon	1.2	71	6	170	17
Holding lagoon	7.0	197	36	255	26

available. Two of these are aerated lagoons and the third a holding basin. Influent figures are on the basis of settled waste because of the inaccuracies inherent to sampling raw waste for BOD determinations because of its suspended solids content. Also, the deinking waste has been combined with paper machine white water prior to treatment which accounts for its low BOD_5 value. It should be noted that the BOD_5 in the effluents averaged as low as 6 lb/ton of product for one of the aerated basins and 36 lb/ton of product for the storage lagoon. Detention time is the major determinant of performance and it can be presumed that results equivalent to those observed for the best installation in operation can be duplicated.

The suspended solids content of the effluents which were all of the same magnitude indicates resistance of the extremely fine suspended matter, such as titanium dioxide, to removal by settling or coalescence by bacterial activity in the oxidation lagoons.

CHEMICAL PULPING

Chemical pulping methods can be used for the dissolution of lignin from between cellulose fibers. Most of the classic chemical pulping methods depend upon the reaction of lignin with simple inorganic salts. These processes generally take prepared wood and digest it in the presence of salts reactive with lignin and hemicellulose to produce a clean pulp. The pulp is screened, washed, bleached, and sent to a papermill.

Process Development

The history of alkaline pulping processes is relatively well documented by Wenzl (1965, 1967) and Shreve (1945). Alkaline pulping processes were first used for commercial production of chemical pulps. Digestion of linen or cotton rags, straw, and other nonwoody fibrous materials was performed in open boilers. Strachan (1941) reported that both NaOH and Na_2S were used for pulping in England during the Napoleonic Wars.

The difficulties of wood delignification retarded its use as pulp feedstock until 1851, when Burgess and Watt found that if birch shavings were boiled with alkali, washed, bleached, washed, and again boiled with alkali, they were reduced to a pulp that could be subsequently bleached. Burgess commercially established this process in the U.S., where he built a mill in which poplar chips were digested with caustic soda. Because of the very large quantity of alkali required, a method for alkali recovery involving incineration of the spent liquor was developed. The U.S. wood pulp and paper industry began with this plant. In 1879 Dahl, in Danzig, introduced a modification of this early soda process by using NaOH and Na_2S in combination as the digestion reagent. The Na_2S obtained as a reduction product of Na_2SO_4 added as chemical makeup. The resultant pulp was known as *kraft*, or sulphate pulp. The term kraft, German or Swedish for strength, is commonly applied to such a pulp and also to the papers made from it. At that time NaOH (caustic soda) was made by the Leblanc process from Na_2SO_4, so that the direct use of this chemical, rather than NaOH considerably reduced the pulp production cost. Moreover, the presence of Na_2S in the cooking liquor resulted in a stronger pulp than when NaOH alone was used. Soda-pulp mills were largely converted to the sulphate process.

Development of an electrolytic process for the simultaneous manufacture of sodium hydroxide and chlorine from NaCl, permitted a pulp mill, without too large a capital investment, not only to manufacture its own digestion reagent (NaOH), but to coproduce a relatively cheap bleaching agent. Because alkaline pulping with a chlorine bleach did not yield a sufficiently white pulp from softwoods, numerous soda-pulp mills were built to produce bleached soda pulp from the hardwoods. This choice produced a pulp of rather low strength properties but gave excellent formation with high opacity and bulk when converted to paper. The dark color of unbleached alkaline pulps resulted in their use being confined to coarse packaging, wrapping, industrial papers and container boards. Kraft pulp was particularly suitable for this use. Consequently, soda pulps are manufactured for mills engaged in fine paper production and kraft pulps are produced for mills producing coarse papers.

Although early plants were markedly different, modern soda and sulphate pulp mills are essentially identical. Differences in the yield of pulp obtainable with the sulphate process can, at least in part, be obtained with the soda process by inclusion of a small amount of Na_2S.

With the advent of multiple-stage bleaching, about 1930, it was found that the alkaline pulps from softwoods also could be bleached satisfactorily. Bleached sulphate pulps are now used extensively in the fine paper industry. With the further improvement of the bleaching agent, chlorine dioxide and other special agents, use of kraft pulp has been extended even further. Application of the full sulphate type digestion liquor to hardwoods has been accelerated because the supply of softwoods has become increasingly short. Sulphate pulps from hardwoods have many excellent properties, giving good formation and being nearly as strong as softwood sulphite pulp.

Expansion of Production

Alkaline pulp production expanded between 1934 and 1942, was decreased by the second World War and resumed again at its close. There are several reasons for this expansion. Development of the chemical engineering skills necessary to operate these plants on a continuous basis improved process economics markedly. The development of multistage bleaching permitted production of bleached sulphate pulps of high brightness from softwoods. These are widely used in the fine-paper field and exhibit greater strength than bleached sulphite, but hydrate considerably less readily. Bleaching costs for sulphate are considerably higher than for sulphite, although the basic pulp-production costs prior to bleaching are lower with the sulphate process. Adoption of chemical recovery in the sulphite process has modified the picture with regard to relative costs.

Digestion

The digestion process is essentially the treatment of wood, in the form of chips, in a pressure vessel called a digester, under controlled conditions of temperature, pressure and time, with a liquor composed mainly of an aqueous solution of inorganic salts. A variety of digestion processes for wood are currently in use, although the kraft process is the major wood pulping process in the U.S. However, most of the major digestion processes follow a similar general pattern of unit operations. The flow sheet for a generalized digestion process is shown in Figure 3.4.

Table 3.6 compares the four classic pulping methods. These methods differ significantly in basic chemistry. Sulfate pulping produces undesirable odors due to

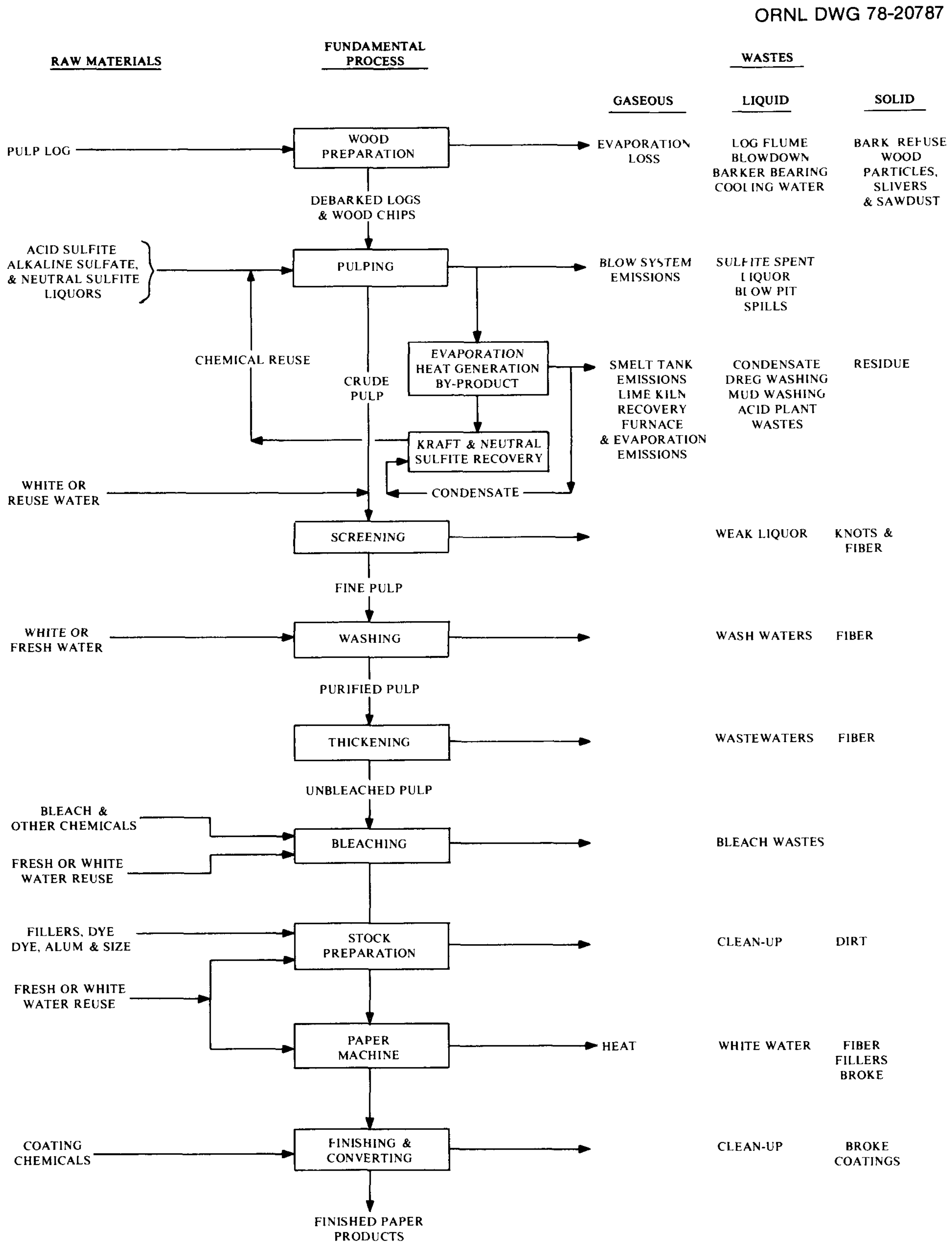

Fig. 3.4. Chemical pulping processes.

Table 3.6 Comparison of the four major wood pulping processes

Parameter	Mechanical pulping	Sulfate pulping	Soda pulping	Sulfite pulping
Wood	Soft coniferous spruce and balsam	Coniferous southern pine, jack pine, spruce, and balsam	Broadleaf poplar birch, and maple	Coniferous spruce most common
Fiber length, mm	1.5	2-3	1.5	3
Digester reaction	No digestion	Hydrolysis of lignins to alcohols and acids Mercaptans formed	Hydrolysis of lignins to alcohols and acids	Sulfation of double bond
Composition of cooking liquor	No digestion	NaOH 40-65 g/l and Na_2S 15-40 g/l as free SO_2	NaOH 85-100 g/l	$Ca(HSO_3)_2$ 45 g/l, 31 g/l as free SO_2
Digester	None. Wood ground to fiber	Unlined steel at 125 psig for 3.25 hr	Unlined steel at 110 psig for 3-4 hr	Cement, crushed quartz, and acid resisting brick lining at 70-160 psig for 10-11 hr
Spent liquor	None	Solids 20% Water 80%	Solids 16.4% Water 83.6% NaOH 1.8%	Spent liquor wasted but SO_2 gas recovered
Pulp fiber quality	Long and flexible but rapid deterioration	Long and strong but variable color	Short, soft and opaque	Long fair strength with good color
Paper types	Newsprint, coarse papers, and boards	Kraft papers and container boards	Books, magazines, and absorbant papers	Books, magazines, and viscose rayon

Source: Shreve 1945

the formation of mercaptans. Both sulfate and soda pulping, which have been coming closer in process conditions across the last few decades, produce alcohols and acids from hydrolyzed lignins. In acid sulfite pulping calcium sulfite is used to produce the sulfite salts of lignins. Sulfate and soda pulping are performed using fairly concentrated alkaline solutions; weak acid sulfite pulping is reacted for a longer time period using a lower concentration of weaker salts in an acid solution.

The chemical pulping processes have similar types of process flow streams. All of these processes have a liquor effluent from the digestion process which contains substantial amounts of dissolved lignins, lignin breakdown products, and carbohydrates. This liquor is generally concentrated and recycled to provide for salt make up. Recycle is accomplished by the combustion of digestion liquors after evaporation. The ash is then used for salt make up. In some cases, spent liquor is also recycled back as digester feed to increase the concentration of combustible products in the digester blowdown.

Chemicals in spent process liquors consist of an organic fraction, which is used for the generation of process heat, and an inorganic fraction, which is used for process liquor make up. Use of the dissolved carbohydrates and lignin breakdown products in spent digester liquor could be economically attractive in that these materials are currently being used for process heat generation, which is a very low valued use. If organic chemicals could be made from a spent process liquor by fermentation or by chemical reaction, it might be possible to return the unused organic material and the inorganic salts to the process. This could represent a considerable economic advantage.

