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