Process Optima

The reactions taking place in the digester involve hydrolysis of lignin and hemicelluloses, resulting in the formation of salts soluble in water or excess alkali. Most extractives, fats, and resins are saponified and dissolved in the cooking liquor. A major problem in the theoretical consideration of the digestion process is the rate of reaction of the different components in the complex mixture called wood. During the two phase reaction involving the dissolution of lignin and hemicellulose between cellulose fibers, for example, the rate of lignin dissolution is low at the start, increases to equal the rate of hemicellulose removal, and then decreases again as the wall around individual fibers is reached. As the rate of lignin removal decreases, the rate of cellulose hydrolysis increases, and the final composition of the pulp reaches a relatively constant state. In order to maximize the weight yield of a pulping process, the highest satisfactory pulp lignin level should be maintained. A number of different researchers studied the pulping process in detail. Much of the work on pulping done by authors around and before World War II led to the development of continuous pulping processes with black liquor recycle currently used. Hajny and Ritter (1941) and Jayme (1942) elucidated the dissolution of holocellulose in pulping operations. The effects of caustic on wood structure and on the dissolution of wood lignin were studied by Jayme, Wegenbach, and Deloff (1939) and Wenzl and Congehl (1932). Ritter studied the structure (1934), arrangement (Ritter and Mitchell 1939), and properties (Ritter and Mitchell 1939) of cellulose fibers and crystals, as well as the carbohydrate and cellulose component of whole maple hardwood (Ritter and Kurth 1933 and Mitchell and Ritter 1940). An invaluable source of information in this area is provided by West (1936, 1937, 1938, 1939, 1940,1941, 1942, 1944, and 1945). A number of different researchers studied the effect of multiple stage pulping, in some cases with prehydrolysis. The use of multiple stages permitted elucidation of the different steps in wood pulping and delignification together with optimization of process conditions for each pulping step. Colombo *et al* (1961, 1962, and 1964) studied the two stage pulping of softwoods, and Richter (1956) and Simmonds (1963) investigated prehydrolysis pulping yields, quality, and characteristics. Meller (1946) investigated the cooking of pine wood by the sulfate process in one and two stages. In a different approach, Chalov *et al* (1962) investigated prehydrohysis using HCl.

In all of the different modifications of the wood pulp digestion process, a large number of variables can significantly affect the yield and quality of pulp. Digestion variables include: the type of wood, the time of digestion, the composition of the cooking liquor, process circulation in the digester, process stream recycle, and air removal from the digester. Pulping methods used in 125 kraft mills in the U.S. and Canada were analysed by Helberg, Neubarger, and Simmons (1976). Results of their survey indicated improved measurement and control systems were needed to optimize process variables and reduce energy requirments.

Waste Treatment

Pulp and paper mills present a unique series of problems in the field of waste water treatment. They have tremendous waste water volumes and a high concentration of relatively undegradable materials, including the colored materials which arise from the breakdown of lignin. Tables 3.7 and 3.8 show the types and amounts of effluents which result from pulping and paper making operations. Table 3.8 illustrates the amounts from older technology mills, where little water conservation or chemical recycle was practiced. Tables 3.8 and 3.9 show the differences in effluent discharge which are possible with water recycle and with more efficent chemical recovery.

Considerable improvement in process water reuse and in process waste discharge has been effected (Parsons 1970). However, the bulk of waste material which is produced by the pulp and paper industry is remarkable. Table 3.10 shows the total amount of waste produced in terms of gross weight and weight per unit commodity versus time. In 1977, the pulp and paper industry was estimated to use around 10^{12} gal of water and to discharge 8 million tons of total solids, including 1.6 million tons of biological oxygen demand. The amount of material discharged is steadily rising, due to increases in the amount of paper consumed outstripping pollution control technology.

Consideration of the amount of wastes per finished dollar of product also indicates that the pulp and paper industry, in particular, the chemical pulping manufacturers, produce a large amount of low cost material. Unless a method to offset the costs of pollution control is found, major increases in the costs for paper manufacture will result. For these reasons, it may be possible to provide the joint benefits of pollution control and chemical manufacture in an economic climate where such processes will be attractive. Even the energy costs of waste treatment are substantial. Table 3.11 shows that the energy costs involved in treating high concentration wastes using conventional activated sludge and aerated lagoon systems were comparable to those required for the fermentation and distillation of ethanol from the same material. The availability of substantial amounts of excess low-level process heat in pulp and paper mills (Kaplan 1977) may make the use of fermentation-distillation processes energetically attractive, since they use heat which would otherwise be discharged, rather than purchased fuel or electricity.

Waters receiving pulp and paper waste discharges can show many toxic effects. Dissolved oxygen concentrations can be lowered due to the biological oxidation of dissolved waste organic materials. The self purification capacity of receiving waters is limited as was determined for a reach of the Kalamazoo river (Michigan State 1958). Organisms in receiving waters can also be adversely affected by chemicals in pulp and paper mill wastes. Leach and Thakore (1976) investigated the toxic constituents of mechanical pulping effluents. They found that 4 to 10% concentrations of mechanical pulping wastewater in receiving waters was capable of producing a 96 hour LC_{50}. The median lethal concentrations of different constituents of this waste are shown in Table 3.12. Further articles by Mueller, Leach, and Walden (1977) and Walden and Howard (1977) explored the methods of dealing with the problem of pulp and paper effluent toxicity. They indicated that, in many cases, treatment of these wastes using activated sludge decreased waste

Table 3.7. Wastewaters from older pulp and paper technology.

	Wasteload, lb/ton						Wastewater,	
Process	Total Solids		BOD		pH		10^3 gal/ton	
	Range	Mean[a]	Range	Mean[a]	Range	Mean[a]	Range	Mean[a]
			Preprocess					
WOOD PREPARATION			~44	44	~7.2	7.2	17-22	12
			Pulping					
GROUNDWOOD	225-450	340	6-25	16	6-8.5		4-16	7
KRAFT								
Blow pit condenser	3-9	6	6-12	8	8-9.4	8.6	0.5	0.5
Uncollected black liquor	80-170	120	12-42	27	8.0-9.8	8.5	1-22	10.5
Evaporator condensate	1.5-7	4	1.2-15	9	6-6.2	6.1	1.8-4.5	3
Causticizing wastes	2-29	9	2-13	7	10.5-12.0	11	0.5-2.5	1.5
Green dreg	15-36	23	0.5-2	1			~4.8	4.8
Subtotal		162		52				20.3
SULFITE								
Digester	51-240	140	99-466	290	2.2-2.9	2.3	4.9-51	12
Other sources	300-3200	2300	30-360	72	2.5-3.7	3.5	1.2-13	2.6
Subtotal		2440		362				14.6
SEMICHEMICAL								
Digester	~5	5	~10	10			~0.5	0.5
Other sources	~150	150	~33	33			11.5	11.5
Subtotal		155		43		6.6		12
			Pulp screening					
GROUNDWOOD								
KRAFT	~80	80	12-25	18	~9.0	9.0	4.5-15	9.6
SULFITE	24-53	35	1-8	5	4.0-6.3	5.2	4.2-14.2	9.1
SEMICHEMICAL	~150	150	~30	30	~6.6	6.6	~7.8	7.8
			Pulp washing					
GROUNDWOOD								
KRAFT	57-180	107	10-49	35	8.9-9.5	9.0	8-15	10
SULFITE	~165	165		19	6.6-7.1	6.7	8-21.8	11
SEMICHEMICAL	~400	400	~85	85	~7.3	7.3	~6	6
			Pulp thickening					
GROUNDWOOD	~107	107	~47	47	~5.0	5.0	~10	10
KRAFT	~71	71	~7	7	~8.4	8.4	~15	15
SULFITE	~108	108	~19	19	6.6-7.1	6.7	~17	17
SEMICHEMICAL	~40	40	~5	5	~7.4	7.4	~14	14
			Bleaching					
GROUNDWOOD							~8	~8
SULFATE	270-520	400			~4.5		28-60	45
SULFITE	200-460	335	17-108	40	2.5-7.2	4.4	23-58	43
SEMICHEMICAL	~1300	1300	~126	126			33-60	45
			Papermaking					
GENERAL	73-380	160	5-44	20	4.4-7.3		17-61	32
RELATED PAPERS								
Fine products								48
Coarse papers								27
Special industrial								94
Sanitary and tissue								18.4

Source Federal Water Pollution Control Administration 1967.

Table 3.8. Wastewaters from present pulp and paper technology.

Process	Wasteload, lb/ton						Wastewater,	
	Total Solids		BOD		pH		10^3 gal/ton	
	Range	Mean[a]	Range	Mean[a]	Range	Mean[a]	Range	Mean[a]
				Preprocess				
WOOD PREPARATION	4-50	13	2-10	3	6.5-8.0	7.0	1-10	3.4
				Pulping				
KRAFT								
Blow tower	~21	21	~1.3	1	~12	12	~1	1
Dirty condensate	6-11	7	6.5-9.0	8	9.5-10	10.0	1-1.9	1.2
Evaporator ejector	1-3	2	1.6-4.5	3	9-10	9.5	0.3-0.6	0.3
Causticizing waste	46-240	101	8.0-10.5	9	9-11.0	10.0	0.6-9.6	2.5
Green dreg	~22	22	~1.0	1	~12	12.0	0.2	0.2
Floor drain	11	11	0.3-1.7	1	11.6-12	12.0	0.3-0.6	0.4
Subtotal		164		23	9.5-12.0			5.6
SULFITE								
Blow tower	36-348	247	29-194	116	2.2-2.9	2.7	1.8-2.0	1.9
Condensate	18-87	47	48-71	66	2.3-3.1	2.6	0.8-1.7	1.1
Uncollected liquor	50-515	105	50-61	53	2.2-2.6	2.4	2-10	
Acid plant wastes	~10	10			1.2	1.2	~0.3	0.3
Boiler blowdown	~22	22				11.0	~0.1	0.1
Subtotal		411		235	1.2-2.9			10.9
SEMICHEMICAL								
Blow tower	~8	8	~1	1		4.0	~1	1
Condensate	~2	2	~3	3		3.5	~2	2
Recovery system	~150	150	~8	8			~2	2
Uncollected liquor	~40	40	~18	18		2.5	~2	2
Subtotal		200		30	2.5-4.0			7
Deinking			11-25				9.7-36	
				Pulp screening				
KRAFT	60-63	62	10-18	14	9-10	10.0	0.9-9.6	3.6
SULFITE		27	22-10.7	8	5.4-5.7	5.6	1.7-14.3	6
				Pulp washing and thickening				
GROUNDWOOD	51-107	75	22-46	33	5.0-6.3	6.0	4.8-10	7.5
KRAFT	94-180	142	10-35	25	8.9-9.4	9.0	3-11	7
SULFITE	68-1037	131	7.4-34	18	2.4-3.9	2.9	1.8-15	7.5
SEMICHEMICAL	42-141	93	10-42	24	7.0-7.9	7.4	2.4-7.8	5.4
				Bleaching				
GROUNDWOOD								4
KRAFT	216-294	240	8-88	30		2.9	12-32	19
SULFITE	131-415	220	17-44	25	2.9-6.8	3.8	9-30	15
DEINKING		125		12		2.2		5.5
				Papermaking				
GENERAL	31-591	119	3-80	16	4.3-6.9	5	5.7-40	13
RELATED PAPERS								
Newsprint			10-20	15			37	
Uncoated book stock		116		16			8-28	14
Fine stock		153	15-40	20			9-40	18
Coarse stock			10-25	15			2-29	10
Special industrial			140-170	155			20-100	
Sanitary and tissue		200	15-30	22			8-37	14

Source: Federal Water Pollution Control Administration 1967

Table 3.9. Wastewaters from advanced pulp and paper technology.

Process	Wasteload, lb/ton						Wastewater,	
	Total Solids		BOD		pH		10^3 gal/ton	
	Range	Mean[a]	Range	Mean[a]	Range	Mean[a]	Range	Mean[a]
			Preprocess					
WOOD PREPARATION	~4	4	~0.2		~6.9	6.9	~1.7	1.7
			Pulping					
REFINER GROUNDWOOD	~50	50	~10	10	~6.9	6.9	2	2
KRAFT								
Causticizing waste	22-56	46	9.0-9.3	9	11.6-12	11.8		2.7
Evaporator ejector	6.3-11	10	8.0-10.0	9	9.2-9.5	9.3		0.4
Green dreg	~20	20	~1.0	1	~12.0	12.0		0.9
Condensate	2.1-6	5	1.6-3.5	2	9-10	9.5		0.6
Subtotal		81		70				4.6
SULFITE								
Digester	36-120	87	10-18	14	2.0-2.2	2.2	0.3-7.1	2.1
Condensate	41-87	65	14-48	31	2.3-3.1	2.7	0.8-1.7	1.1
Acid plant					~0.5	0.5	~1.1	1.1
By-product plant	~153	153	~21	21	~4.5	4.5	2	2
Other operations				4				
Subtotal		305		70				6.3
			Pulp washing and thickening					
REFINER GROUNDWOOD	5-51	27	2-22.3	10	6-6.5	6.2	0.2-4.8	1.9
KRAFT	2.3-94	50	2.0-12	8	9-10	9.5	1-2.4	2
SULFITE	42-93	68	3.9-18	11	2.4-4.7	3.9	1.8-7.8	4.1
			Bleaching					
KRAFT	~125		~8		2.7-6.1	4.4	11-12	11.5
SULFITE	~90		6-8	7	~7.0		5.2-6.8	6
			Papermaking					
GENERAL	26-104	70	2-16	10	~4.5		4.5-11	7.5

Source: Federal Water Pollution Control Administration 1967.

toxicity markedly. However, as shown in Table 3.13, there are a number of toxic compounds in paper wastes which require treatment and monitoring.

It is not new for pulp and paper waste disposal to receive concentrated and skilled technical consideration. For example, Bloodgood (1947, 1948, 1949, and 1951; Bloodgood and Erganian 1947) studied the treatment of strawboard waste for the National Council on Air and Stream Improvement, a pulp and paper industry environmental improvement association. Gehm and Morgan (1949) also investigated strawboard waste treatment. Nemerow (1952a, b, c, d, e, and f; Rudolfs and Nemerow 1952; Rudolfs 1953) studied the composition and treatment of the effluents from rag, rope, and jute pulping industries. Although the effort devoted to the treatment of pulp and paper industry wastes has been considerable, and has persisted with industry funding and cooperation across several decades, there is still a considerable effluent treatment problem. This arises from the diverse nature of pulp and paper wastes (as typified by the two series of reports above), variations within different mills performing the same type of pulping, toxic consitituents which make biological treatment difficult, and the continuously changing nature of industrial practices. The currently recommended approach to pulp and paper mill effluent treatment seems to be an increase in internal water reuse combined with aerobic biological treatment of the effluent produced, as described by Betts *et al* (1954), Betts *et al* (1956), Pearman and Burns (1957), Rice and van Soest (1975), the National Council on Air and Stream Improvement (1968), and Edde (1968). The pulp and paper effluent may also be combined with municipal sewage prior to treatment. As early as 1949 Gehm investigated the effect of paper mill wastes on sewage plant operation. Brosig *et al* (1971) investigated the joint treatment of pulp and paper effluents with municipal sewage in an activated sludge plant. Combined treatment of NSSC pulping waste and sewage was considered by Opferkuch (1951) and the Federal Water Pollution Control Adminstration (1969). However, as shown in Table 3.11, the energy requirements for this type of treatment, which are as high as those for fermentation and distillation to produce ethanol from

Table 3.10. Pulp and paper industry wasteloads.

	Wasteload				
Year	Suspended solids, lb	Dissolved solids, lb	Total solids, lb	BOD$_5$	Wastewater, gal
		Wastes/ton product			
1972	125	485	610	120	41,000
1977	120	440	560	110	36,000
		Wastes/dollar of product			
1972	123	479	602	118	405
1977	129	475	604	118	387
		Gross waste × 10^{-9}			
1968	282	111	138	271	930
1969	287	112	140	275	942
1970	292	114	142	280	960
1971	296	115	146	284	975
1972	303	118	148	291	990
1977	350	129	163	321	1050

Source Federal Water Pollution Control Administration 1967

Table 3.11. Waste treatment-ethanol production energy requirements.

Carbohydrate %w/v	Surface aerators, kwh/10^3gal feed	Turbine aerators, kwh/10^3gal feed	Potential ethanol, %v/v[a]	Energy, lb steam/10^3 gal feed
4	142	213	2	1427
6	213	319	3	1480
8	284	427	4	1462
10	354	532	5	1551
12	425	639	6	1593
14	496	745	7	1656
16	566	851	8	1699
20	708	1064	10	1811

[a] Based on original feed volume

Source Griffith and Compere 1977

Table 3.12. Toxicity of groundwood compounds to rainbow trout.

Compound	96 hr LC_{50}, mg/l
Resin acids	
Dehydroabietic	1.1
Pimaric	0.8
Abietic	0.7
Palustric	0.5
Isopimaric	0.4
Diterpene alcohols	
Abietol	1.8
dehydroabietol	0.8
Isopimarol	0.3
Pimarol	0.3

Source Leach and Thakore 1976

an equivalent effluent, may discourage aerobic treatment as energy costs rise.

An alternative waste disposal method that has received some attention is land application. Guerri (1971) investigated the land disposal of NSSC waste liquor from Weston's Terre Haute, Indiania mill. Koch and Bloodgood (1959) studied the spray irrigation of paperboard mill wastes.

Pulp and paper industry wastes are now a major national problem (Vogt and Kenih 1976); with the development of innovative methods which use these materials as a starting point for the synthesis of needed compounds, they can be a major national resource.

Table 3.13. Fish toxic compounds in pulp mill effluents.

	Contribution		
Compound	Major	Intermediate	Minor
Acids			
Resin	KP, D, M, S		
Chlorinated resin		KC	
Unsaturated fatty		KP	D, M
Other		KC	
Neutral compounds			
Diterpene alcohols		M	D
Juvabiones			M
Other			D
Lignin derivatives			
Degradation products		S	

Abbreviations K=Kraft, P=Pulping, D=Debarking, M=Mechanical, S=Sulfite pulping, C=Caustic

Source Walden and Howard 1977

4. Chemical Products

The pulp and paper industry has practiced chemical recycle for almost a century. Every year it produces per capita between 600 and 700 lb of finished paper from nearly 1 ton of wood. Finished paper is an inexpensive material made to close tolerances from a renewable resource managed on a continuous production basis. To meet these standards, most of the inorganic salts used in the complicated process of paper production are recycled. The organic materials liquefied during the production of cellulose fibers from wood are burned to provide process heat. With increasing uses for chemical raw materials, the pulp and paper industry has been able to recover several types of chemicals from process streams. These products, to date, have generally been lignin derived materials, such as lignin sulfonates, and vanillin, or rosin based materials, such as black liquor soaps and tall oils. As the desire to produce chemical intermediates from renewable resources, rather than petroleum, increases, the pulp and paper industry can logically be expected to turn more of their process streams into raw materials for chemical production.

To get a feeling for the magnitude of this resource, consider only one of the many types of paper processes. McCarthy (1946) estimated that 2,000 gal of sulphite waste liquor with 12% solids could be recovered per ton of sulphite pulp. Of the solids, as much as 65% may be lignosulphonic acid, 20% reducing sugars, 8.4% sugar-sulphur dioxide derivatives, and 6.7% calcium. In 1975 the U.S. produced about 5,714 ton/day of sulphite pulp, or about 2 million tons per year. Consequently the total volume of waste liquor was approximately 4×10^9 gal/yr. The dissolved components of the wood would weigh about 2.5 million tons. Based on the average composition, the lignosulfonic acids thus made available would exceed 1.5 million ton/yr and the reducing sugars would approach 0.5 million ton/yr. These levels of chemicals are comparable to those needed for enhanced oil recovery. And sulfite pulping is only one of many types of chemical processing performed by the paper industry.

INTERNAL CHEMICAL RECYCLE

Recovery methods to recycle chemicals found in the waste streams from sulfite pulping has been extensively studied. References to many of these studies can be found in the comprehensive bibliographies prepared by Collins and Shick(1970a, 1970b, 1970c, 1971a, and 1971b).

Direct recycle of black liquor from the digestor is generally practiced. This increases the concentration of solids in the stream going to the digester and provides some direct process improvement in digestion. Increasing the concentration of black liquor decreases required evaporator process heat. After evaporation, salts are also recovered from the fired boiler ashes for process reuse. These methods of internal chemical recycle and reuse contribute significantly to pulp process economics.

From 10 to 60% of the total digester charge may be recycled black liquor. Typical inorganic compositions for black liquor are presented in Table 4.1. Opinions vary as to the advantages and disadvantages of the use of black liquor in the digester liquor charge. Process advantages include higher yield and better pulp quality and lowered chemical consumption.

Wells, (1925, 1941) and Woodhead (1925) claimed that wood impregnated with black liquor under pressure and then digested with

Table 4.1 Inorganic constituents of black liquor

Mill	Na_2CO_3, %	Na_2SO_4, %	Alkali, % Na_2O	Na, %	K, %	S, %	Ash, %[a]	Ca, ppm[b]	Mg, ppm	Si ppm[c]	Al, ppm	Fe ppm	Mn, ppm	B ppm
1	8.3	1.5	4.8	17.2	2.4	2.56	60.3	1080	190	3850	140	94	94	180
2	10.5	1.0	6.35	19.6	0.88	0.35	63.3	1020	220	1710	120	71	110	89
3	10.7	4.3	5.45	19.4	1.0	3.96	63.4	690	180	1090	220	78	73	49
4	9.1	2.6	6.5	18.6	0.93	3.49	62.3	300	180	2780	73	90	96	120
5	6.8	2.6	5.9	17.2	2.7	4.28	60.4	730	175	2460	96	87	120	110
6	10.3	4.1	4.25	18.9	0.8	3.05	59.8	170	160	2140	300	86	140	100
7	8.3	4.3	6.3	18.9	1.0	4.58	62.4	330	240	2780	220	120	70	380
8	7.5	3.8	6.0	18.0	0.92	3.68	59.4	450	170	1430	240	71	88	68
9	9.9	5.8	5.8	19.6	2.5	4.61	66.9	550	240	3210	80	110	220	180
10	9.9	2.9	5.0	18.7	1.0	3.89	60.4	170	160	3420	220	98	84	140
11	12.3	3.2	7.75	20.5	1.4	4.29	69.2	210	200	980	80	100	45	680
12	9.4	2.2	6.0	18.7	1.8	3.92	63.2	120	170	2140	75	95	120	260
13	7.1	2.3	5.3	17.3	1.2	3.35	59.0	170	140	2990	62	98	48	92
14	6.9	8.3	6.0	19.8	1.1	6.24	63.9	250	180	2570	84	100	69	120
15	8.4	4.6	6.8	18.4	1.2	3.95	62.5	280	140	2990	260	110	75	260
16	9.0	1.6	6.25	17.9	1.5	3.30	60.3	250	190	3850	240	100	100	120
17	9.6	4.6	4.9	19.3	1.5	4.82	62.9	180	170	2570	170	110	82	600
18	7.0	2.5	5.55	17.4	0.97	3.38	57.3	270	200	2990	220	80	130	300
19	10.9	3.2	4.05	18.1	0.88	3.77	60.1	280	170	3420	190	89	42	120
20	8.7	3.9	7.4	19.4	2.2	3.49	65.1	490	240	2990	170	120	140	170
21	8.1	4.5	3.9	18.2	1.8	3.79	60.6	230	140	3210	68	88	120	130
22	7.8	3.2	6.05	18.6	2.1	3.51	63.3	300	230	1540	42	98	100	120
23	6.7	3.3	6.3	18.6	1.1	4.45	61.1	520	170	1350	140	58	64	450
24	7.8	0.9	7.3	19.2	1.6	4.02	63.2	220	160	2140	51	86	100	100
25	9.1	2.6	5.55	18.0	0.44	3.69	59.0	170	150	2990	100	100	46	100
26	8.9	2.8	5.6	18.3	1.2	3.95	6.13	90	170	510	32	56	78	260
27	6.6	2.7	6.85	18.5	1.2	5.57	61.9	190	180	2140	120	93	97	230
28	7.3	1.5	8.6	20.5	0.86	3.28	65.3	260	230	2140	76	79	130	140
Avg	8.7	3.2	5.95	18.7	1.36	3.83	62.1	360	184	2440	139	91	96	202

[a] Measured sulfated ash

[b] Measured by atomic absorption

[c] As SiO_2

Source Grace, Sachs, and Grady 1977

white liquor produced an improved pulp yield and strength. Black liquor as a digester feed diluent, rather than water, permitted more rapid wood component dissolution. In experiments using balsam fir and hemlock, Crandall and Enderlein (1946) added black liquor as diluent using up to 75% of the total cook liquor volume. Active alkali in the white liquor was reduced correspondingly to compensate for that analytically determined in the black liquor. They reported that the permanganate number, the screenings, and the yield passed through local maxima with 50% black liquor volume, while at 60% black liquor local minima were observed. Higher pulp strength was also observed as the content of black liquor increased. Hart and Strapp (1948) using spruce, maintained the active alkali constant at a nominal 21% Na_2O (based on the wood) while increasing the black-liquor volumes from 0 to 60%. They concluded that the yield, screenings and permanganate number increased with increasing black-liquor volumes and that the screened pulp yield and strength values remained virtually constant.

Under normal conditions the black liquor recycle stream contains from 15 to 20% total solids depending on the digestion conditions and the number of stages of pulp washing provided.

The process for black liquor concentration and chemical recovery is relatively simple in conception. Black liquor is first evaporated in a multiple effect evaporator to a concentration of 45 to 55% w/w total solids. Further evaporation to 60 to 70% total solids is carried out in a cascade-type evaporator or a cyclone-type. Concentrated black liquor leaves the evaporator, and passes through a direct steam primary heater where the temperature is raised from 1800 to 2100°F. In the sulphate process, makeup salt cake, Na_2SO_4 is added and mixed into the black liquor. In the soda process, the makeup salt cake, Na_2CO_3, is added to the green liquor in a dissolving tank, or NaOH can be added elsewhere to the white liquor.

The concentrated black liquor goes through a secondary heater and the temperature is raised to 2200 to 2400° F. By steam or mechanical atomizing the dehydrated liquor, or black ash accumulates on the char bed. In either the sulphate or soda process, the black liquor, is burned out and the inorganic salts are melted and are discharged.

In the sulphate process the sodium salts are also reduced in the presence of carbon and a highly reducing atmosphere. About 95% of the sodium salts are Na_2S. The green liquor, after having reached the desired concentration, goes to the causticizing house, where it is treated with $Ca(OH)_2$, to convert the Na_2CO_3 in the green liquor to NaOH for use in makeup of new white liquor for the digesters.

It may be possible to use black liquor as a source for the recovery of organic chemicals. The inorganic fraction is currently recovered from ash. However, the removal of organic components ahead of the the ashing process should affect the recovery of process heat, rather than the ashing and causticizing processes.

In other chemical pulping processes where chemicals in the waste stream generally are not independently recycled, alternate recovery methods have been proposed. The use of mixed magnesium and ammonia bases in NSSC mills was proposed by Sanyer and Keller (1971). In another recent study, Lowe (1968) evaluated submerged evaporation of NSSC spent liquor.

CHEMICAL MIXTURES

In many cases, black liquor and other wood process components are used as a basis for the manufacture of relatively unrefined chemical mixtures. There is a limited demand for them. A major problem in the development of uses for waste pulp and paper process streams has been the huge volume of material produced.

Waste liquor itself is concentrated and sold either on a 50% solids basis or as a dry product. However, its commercial uses are limited. It may be used as an adhesive either alone or modified with fillers. It can be used as a binder in making briquettes or mixed with coke, clay, quartz, and cement as a core binder. Sulphite waste liquor suitably modified is said to harden cement, improve durability, and decrease time for setting. It has similar applications in the ceramic field. Sulphite waste liquor solids are reported to condition the soil and to improve the quality and yield of a crop. It finds use in laying dust on gravel and dirt roads. Small amounts are used in electroplating zinc or cadmium. Lignosulphonic acids in the waste liquor make it useful as an inexpensive dispersing agent in a number of fields; and further refinement of the product may extend this use. A possible series of petroleum recovery uses includes addition of lignosulfonates to drilling muds and as a sacrificial agent in micellar floods.The materials are also used in the manufacture of cation exchange materials. This suggests that the use of lignosulfonates as competitive sorbants for divalent and trivalent cations in well brines may be possible.

Constituents of sulfite waste liquor are used in tanning, with vegetable tannins. Synthetic tanning agents have been made by combining sulphite waste liquor with various phenols and aldehydes, but further improvement is necessary before condensed waste liquor or the lignosulphonates can replace the vegetable tannins. Sulphite waste-liquor solids are also being used in the manufacture of base-exchange materials.

The alkaline processes produce a black liquor differing in many respects from the waste liquors of the sulfite process. Lignin has been changed to thiolignin, or alkali lignin, which behaves as the alkaline salt of a weak acid. The carbohydrates, following hydrolysis, are oxidized to yield sugar acids and other related products. The extractives in the wood are in part recovered from the digester blowdown as sulphate turpentine and in part converted to the sodium salts of resin and fatty acids. These latter materials are later changed to free acids and, together with small amounts of unsaponifiable compounds, are the principal components of tall oil.

REFINED PRODUCTS

Some wood derived chemicals are produced for use as chemical intermediates. These materials include rosin derived oils and acids, saponified oils, purified lignin derivatives used as fillers in plastics, turpentine, cymene, and conindendrols. The market values of these materials range from a few cents per pound to several dollars per pound. The materials currently produced fill a wide variety of uses, and indicate the wide diversity of process streams which can be tapped.

Investigations of rosin extraction in kraft pulping process were made by Jayme and Groegaard (1940).

The collection of sulfate terpentine was discussed by Lawerence (1947). Sulfate turpentine can be recovered in yields of 0.5 to 5.0 gal/ton of pine sulphate pulp. It is sold largely to the paint industry but may also be useful as an intermediate for the production of terpineol or camphor. After suitable purification, it has also been used as fuel in internal combustion engines.

Tall (pine) oil is obtained from sulphate black liquor skimmings by acidification. Crude tall oil may be sold directly to the chemical industry for further refining. Refining can also be carried out by the pulp industry to produce a refined tall oil product. With the shortage of fats during World War II, the chemical industry began to use tall oil. Tall oil skimmings, which would normally be burned in the sulfate recovery system, are now in use as a source of crude and refined tall oil and of fatty and resin acids. The degree of refinement followed depends upon the particular application. It is possible to refine the tall oil so as to provide a 95% pure fraction of either resin or fatty acids. Liquid crystals in systems of rosin and fatty acids and their implications for tall oil recovery was discussed by Roberts *et al* (1976). The fatty acid fraction consists principally of linoleic acid and oleic acid. Linoleic acid is a principal constituent of cottonseed, linseed, and soybean oils. The two main constituents of the unsaponifiable fraction of tall oil are sterols mixed with lignoceryl alcohol.

Tall oil is sulphonated for the preparation of soluble soaps and used directly in the manufacture of industrial and laundry soaps, as an emulsifying agent in the preparation of asphalt emulsions and cold-water paints, and largely as flotation aids in the concentration of phosphate and other ores. Improvements in the quality of tall oil and of its separated constitutents should widen the fields in which tall oil finds uses. These improvements include: color, odor, heat, light and air stability. Fatty acids, free of resin acids, may find other uses.

Resin soaps formed during cooking are nearly insoluble in black liquor and tend to separate and float on the surface. This separation occurs in the weak liquor during storage. This tendency of soap to separate in the evaporator has been a source of much difficulty since it fouls the heating surfaces. Most evaporators are now arranged so that liquor is withdrawn from the effect where the concentration is such that maximum soap recovery is obtained; generally at a point in the system where the liquor concentration is about 25 to 28% solids and at a temperature of 160 to 180° F. The liquor flows to settling tanks where the soap is skimmed off and sent to the tall-oil plant. The remaining hot liquor is returned to the evaporator system. During normal operation of a sulphate mill operating on southern pine, it is usual to obtain as much as 150 to 200 lb of soap per air-dried ton of pulp.

Ying-Chech Chiu (1978) indicated that tall oil pitch, a bottom product of tall oil fractionation, could be used for chemical tertiary oil recovery. Chiu used a solution of tall oil pitch digested at 70°C with concentrated alkali. This increased the amount of fatty acids in the solution, and, thereby, its activity. This material was capable of scavenging a high percentage of oil from Berea sandstone cores during testing. There was a marked incompatibility of the pitch solution with brines, but this was decreased by the use of inorganic scale prevention compounds. The tall oil pitch solution functioned as both surfactant and coagent under the conditions mentioned.

The market value of fatty and resin acids has led to the reclamation of these materials from the crude soap present in black liquor. Tall oil consists of a heterogeneous and extremely variable mixture of fatty acids, resin acids, and unsaponifiables, all of which are practically non-volatile under conditions of the alkaline pulping processes, which range between 150 to 350°F. In pulping pine, the fatty and resin acids dissolve in the cook as sodium soaps. The soap, or crude tall oil, skimmings contain approximately 50% resins and fatty acids.

With increasing demand for tall oil, mills have installed recovery units. A theoretical yield of 180 - 200 lb of soap per air-dry ton of pulp from loblolly pine and as high as 300 lb / ton from longleaf pine has been reported. For a mill producing 1,000 tons/day this corresponds to the recovery of 10,500 to 17,500 gal of crude tall oil per day.

POTENTIAL PROCESSES

Black liquor recycle, tall oil production, and turpentine recovery are at present the major types of by-product recovery practiced by the pulp and paper industry. Other materials are recycled to a smaller extent to provide specific industrial chemical process feeds, such as vanillin. It is clear that there is a competitive market for turpentine and tall oils. Products which are made from these two sources will have to compete for their share of the resource market, and may suffer price increases accordingly. However, materials which can be made from black liquor without harming the salt-recycle processes may be made in large amounts without much shifting of prices in that the supply of black liquor is very large relative to the amounts of various different chemical intermediates currently produced.

A potential use for spent sulfite liquor is the manufacture of resins for use in the production of panel wood products (Fung, Calve, and Shen 1977). The spent sulfite liquor was acidified with sulfuric acid. This resulted in the formation of lignosulfonic acid, which served as a resin crosslinking agent. The resin does not require addition of a phenolic compound for strength. An excess of 50% of the spent sulfite liquor over resin is required for the same finished waferboard strength.

The production of low molecular weight organic compounds from pulping liquors is a potential chemical production process which has been explored in several ways by different authors. Aronovic, Crowell, Whalen, and Burnett (1971) considered the production of low molecular weight organic acids from pulping liquors. Table 4.2 shows the results found by these authors in the analysis of several different black liquors. It appears that there are substantial amounts of sodium acetate in neutral sulfite semichemical pulping liquor and of sodium acetate and glycolate in Kamyr hardwood liquor. Glycolic acids have a potential use in tertiary oil recovery as sequestering agents. Acetic acid is a major industrial chemical intermediate which forms the basis for many syntheses.

Lang and DeHaas (1970) indicated acetic acid is also a component of sulfite liquor. Spent sulfite liquor contains 0.2 to 0.8% acetic acid on a weight basis. A recovery process was tested in a pilot plant attached to the Cosmopolis, Washington, acid sulfite pulp mill of the Weyerhaeuser Corporation. The system provides for the removal and recycle of sulfite with the concurrent production of acetic acid. The acetic acid produced met all of the American Chemical Society tests for reagent grade glacial acetic acid. However, the quantities of acid which could be produced at a single acid sulfite paper mill were smaller than those which could be produced at a synthetic glacial acetic acid plant. This might have an effect on the economics of product sale, unless an internal use for the product was found.

Schalegar and Brink (1977) investigated the production of chemical intermediates from lignocellulose at 4 temperatures ranging between 160-220° C and 225 to 500 psig using wet oxidation. Table 4.3, taken from Bicho (1971) shows the yields of major products from hammermilled wet oxidized wood. Schalager and Brink (1977) indicated

Table 4.2. Low molecular weight organic acids in pulping liquors.

	Component				
Liquor	Solids, %	Sodium formate, %	Sodium acetate, %	Sodium lactate, %	Sodium glycolate, %[a]
Heavy black	47.8	5.4	4.3	3.2	3.7
Oxidized black	49.3	5.5	4.7	3.0	3.7
NSSC	9.0	2.7	21.1	0.2	0.6
Kamyr hardwood	14.4	5.5	8.4	2.0	9.0
Polysulfide	12.2	6.6	4.3	3.6	8.2
Bleach	0.3	1.9	0.7	0.3	1.3

[a] Includes sodium glycolate and sodium α-hydroxy butyrate

Source. Aronovic, Crowell, Whalen, and Burnett 1971.

Table 4.3. Yields of chemical products from wet oxidation solubilization of 100 g hammermilled wood.

	Wet oxidation temperature, °C		
Compound	160	180	200
Formic acid	12	16	12
Acetic acid	7	7	5
Glycolic acid	5	10	8
Oxalic acid	1	4	1
Levulinic acid	1	2	2
Succinic acid	1	2	2
Glucose	10	8	5
Mannose	10	4	1
Xylose	6	3	2
Methanol	6	5	3
Galactose	4	1	tr
Arabinose	2	tr	tr

Source Schaleger and Brink 1977

that a three step process in which five carbon sugars, six carbon sugars, and organic acids were produced sequentially would probably represent the best commercial process for the production of organic chemical intermediates. They were interested in employing the process offstreams for the production of *Candida utilis* yeast as a single cell protein food supplement.

Harris (1977) considered the coproduction of furfural, cellulosic residue, and acetic acid. He states that the production of all U.S. domestic furfural from wood would require use of the process streams from less than 2,000 ton/day — equivalent to one or two modern pulp mills. The furfural produced could be used as a substitute for phenols in some applications. Acetic acid and a partially degraded cellulosic resdue could also be recovered from process effluents. Harris suggested that the production of furfural from a wood source, rather than from the conventional sources, might be economically attractive. This particular reaction might also be performed on conventional wood process offstreams, such as those from the pulping of wood for viscose rayon, since it uses solubilizied xylans as a feed material for the production of furfural.

Particularly interesting side products from pulping liquors are reducing sugars. These materials can be fermented for the production of a wide variety of chemicals and for human or animal feedstuffs. A major difficulty with the use of pulping liquors for the production of such compounds has been the presence of lignin and lignin derivatives in the pulping liquors. The smaller lignin derivatives may have a significant level of biotoxicity (Rogers, *et al*, 1975). Reducing sugar purification by ultrafiltration was investigated by Collins *et al* (1973). Further investigations were carried out by Boggs (1973) and Bar-Sinai and Wayman (1976). Boggs employed methanol precipitation of sugars, ultrafiltration, and ion exclusion for the purification of sugar solutions. He was able to recover high-xylose solutions from birchwood pulping liquors. Bar-Sinai and Wayman used acid hydrolysis followed by ultrafiltration to separate reducing sugars and lignin compounds in spent sulfite liquor. Use of such an ultrafiltration process would provide the lignin for use in process heat recovery or for chemical production, and permit the fermentation of the sugars recovered.

The concentration of lignin species and other chemicals in pulping wastes that are too dilute for concentration by economical evaporation may become economical using hyperfiltration or ultrafiltration processes. The Institute of Paper Chemistry has conducted laboratory and pilot-plant tests of tubular cellulose acetate membrane systems (Wiley *et al* 1970; Wiley, Dubey, and Bansal 1972; Wiley, Scharpf, Bansal, and Arps 1972; and Collins, Boggs, Webb, and Wiley 1973). Both tubular and spiralwound configurations were evaluated by the Green Bay Packaging Company (Morris, Nelson, and Walraven 1972). Beder and Gillespie (1970) demonstrated color removal from the bleach-plant effluent with ultrafiltration film membranes, and extensive tests were carried out at the Champion International plant at Canton, North Carolina (Fremont, Tate, and Goldsmith 1973). Dynamic hyperfiltration and ultrafiltration membranes have been studied by Perona *et al* (1967), Csurny *et al* (1967), Johnson, Minturn, and Moore (1974),and Minturn (1974). Dynamic membranes and more recently developed conventional membranes have the advantage of allowing operation at the elevated temperatures of these process streams in the plant. Recycle of the hot filtrates can result in additional energy conservation. Pilot scale work using dynamic membranes for the filtration of bleach plant effluents has been reported by Breithaupt (1975 to 1977). The work was performed in the Moss Point, Miss., plant of International Paper Company under the supervision of L. J. Breithaupt, Jr. using dynamic membrane modules designed by Selas Corp., in test units fabricated at Oak Ridge National Laboratory.

None of the configurations now available appear to have sufficient long term performance or to be available at low enough cost to entice large-scale application. However, rising pollution control standards and continuing improvement in membranes and equipment seem likely to overcome these barriers. The concentrated streams produced should be a source of useful sugars and chemicals (Bar-Sinai and Wayman 1976).

MICELLAR FLOOD CHEMICALS

Some currently available wood derived chemicals are suitable for use in selected micellar floods. For example, the tall oil acids could potentially find use as surfactants in micellar floods under conditions where the well brine had a limited concentration multivalent cations. Lignin sulfonates might find a use as sacrificial agents which would be used early in a surfactant flood to prevent the deposition of a surfactant on the well formation. Preliminary tests reported by Baldwin *et al* (1977) indicated that the acids of simple carbohydrates found in pulping liquor could be used as sequestering agents for the complexing of multivalent cations. These materials are either current market products or readily recovered present process chemicals.

In other cases, currently produced process streams could be used as feedstocks for the production of materials to be used in micellar flooding. The purification of glycollic acids from wet oxidiation streams would provide sequestering agents for use in brines where the multivalent cation content is high enough to cause the formation of calcium, magnesium, or aluminum soaps. The isolation of high carbohydrate streams from wet oxidized wood pulp streams or from weak acid sulfite liquor could provide feedstocks for fermentation produced chemicals, including sequesterants, alcohols, high viscosity polymers, and chemical process intermediates. Lignin sulfonate streams could also be alkylated to produce surfactants for use in forming oil emulsions. If the proper economic incentives were provided, it might be possible to commercially establish some of these processes.

The carboxylic acids found in crude tall oils are another promising material which have a potential use in micellar flooding (Baldwin and Neal 1978). Although the use of these materials is now restricted to formations having low-hardness brines, they are made in large quantities cheaply. Package plants for the purification of tall oils from black liquor soaps are available. Chemical modifications of tall oil structure to decrease response to hardness may make this material a major source of micellar flood surfactants, as suggested by Baldwin (1977) and Chiu (1978).

It is difficult to predict the types of processes which might grow out of a thorough bench-scale investigation of the pulp and paper waste streams. However, the organic materials contained in these streams are very high. It might be possible to provide many of the materials which would be used for tertiary oil recovery using micellar flooding from this single industry.

5. Fermentation Processes

The production of industrial chemicals from pulp and paper industry process streams by fermentation was accepted practice during World War II. In the decades afterward, the cost balance gradually shifted to favor production of U.S. industrial chemicals from petroleum by chemical synthesis. Recent increases in energy, petroleum, and wastewater treatment costs could swing the economic balance toward recovery of some industrial chemicals from pulp and paper industry streams. From the standpoint of tertiary oil recovery, this is particularly advantageous in that the chemicals would be derived from a non-petroleum source, providing a potential net gain in petroleum recovered.

The pulp and paper industries are experienced in the recycle and recovery of process and by-product streams; the use of low valued process and waste streams as feeds for the production of industrial chemicals could be economically attractive to this industry. However, the modern methods used in pulp and paper mills will probably require changes in earlier biological production methods to fit the new streams and process conditions as well as to take advantage of advances in fermentation technology.

The fermentations which will be considered can be divided into several groups based on the nature of the fermentation and its principal products. Because of previous research and industrial experience, detailed descriptions of many of the fermentations can be found. The major fermentation groups which will be discussed are the acetone-butanol-isopropanol fermentation, the aerobic and anaerobic citric acid fermentations, the lactic acid fermentation, and the aerobic polymer fermentations. These represent potential sources of cosurfactants, sequestering agents, chemical intermediates for mobility control polymer synthesis, and mobility control polymer, respectively.

ACETONE, BUTANOL, AND ISOPROPANOL FERMENTATIONS

The acetone, butanol, and isopropanol fermentations are groups of fermentations which start from a common point, pyruvic acid, as shown in Fig. 5.1. These fermentations produce, depending upon the organism and growth conditions, varying amounts of butyric acid, butanol, acetone, and isopropanol. Small amounts of other fermentation products, including both volatile acids and some other neutral solvents, are produced. As a group, the

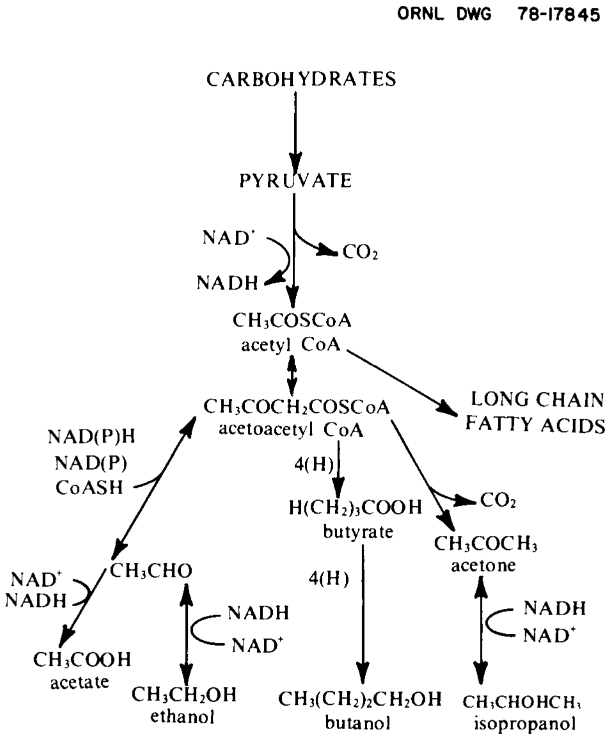

Fig. 5.1. Butanol fermentation pathway.

fermentations are referred to as butyric-butylic fermentations. The history of the fermentation itself is long: Louis Pasteur made the first investigations of the production of butyl alcohol from lactic acid and calcium lactate (Pasteur 1862). During the better than one century in which these organisms have been studied, they have borne a variety of names, including *Bacillus butylicus*, *Bacillus amylobacter*, *Bacillus orthobutylicus*, *Granulobacter butylicum*, *Amylobacter butylicus, Amylobacter ethylicus,* and *Clostridia.* In most cases, the cultures have contained spore forming rod shaped organisms able to ferment a wide variety of carbohydrate materials.

The commerical fermentation organisms which were used between 1915 and the present fall into three main categories (Monick 1968). The products of fermentation of these different organisms are shown in Table 5.1. of butyric acid for every 100 input moles of glucose fermented. The acetone-butanol producing organisms make almost 20 times less butyric acid, and are capable of making 56 moles of butanol, 22 moles of isopropanol, and 14 moles of acetic acid per 100 moles of supplied glucose. The isopropanol-butanol fermentation organisms are able to make 59 moles of butanol, 12 moles of isopropanol, and 17 moles each of butyric and acetic acids from 100 moles of input glucose. A typical acetone-butanol fermentation will start with a molasses solution diluted to about 5% sugar. The fermentation will generally take about 48 hours. The final yield of mixed solvents will be about 30% by weight of the input sugar, and will contain butanol, acetone, and ethanol in the approximate ratios 6:3:1.

Table 5.1. Fermentation balances from different *Clostridia* species.

Products	*Clostridium butyricum,* mole %	*Clostridium acetobutylicum,* mole %	*Clostridium butylicum,* mole %
Butyric acid	76	4	17
Acetic acid	42	14	17
Ethanol		7	
Butanol		56	59
Acetone		22	
Isopropanol			12
Acetylmethycarbinol		6	
Carbon dioxide	188	221	204
Hydrogen	235	135	78
Carbon recovery, %	96	100	96

Source Wilkinson and Rose 1963

The political and economic history of the acetone-butanol-isopropanol fermentation is a long and interesting one (Prescott and Dunn 1940). After nearly 50 years of industrial research on synthetic rubber, the firm of Strange and Graham, Ltd., decided to pursue the synthesis of rubber by the polymerization of butadiene or isoprene. Their chosen method required the use of isoamyl alcohol or n-butyl alcohol. They recovered the isoamyl alcohol from the fusel oil content of ethanol fermentations. In order to increase their potential production, this firm retained Professor Perkin and an assistant, Weizmann, of Manchester University and Professor Fernbach and his assistant, Schoen, of the Pasteur Institute, to find fermentation methods for meeting their synthetic rubber intermediate needs.In 1911, Fernbach and Weizmann discovered bacteria that were capable of fermenting potato starch to yield amyl alcohol, butyl alcohol, ethyl alcohol, and acetone. In 1912, Weizmann left the employment of Strange and Graham, Ltd., and pursued his research on bacteria which were able to make higher alcohols and acetone. He was able to isolate an organism which produced 4 times as much acetone as previous organisms and which was able to ferment a variety of starches. The organism bore several names, and is currently called *Clostridium acetobutylicum* Weizmann. Strange and Graham, Ltd., continued to build plants for the production of solvents during the period between 1912 and the first World War.

During World War I, the industrial use of acetone increased since it was used for the production of cordite and airplane wing dopes. The Strange and Graham, Ltd., plants which produced solvents were unable to meet the demand with their potato-based fermentation. A government order required the substitution of the Weizmann organism, which could ferment a wide variety of starches, including maize. The process and the patents were used in England, Canada, and the United States during the first World War. After the end of the first World War, the production of acetone and butanol dropped for a period, and was then resumed to meet new industrial uses in organic chemical and automobile paint manufacture.

During the period between the two World Wars, a fermentation process for the preparation of acetone and butanol which used molasses, rather than a grain based feedstock, was developed. At this time, molasses was regarded as a waste material which had little commerical value (Monick 1968). This made the butanol-acetone fermentation process more attractive. With the decrease in the availability of cheap Cuban molasses which occurred after the Korean War, the amount of butanol produced by the acetone-butanol fermentation process has dropped. In 1944, roughly 80% of the butanol used in the U.S. was made by fermentation, and in 1966, only 20% of the butanol made was fermentation produced. The replacement chemical process is a synthetic process which uses acetaldehyde via an aldol condensation.

Another problem which occurred during the middle 1950's and which substantially hindered acetone butanol production was due to the contamination of some commercial fermentation installations with a bacteriophage which caused lysis, or disintegration, of the fermentation cultures. This problem was remedied by the development of bacteriophage resistant cultures by the Northern Regional Research Laboratory of the Department of Agriculture in Peoria, Illinois. The resistant cultures are available from this institution.

Primarily n-butanol is used in the coatings industry for the formulation of nitrocellulose lacquers. It imparts good viscosity characteristics to the lacquer and acts as a cosurfactant to the nitrocellulose solvents used (Monick 1968). Other uses include cellulose-ester finishes, melamine plastics, urea-formaldehyde resins, alkyl-resin coatings, shellac, and spirit varnishes. It is used as a selective solvent or extractant in a variety of industrial processes, and as a blending agent for some mixtures, including petroleum naptha, ethanol, resins, and gums. It is an organic intermediate for a variety of compounds, including butyraldehyde, butylamine, butyl stearate, butyric acid, and butylene.

Several cosurfactants, including polyglycols, low molecular weight sulfonated naptha compounds, and 3 to 5 carbon alcohols, are used in tertiary oil recovery. The choice of cosurfactant varies with the reservoir, crude oil, and with the surfactant system used. Normal butanol, produced by these fermentations, is a possible cosurfactant in many systems. If it is employed in this fashion, it would be used in formulations applied at amounts ranging between 5 and 10 pounds of cosurfactant per barrel of incremental oil.

There does not appear to be a beneficial use for the acetone which might be produced in the acetone-butanol fermentation in tertiary oil recovery. There is, however, a potential use in the paper industry for acetone: it could be employed in *organosolv*, or organic solvent based, pulping processes to increase pulp yields and decrease pollution. Other organic materials (Cox and Worster 1971) can also be used in this type of process. Ethanol-water pulping systems, as described by Kleinert (1975) can also be used. This provides a potential use for ethanol which is produced with butanol and acetone. If organic solvent based pulping methods become widely used, it is possible that there may be a use for excess n-butanol for pulping in that Bowers and April (1977) indicate that n-butanol is also a good delignification solvent.

A variety of materials could be suitable fermentation feedstocks for the acetone-butanol or isopropanol-butanol fermentations. Several main requirements appear to exist. The feedstock must have at least 3 or more percent fermentable carbohydrate. It would be desirable to the feedstock to have a higher amount of carbohydrate, if possible, to cut down on process energy losses during distillation. A feedstock having a substantial amount of nitrogen-containing compounds, such as proteins, amino acids, urea, or ammonia would decrease the cost for nutrient supplementation, although supplements can be added to a feedstock which is deficient. It would be desirable for the feedstock chosen to be relatively free from heavy metals and soluble sulfides, in that these materials are common fermentation toxicants. Heavy-metal-resistant strains of organisms can be developed, but this may represent a substantial research expense. Feed pH can be adjusted. If, however, the feed pH falls in the 5 to 7 range and if the feed is buffered in excess of 100 meq, little or no pH adjustment will probably be required during the fermentation. Feeds containing carbohydrates having a high degree of polymerization may require pre-process treatment. These carbohydrates include: celluloses, long-chain starches, hemicelluloses, plant fibers, and xylans. A major problem may be the presence of organic compounds, such as substituted phenols, which can be derived from lignin breakdown and which can be present in a variety of wood wastes.

The butanol fermentations are reasonably tolerant in their acceptance of carbohydrates. In the past, starches derived from maize, potatoes, and horse-chestnuts were used as feedstocks (Prescott and Dunn 1940). Small cultures tested were able to ferment a variety of wood hydrolyzates, including some from soft woods. Both black strap and high-test molasses were used as commerical feedstocks for butanol production. Industrial wastes which may be able to provide satisfactory feedstocks include wood molasses, citrus molasses, wood chip cooking wastes, vegetable canning wastes, starch manufacturing wastes, and dairy wastes. Hydrolyzates of a variety of materials may also be suitable for use. Strains of organisms able to use partially hydrolyzed celluloses and soluble hemicelluloses as feeds may also be developed. Veldhuis, Christensen, and Fulmer (1936) reported the production of ethanol at high temperatures from cellulose using similar organisms.

SEQUESTERING AGENTS

Sequestering agents form complexes with those multivalent cations in well brine which interfere with surfactant activity or with viscosity elevation by polymers, such as partially hydrolyzed polyacrylamide. Some common interfering multivalent cations are calcium, magnesium, iron, and aluminum. Because of the composition of the porous rock through which the fluids are flowing, calcium and magnesium will probably be the most common interferences. Sequestering agents used are generally multivalent organic acids. A well known seqestering agent is EDTA, ethylene dinitriloacetic acid. Some other materials which can be produced using fermentation technology can be efficient sequestering agents. These compounds include the components of the Krebs cycle, dicarboxylic amino acids, sugar acids, and humic acids. Some of these compounds, notably the sugar acids and the humic acids, can be products of wood wastes. It is possible that some other materials, such as some of the acidic components of marine algae, can be used as sequestering agents. Based on previous industrial experience, it will be possible to produce sequestering agents which can reduce the precipitation of the surfactants used for micelle formation. However, it may be difficult to produce these compounds in the high quantities required at prices which make their use in tertiary oil recovery economic.

The Krebs cycle and the glyoxalate shunt are shown in Fig. 5.2. These processes are common to most aerobic organisms. They are a part of the primary metabolism of the organism, and supply chemical intermediates which are used in the manufacture of a variety of necessary biological compounds.The multicarboxylic acids which form the bulk of this cycle are often good sequestering agents. Citric acid is the best known and least expensive of these compounds.

In general, processes for the industrial production of citric acid involves the conversion of inexpensive sources of sucrose or of glucose to citrate using selected *Aspergillus niger* strains (Martin 1963). The sources of sucrose which are used include both beet and cane molasses. For the most part, the processes used are proprietary. Many strains of *Aspergillus niger* show the ability to grow on five carbon sugars, indicating that these materials have a potential for use as substrates for citric acid production. With a six carbon sugar, or a polymer containing exclusively six carbon subunits, the production of citrate approaches theoretical, and the organism shows almost no synthesis of carbon dioxide relative to the amount of citrate which is produced.

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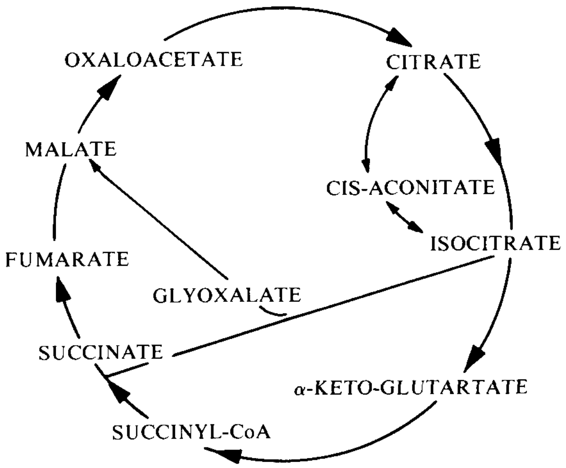

Fig. 5.2. Citric acid cycle.

Citric acid production historically presents a contrast to acetone-butanol-isopropanol production. Prior to 1923, almost all of the citric acid produced on a world-wide basis was produced from waste vegetable and fruit materials. Over 90% of this material was produced in Italy. Production of citric acid on a commerical basis used a mold started in the United States in 1923, and in England in 1929.Both shallow tray and submerged fermentations are used for the production of this material. With time, increasing amounts of this material have been made, with more of it being produced by molds from sugars having six-carbon subunits. Citric acid is widely used in the food and pharmaceutical industries because of its ready availability, palatability, low toxicity, and ease of assimilation. It is used in carbonated beverages, jams, jellies, and gelatin preparations. Citric acid and citric acid salts are used as both preservatives and emulsifiers and stabilizers in different foods. They are also used as antioxidants. They are a major ingredient of effervesecent powders. Citric acid is also a major constituent of non-ferrous plating solutions. A variety of smaller uses for the material, such as paints and inks, also exist. However, for the most part, citric acid is a food constituent and is manufactured in a high purity form for this application.

There are three major methods used to make citric acid with an *Aspergillus* mold: tray fermentations, submerged fermentations, and solid-phase fermentations. In the tray fermentation method, sucrose, high-test cane syrup, or beet molasses are diluted with water to form a 20 to 25% sugar concentration. Inorganic nutrients, including magnesium sulfate and phosphate, are added to the culture broth. Ammonium salts of strong mineral acids, i.e., ammonium sulfate, are added to the fermentation broth, and the pH is reduced to between 3 and 5. The material is aliquotted into shallow trays and innoculated. Warm air is passed across the surface of the trays. After a few days, the mycelium forms a thick mat. After 8 to 10 days of incubation, the mycelium is separated from the fermentation broth containing the citric acid, the mycelium is washed, and the washings are added to the broth. The citric acid is then purified. The Japanese favor use of a tray method in which the mold is grown on moist bran, rather than on the surface of a liquid medium. After several days, the bran is extracted with water, and the citric acid is then purified and recovered. Traces of gluconic acid and oxalic acid are formed with the citric acid when the Japanese method is used. In submerged culture, the mold culture is grown mixed with the fermentation broth under conditions where the aeration, pH, and constituents of the medium can be continuously manipulated. Otherwise the fermentation times and conditions are similar to those used for the tray fermentation. Citric acid production from hexose sugars is essentially stoichiometric.

The efficiency of citric acid production is closely related to the maintenance of low levels of iron, generally in the range of 20 mg/l or less, and in the maintenance of phosphate levels of 0.1 % or less. Once citric acid production begins, the low pH of the medium discourages contamination of the fermentation by other organisms. Although the fermentation is a long one, ranging between 7 and 15 days for completion, the concentration of the citric acid produced, around 10%, is high, and the efficiency of the fermentation approaches theoretical yield.

Fermentation processes for the production of other Krebs cycle acids are similar, in that they produce high yields of major cell metabolites from concentrated sugar solutions at very low pH values. The technology used to perform these fermentations is essentially equivalent to that for the production of citric acid. Other Krebs cycle intermediates which may be suitable sequestering agents include succinic, fumaric, malic, itaconic, and isocitric acids.

Anaerobic methods for the production of these compounds from a variety of substrates have also been tested at a bench scale. A major advantage of the use of an anaerobic fermentation for the production of an aerobic Krebs cycle intermediate is that a wider range of substrates and production conditions may be suitable for the production of some of these compounds. Table 5.2 shows the production of succinic acid anaerobically by *Bacteroides succinogenes*, a bacterium isolated from cattle rumens. Other than the types of *Clostridia* which produce butanol and acetone, the large scale culture of rumen organisms has not been demonstrated. However, they are able to ferment cellulosic waste materials,

Table 5.2. Anaerobic production of organic acids from cellulose.

Cellulose used, as 10^{3} M glucose	Formic acid, 10^{-3} M	Acetic acid, 10^{-3} M	Succinic acid, 10^{3} M	CO_2 used, 10^{-3} M	Source
0 554		0 28	0 458	0 125	Hungate 1950
0 531		0 208	0 424	0 148	Hungate 1950
1 72	0 23	0 86	0 89	0 69	Bryant and Doetsch 1954
1 78	0 21	0 61	1 26	0 83	Bryant and Doetsch 1954
2 73	0 28	1 00	2 46		Bryant and Doetsch 1954

Source Hungate 1966

and, therefore, may have a good potential for the fermentation of paper wastes.

A desirable substrate for the aerobic production of citric acid would have no less than 20% carbohydrate.Major decreases in the production of citric acid are noted when the feed has over 10 mg/ liter of iron or over 1 g/liter of phosphate (Lockwood and Schweiger 1967). Therefore, a feed which is low in trace elements and phosphate would be desirable. Because ammonium salts of strong mineral acids are used for pH control in many of the fermentation methods, it would, depending on the method chosen, probably be desirable to have a feed very low in organic nitrogen compounds, which the mold might use preferentially to ammonium salts. A feed material which had a high pH and a high buffering capacity would probably be unsuitable for the production of citric acid in that a very low medium pH — generally 1.5 to 2 — is required for citric acid synthesis. The Krebs cycle acids are produced from both 5 and 6 carbon sugars (Martin 1963).

LACTIC ACID

Lactic acid has the distinction of being the first industrial fermentation compound in the U.S. It was first manufactured by fermentation of a commerical basis in 1881 (Peppler 1967). At present, it can be manufactured by either fermentation or by synthetic routes. The fermentation route generally employes a low-valued carbohydrate, and the synthetic route is as a by-product from the synthesis of acrylonitrile (Mark, McKetta, and Othmer 1968). Lactic acid is a common metabolite in both aerobic and anaerobic organisms. Many organisms capable of producing high yields of lactic acid are available from U.S. culture collections. The major difficulty in the synthesis of lactic acid is the current market situation, in which the lactic acid manufactured is provided for high-cost, high-purity applications, generally requiring formulations meeting the U.S. Pharmacopia standards. These applications require only small amounts of material.

Lactic acid is primarily used in the food and beverage industry as an acidulant or a preservative. It is used in the vegetable tanning of sole leathers. It can be used as an intermediate for the synthesis of lactic acid esters. Lactic acid is used in the acid dying of wool and other textiles, and in a variety of proprietary formulations. Calcium, sodium, and aluminum salts are used in fermentations and in pharmaceutical preparations. Lactic acid can also be dehydrated, using calcium sulfate as a catalyst, to form acrylic acid, the monomer base for acrylic mobility control polymers (Holmen 1958).

Lactic acid is commercially prepared from a variety of cheap carbon sources, including starch hydrolysate, whey, and molasses (Peppler 1967). Refined sugar based media can also be employed where a high purity lactic acid is required. Appropriate buffers and nitrogen compounds are added to the medium so that the pH is kept above 5. In a typical commerical fermentation, a medium containing 15% glucose, 10% calcium carbonate, 0.375% malt sprout, and 0.25% diammonium phosphate is fermented for 4 to 6 days at a temperature of 50C by *Lactobacillus delbrueckii*. The yield from such a fermentation is 93% to 96% of theoretical.

For use as a chemical intermediate for the synthesis of acrylic acid, an impure grade would suffice. The patent by Holmen (1958) indicates that aqueous concentrations of 10% or less of lactic acid can be converted to acrylic acid after heating and passage through a gypsum catalyst. Tests to determine the amount of other acids and chemical impurities which can be tolerated by the catalyst without unacceptable decreases in efficiency are required. If relatively crude materials can be processed to form acrylic acid, contaminant substances would be expected to be excluded from the acrylic acid polymer which can be formed from the monomer.

A method for the production of crude lactic acid solutions, such as feeds described in the Holmen patent, from wood molasses using a continuous process was developed (Compere and Griffith 1976, 1977; Griffith and Compere 1977). Although this process is less efficient in the production of lactic acid than is the process described by Peppler (1967), it is able to produce lactic acid continuously from very crude feeds: wood molasses is a 5 to 10% solution having either a concentrated prehydrolysis washwater from hardwood pulping or a wastewater from hardboard production as an input stream. Results from a series of bench scale runs are shown in Table 5.3. An additional benefit which can be derived from the use of such a process is the obviation of some of expensive waste treatment required to dispose of these wastes as they are now produced.

Lactic acid can be formed from a wide variety of materials, including long chain polysaccharides, pentoses, pentosans, hexoses, and carbohydrate derivatives, such as sugar alcohols. Lactic acid synthesis from two waste materials, wood molasses and sour whey, is satisfactory (Compere and Griffith 1977). The fermentation can be performed either aerobically or anaerobically (Peppler 1967). Table 5.4 shows the wide range of different substrates which can be fermented by a variety of different types of *Lactobacilli*. Depending upon the desired concentration of lactic acid in the beer, carbohydrates having between 4 and 15% carbohydrate may be suitable for fermentation. Nitrogenous compounds, such as salts of ammonia or nitrogen containing organic compounds, are required for the nutrition of *Lactobacilli*. The fermentation medium should be heavily buffered so that the pH during the whole fermentation ranges between 4.5 and 6. If possible, a feed containing calcium carbonate is desirable in that it will provide the necessary buffering capacity as needed by dissolution. If the fermentation is continuous, the presence of B vitamins in the medium will be required to provide for continued growth of the organisms. The *Lactobacilli* which have been commerically developed are resistant to a variety of toxic materials, and services supplying starter cultures for a variety of applications are available (Sellars 1967). A major problem in the production of lactic acid, however, is the occasional presence of culture-lysing bacteriophages in the feed.

Table 5.3. Fermentation patterns of several *Lactobacilli*

	L. delbrueckii	*L. leichmannii*	*L. jensenii*	*L. lactis*	*L. bulgaricus*	*L. helveticus*	*L. acidophilus*	*L. salivarius*	*L. casei*	*L. casei* subsp. *tolerans*	*L. casei* subsp. *pseudoplantarum*	*L. xylosus*	*L. plantarum*	*L. curvatus*	*L. coryniformis* subsp. *coryniformis*	*L. coryniformis* subsp. *torquens*	*L. homohiochii*	*L. fermentum*	*L. cellobiosus*	*L. brevis*	*L. buchneri*	*L. viridescens*	*L. coprophilus*	*L. hilgardii*	*L. trichodes*	*L. fructivorans*	*L. desidiosus*	*L. heterohiochii*
Amygdalin	–[a]	+	+	–	–	–	+	–	+	–	+	+	+	–	–	–	–	–	+	–	–	–	0	–	0	–	0	–
Arabinose	–	–	–	–	–	–	–	–	–	–	–	–	d*	–	–	–	–	d	+	+	+	–	+	–	–	–	+	–
Cellobiose	–	+	+	–	–	–	+	–	+	+	+	+	+	+	–	–	–	–	+	–	–	–	+	–	0	–	–	–
Fructose	+	+	+	+	+	#	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	0	+	+	+	#	+
Galactose	#	–w	+	+	+	+	+	+	+	+	+	+	+	+	+	+	–	+	+	#	#	–	0	d	–	–	#	–
Glucose (acid)	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	#	#	+
Glucose (gas)	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–	+	+	+	+	+	+	+	+	+	+	+
Gluconate	–	–	–	–	–	–	–	–	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	0	+	0	+
Lactose	–	+	–	+	+	+	+	+	*	+	+	*	+	d	–	–	–	+	#	#	#	–	–	d	–	–	–	–
Maltose	d	+	+	+	–	+	+	+	(d)	–	+	+	+	+	+	+	+	+	+	+	+	+	+	+	d	#	–	–
Mannitol	–	–	–	–	–	–	–	+	+	–	+	+	+	–	+	+	+	–	–	(#)	(#)	–	–	–	–	–	–	–
Mannose	+	+	+	+	–	#	+	+	+	+	+	+	+	+	+	d	+	w	#	–	–	+	0	–	–	–	–	–
Melezitose	–	–	–	–	–	–	–	–	+	–	+	–	d	–	–	–	0	–	–	–	+	–	–	–	0	–	0	–
Melibiose	–	–	–	–	–	–	d	+	–	–	–	–	+	–	d	–	0	+	+	+	+	–	–	–	0	–	0	–
Raffinose	–	–	–	–	–	–	d	+	–	–	–	–	+	–	d	–	–	+	+	#	#	–	–	d	–	–	–	–
Rhamnose	–	–	–	–	–	–	–	*	*	–	–	–	–	–	+	–	–	–	–	–	–	–	0	–	0	–	–	–
Ribose	–	–	–	–	–	–	–	–	+	+	+	+	+	+	–	–	–	+	+	+	+	+	+	+	0	–	0	+
Salicin	–	+	+	+	–	–	+	*	+	+	+	+	+	+	d	–	+	–	#	–	–	–	d	–	0	–	–	–
Sorbitol	–	–	–	–	–	–	–	+	+	+	+	–	+	–	d	–	–	–	–	–	–	–	–	–	0	–	–	–
Sucrose	+	+	+	+	–	–	+	+	(d)	–	+	+	+	–	+	–	–	+	+	d	d	d	+	d	d	#	–	–
Trehalose	–	+	+	+	–	*	+	+	+	–	+	+	+	–	–	–	–	d	+	–	–	d	0	–	0	–	–	–
Xylose	–	–	–	–	–	–	–	–	–	–	–	+	d*	–	–	–	–	d	d	d	d	–	+	+	–	–	0	–
Esculin	–	+	+	#	–	–	+	*	+	–	+	–	+	+	d	–	0	–	+	d	d	–	+	–	0	–	0	0

[a] The symbols used are + = positive reaction by 90% or more strains; d = some strains +, others – (about 89–11% positive), – = negative reaction by most strains (90% or more); ( ) = delayed reaction; w = weak reaction; # = weak, slow or negative; * = see text; 0 = not tested. Combinations of symbols, e.g. (–) = rarely positive, and then slowly, –w = negative or weak reaction.

Table 5.4. Continuous lactic acid production from wood wastes.

Source	Feed,%	Residual reducing sugar,%	Lime buffer, meq	Lactic acid, g/l
MC	4	0.25	75	13
MC	6		250	25
MC	8	1.0	125	26
MC	8	0.75	250	50
IPC	6	0.25	250	32

Abbreviations MC=Masonite Corporation, IPC=International Paper Company.

Source Griffith and Compere 1977

Commercial services provide mixed cultures which are rotated so as to decrease this problem.

MOBILITY CONTROL BIOPOLYMERS

A major chemical need for micellar flooding is mobility control polymers. Some biologically synthesized polymers, such as xanthan gum, appear to have satisfactory characteristics as mobility control agents. These materials would be used to improve sweep of the reservoir by the surfactant by providing a high viscosity chaser. Alternative high-viscosity materials are hydrolyzed polyacrylamide polymers.

The aerobic microbial or fungal production of high viscosity gums is a relatively new process (McNeely 1967). Much of the development work in this area has been done by the Northern Regional Research Laboratory of the Department of Agriculture at Peoria, Illinois. This research provided a basis for the commercialization of the production of xanthan gum, which is the microbial polysaccharide most frequently projected for use in micellar floods (Jeanes, Pittsley, and Senti 1961). This material is used in a variety of foodstuffs, in thickening agents, and in drilling muds, as well. It is primarily manufactured by Kelco, although other industries have shown an interest in the field synthesis of xanthan gum for mobility control in tertiary petroleum recovery. Kelco produced this material at pilot scale in 1960, semi-commercial scale in 1961, and full commercial scale in 1963.

A typical fermentation for commericial use, as described by Rogovin, Anderson, and Cadmus (1961) used 2.5 to 3% input glucose, 0.4% distillers dried solubles, 0.5% dipotassium phosphate, and 0.01% magnesium sulfate heptahydrate. The fermentation was performed for 96 hr at 28° C. Final yield represented a 50% conversion input glucose to biopolymer. The fermentation broth was purified and the polymer precipitated with methanol in the presence of 2% potassium chloride. A variety of methods for the synthesis and recovery of the polymer have been developed by the research staffs at the Northern Regional Research Laboratory. Albrecht, Sohns, and Rogovin (1963) developed a process for the isolation of xanthan and other microbial polysaccharides using quarternary ammonium compounds to force the high-molecular weight materials from solution. Investigations of the kinetics of the polysachharide fermentation (Moraine and Rogovin 1966) and conditions for optimum production of xanthan (Moraine and Rogovin 1971) were investigated. Methods for producing lower cost industrial grade polysaccharide were also developed (Rogovin, Albrecht, and Sohns 1965).

In the area of enhanced oil recovery, major concerns have been the removal of the bacterial cells, which are around 1 μm long, from the purified polymer, and development of methods for field production which eliminate precipitation and resuspension of the polymer. The continuous production of xanthan polymer, which has been demonstrated by NRRL (Silman and Rogovin 1970, 1972), will help to decrease the cost of the polymer in that it will eliminate some of the more expensive purification steps.

McNeely (1967) indicates that xanthan gum can be produced from glucose, sucrose, hydrolyzed starch, and starch. This organism is limited primarily to the hexoses and their polymers as substrates.

The production of polysaccharides from fungi was investigated by the Pillsbury Corporation. They developed *Sclerotium* fungi which were able to produce high-viscosity polysaccharide from a variety of substrates in submerged culture. These organisms were able to produce polysaccharide at roughly 50% yield from a fermentation broth containing 0.3% nitrate, 0.1% yeast extract, 3% sucrose, 0.05% KCl, 0.05% magnesium sulfate, and trace elements. The fermentation required 72 hr and 25 °C, and the polymer was precipitated and purified in a fashion similar to that used for xanthan gum except that the larger cell sizes permitted easier separation of the polysaccharide and organism. The carbohydrate tolerances of some of these fungi are shown in Table 5.5, which was derived from the Pillsbury base patent. The patents have since been sold by Pillsbury to a French concern, Ceca, which is marketing the polymers produced by the *Sclerotium* molds from sucrose for enhanced oil recovery in the U.S.

Production of scleroglucans on a continuous basis is under investigation at ORNL (Griffith and Compere 1978). Continuous production of scleroglucans may eliminate the isopropanol precipitation step in scleroglucan production and should permit production of 6 times as much material from the same equipment. Production methods for scleroglucan from agricultural wastes have also been investigated (Compere and Griffith 1978) and some of the results are shown in Table 5.6.

A major research need in this area is a clear definition of the carbohydrate requirements of the polymer producing strains. The different strains of biopolymer producing organisms require at least 2 but less than 10% input carbohydrate in the feed stream, although different types of polymer producing organisms have different fermentation substrate and pH requirements. A xanthan producing organism would require a feed

Table 5.5. Fungal production of glucans.

Organism	Strain	Sugar	Concentration, g/l	Polymer g/l
Sclerotium glucanicum	NRRL 3006	Sucrose	30	8.2
Sclerotium delphinii	ATCC 15199	Mannose	20	3.6
Sclerotium delphinii	ATCC 15197	Dextrose	20	5.4
Sclerotium delphinii	ATCC 15197	Fructose	20	5.0
Sclerotium delphinii	ATCC 15197	Mannose	20	5.1
Sclerotium rolfsii	ATCC 15195	Fructose	20	5.0
Sclerotium rolfsii	ATCC 15205	Dextrose	20	5.4
Sclerotium rolfsii	ATCC 15205	Sucrose	20	5.0
Sclerotium rolfsii	ATCC 15205	Maltose	20	4.9
Sclerotium rolfsii	ATCC 15201	Maltose	20	5.5
Sclerotium rolfsii	ATCC 15201	Sucrose	20	5.0
Sclerotium rolfsii	ATCC 15206	Maltose	20	6.0

Source Halleck 1967

which had a pH near 7, while a fungus which produced glucan would have a pH requirement of <4 for feedstocks. The usable sources of nitrogen to the two different organisms are different, since the mold is able to use nitrate with minimal supplementation, while the *Xanthomonas* requires organic nitrogen compounds in the feed. This is an area in which research will have to be performed to determine requirements and suitability. However, candidate feeds would include those having between 2 and 10% carbohydrate, a low level of toxic materials, such as phenols and heavy metals, and a pH suitable to one of the classes of polymer forming organisms.

Table 5.6. Scleroglucan production from cellulosics at 26°C.

Organism	Strain	Feed	Concentration, g/l	Polymer, g/l
Sclerotium glucanicum	NRRL 3006	beet pulp	40	8 14
Sclerotium glucanicum	NRRL 3006	starch	40	18 20
Helotium sp	NRRL 3129	starch	40	8.15
Sclerotium delphinii	ATCC 15196	starch	40	13.87

Source Compere and Griffith 1978

6. Choices

Pulp and paper industry process streams for investigation as sources of chemicals for use in enhanced oil recovery have been discussed. The pulp and paper industry includes a wide diversity of processes and process streams. Many of these streams are poorly characterized. The candidate streams which might be picked for further testing may be unsuitable for some reason which cannot be determined at the time of choice, and other process streams may be more suitable for use. However, in order to evaluate the suitability of wood processing streams as feedstocks for the production of chemicals and chemical intermediates used in tertiary oil production, it is necessary to establish a starting point. The streams discussed below appear to be most promising for investigation as feedstocks for the production of different micellar flood chemicals. There are no guarantees that these streams will, in the long run, be the most suitable for the uses covered. Bench, pilot, and full-scale experience are required to develop a process.

LIGNIN SULFONATES

Lignin sulfonates have several potential applications in tertiary oil recovery. These materials might be used as sacrificial agents to inhibit the deposition of surfactants contained in a micellar dispersion contained in a reservoir matrix. This could decrease the requirement for surfactants, and may reduce the cost of required chemicals. According to Kalfoglou (1977), the process normally would be carried out by first injecting an aqueous solution of lignin sulfonates into the formation through the injection well and following them with a micellar dispersion which may contain lignin sulfonates.

It is also theoretically possible to produce a surfactant by alkylating a lignin sulfonate. This material might be used by itself or in combination with other surfactants to lower the surfactant cost of a barrel of oil.

Lignin sulfonates have the advantage of a low cost, since they range in commerical price between $0.035 and $0.05/lb. Billions of pounds of this material are produced annually by major U.S. pulping processes. This material is currently burned for the production of process heat which is a relatively low valued use for a chemical. However, some barriers to the use of lignin sulfonates exist. The black liquor containing lignin sulfonates is a heterogeneous mixture of inorganic salts, lignin sulfonates, carbohydrates, and lignin or carbohydrate hydrolysis products. The inorganic process solution salts are recycled as a part of pulping process economics. The cost of lignin sulfonate purification for any oil recovery use needs to be evaluated in consideration of its use as a process chemical.

SACCHARINIC ACIDS

Saccharinic acids are formed from low molecular weight carbohydrates. They are able to function as sequestering agents for multivalent cations. They are major constituents of spent pulping liquors. Because of the mixture of compounds in spent pulping liquors, the purification of saccharinic acids may be a difficult proposition. However, it may be possible to recover a mixture of low molecular weight lignin sulfonates, saccharinic acids, and inorganic salts using a technique such as ultrafiltration. This mixture might be able to function as both a surfactant sparing and a multivalent cation sequestering agent.

Saccharinic acids are usually burned for process heat and salts recovery. Therefore, any use of these materials for enhanced oil recovery operations should consider the loss of process heat and provision of makeup salts as a part of the cost of using saccharinic acids.

CARBOHYDRATES

Fermentation of wood pulping liquors for the production of alcohols has been practiced for a long period of time. The production by fermentation of volatile solvents from pulping liquors offers a process advantage in that carbohydrates can be fermented to distillation recovered solvents leaving a process flow stream containing all of the input lignins and most of the input salts. The process stream could be diverted prior to the evaporator, processed to produce solvents, distilled, and returned to the evaporation step for process heat and salts recovery. The alcohols which are produced are known and preferred coagents for micellar flooding.

Fermentation has the process advantages that it provides for heat and salts recovery in conjunction with the recovery of the solvents distilled. The concentration of carbohydrates in wood pulping process streams is on the low side of that usually used for fermentation. This may cause some inefficiency in distillation of the solvents produced. However, from a fermentation standpoint, there are only three major difficulties with the fermentation feed streams from wood pulping operations: toxicity from lignin breakdown products, high concentrations of salts and difficulties with the degradation of some of the complex carbohydrates in solution.

Fermentation can also be used for the production of sequestering agents, including citric acid cycle intermediates and succinic acid; lactic acid, which could be a feed for acrylic acid synthesis; and high viscosity polymers. As with lignin sulfonates and saccharinic acids, the separation of the finished products from the complex wood process stream and the recycle of process salts may represent a process problem. However, it may be possible to develop a process for the coproduction of several different products so that separation and recovery is not necessary.

FEEDSTOCK SEPARATION

One possible solution to the cleanup of carbohydrates and lignin sulfonates for recovery operations is the use of an ultrafiltration process for the concentration of these materials. This type of a process could produce a sterile solution of carbohydrates, salts, saccharinic acids, and fatty acids for fermentation. This might provide the base feedstocks for chemical synthesis in a form where they are suitable for use. Investigation of this type of separation on a bench scale might be very profitable, since it represents a potentially attractive application for manufacturers of ultrafiltration equipment and for paper mill operators.

The wet oxidation of pulping process streams for the production of organic acids and 3 to 7 carbon alcohols is attractive. Without tests of the complicated alcohols produced from lignins during wet oxidation, it is difficult to determine whether they might make good coagents for available surfactants. If tests on these materials indicate that they might be good coagents for use in micellar flood operations, their recovery from pulp and paper waste streams should be investigated. As a technology, wet oxidation has the advantage that it is used and understood by pulp and paper mill staff. This would make the scale up and technology transfer easier and simpler.

7. Summary

Using advanced petroleum recovery techniques, it may be possible to produce half as much oil from existing U.S. wells as had been previously produced. Even limited use of advanced oil recovery methods could add measurably to U.S. domestic oil production and could decrease U.S. dependence upon foreign energy imports.

Micellar flooding, a promising technique for enhanced oil recovery, requires substantial amounts of chemicals which now account for an estimated $10.68 per barrel of incremental oil. The availability of better, cheaper chemical materials for this process could decrease the overall cost and increase its use. If the process is used on a large scale without development of new production techniques for the chemicals required, there could be substantial market dislocations in that the amounts of chemicals required for even an increase equivalent to 5% of U.S. oil consumption can be in excess of the national production of butanol, surfactants, high viscosity polymers, and sequestering agents. Synthesis of micellar flood chemicals from wastes materials could meet the requirements of low cost chemicals without large scale market dislocations.

With the exception of petroleum, wood is the largest single U.S. commodity: roughly one ton of wood per capita per year is processed to produce 500 to 700 lb of paper and paperboard products. This results in a roughly equivalent amount of dissolved organic material in process streams, since the yield from chemical pulping processes is roughly one-half of the dry weight wood processed. Because this rapidly growing industry—the production doubling time is 15 to 17 yr—is experienced in chemical recovery and has major unexplored landholdings, it is a good potential source for micellar flood chemicals.

There are several different types of pulping processes; each of these processes is designed to separate clean cellulose fiber from other wood constituents using chemical or mechanical means. Goundwood is the major purely mechanical pulping process. Chemigroundwood processes are hybrid chemical-mechanical methods which combine the features of the groundwood and chemical pulping processes. The groundwood processes have a high pulp yield and relatively low wastewater discharges. An analogous process is deinking pulp which involves the washing of pulp and paper for reuse.

Chemical pulping is the principal method for pulp production currently in use. The principal processes are sulfate pulping (kraft), soda pulping, and sulfite pulping. Although early plants were markedly different, modern soda and sulfate pulp mills are essentially identical. These plants account for the bulk of chemical pulp production. Both sulfate and soda pulping produce alcohols and acids from hydrolysed lignins. In acid sulfite pulping, calcium sulfite is used to produce the sulfite salts of lignin. The chemical pulping processes have similar process flow streams. All of these processes have an effluent stream which contains substantial amounts of dissolved lignins, lignin breakdown products, and carbohydrates. These liquors are generally concentrated and recycled for chemical recovery of the inorganics. The organic fraction is usually burned during an evaporation step to produce process heat. A considerable economic advantage to the pulp and paper industry might accrue if some of the carbohydrates and lignin derivatives were separated from the recycle stream and used to produce organic chemicals, including polymers, alcohols, surfactants, and sequestering agents. It could also provide waste treatment and chemicals for micellar flooding.

The development of processes which produce useful materials from pulp and paper wastewater streams is important in that these streams have a tremendous volume and contain a high concentration of materials, including lignins, which are highly colored. The streams also have a high concentration of soluble carbohydrates, which are fermented in receiving waters. Although major decreases in waste volumes and concentrations have been effected, pulp and paper industries still represent a vast source of dissolved organic materials: in 1977, this industry discharged one trillion gallons of water and 16 billion pounds of solids having a biological oxygen demand of 3.2 billion pounds. These materials can either represent a major renewable resource or a pollution problem whose treatment will add to the cost of finished paper.

The pulp and paper industry has practiced chemical recycle to decrease the cost of finished paper and the amount of waste discharged for almost a century. The largest chemical recycle processes are the internal recycle of inorganic salts for reuse in pulping. This is coupled with the use of waste organic compounds in the liquor as a fuel for directly-fired evaporation processes. This results in both the recycle of salts and the generation of process heat. Diversion of streams for chemical recovery using fermentation, purification, or synthesis methods with subsequent return to the wet combustion process may be feasible.

Some chemical recovery processes are being used in the pulp and paper industry. Nearly one billion pounds of lignin sulfonates are sold annually. Vanillin and other lignin derivatives are sold for flavoring and pharmaceutical uses. Tall, or pine, oils are recovered, refined, and sold in a variety of forms. Turpentines are also currently recovered for sale from a variety of different pulping processes. With the use of new recovery processes, a variety of different products could be made from these streams. For example, volatile acids, such as acetic acid, could be recovered from sulfite liquor streams. Wet oxidation processes for the production of volatile acids from wet hammermilled wood have been developed at a pilot scale, and can be scaled up for larger production. Sugars produced by wet oxidation and by ultrafiltration concentration from liquid wastes can serve as feedstocks for fermentation processes. Furfural can also be produced from wood wastes. Some of the recovered chemicals are of particular interest for use in micellar flooding. Lignin sulfonates may be suitable for use as sacrifical agents to decrease detergent requirements in micellar floods and also as feedstocks for the synthesis of alkylated lignin sulfonate detergents. Some of the sugar acids, such as saccharinic acid, found in pulping liquors can be used as sequestering agents in reservoirs where there are large amounts of multivalent cations in the flood brine. Tall oil acids and their derivatives can be used as surfactants in some reservoirs. The development of processes for the production of chemicals, including those chemicals used in micellar floods, from pulp and paper industry waste and low-valued process streams could provide economic benefit to the industry and to the nation.

Fermentation methods for the production of chemicals from pulping streams are also attractive means of chemical production. Fermentation methods were used for this purpose during the World Wars; however, the cost balance has currently shifted to favor the production of these chemicals, including alcohols, high-viscosity polymers, lactic acid, and sequestering agents from other sources or by chemical processes. The development of organisms producing these compounds from wood wastes coupled with the development of modern, continuous fermentation processes could swing the cost balance back to favoring synthesis of chemicals from wood wastes by fermentation. An added benefit is the potential use of these materials in low-pollution pulping processes, called organosolv, in which lignin is dissolved from wood using organic solvents but without the use of sulfur compounds.

Although the fermentation of wood pulp streams has been used in the past, there are some difficulties in adapting fermentation processes to pulp and paper streams. Three difficulties foreseen include the toxicity of phenolic lignin derivatives, high concentrations of inorganic salts in some streams, and difficulties with the fermentation of mixed, complex, or relatively unstudied carbohydrates. One particularly attractive solution to the cleanup of carbohydrates is the use of an ultrafiltration process for the separation and concentration of these materials. This type of process could also be used to separate a solution of carbohydrates, salts, saccharinic acids, and fatty acids for fermentation and return the stream of relatively concentrated lignins to the pulping process.

Although some difficulties in adapting classic or bench scale processes to full scale operation in a pulp or paper mill are anticipated, there is considerable potential in the development of methods for the production of micellar flood chemicals from mill waste streams. Even under the assumption that micellar flooding is an unsuccessful technique and that only a few of the proposed chemical recovery techniques are successful, the pulp and paper industry will have been steered in the direction of production of industrial chemicals from a renewable, continuously harvested resource. This innovative industry is, at present, the U.S. renewable resource manager, producer, and developer. Production of industrial chemicals from this domestic source, rather than by purchase from foreign sources, can only increase U.S independence from foreign oil producers.

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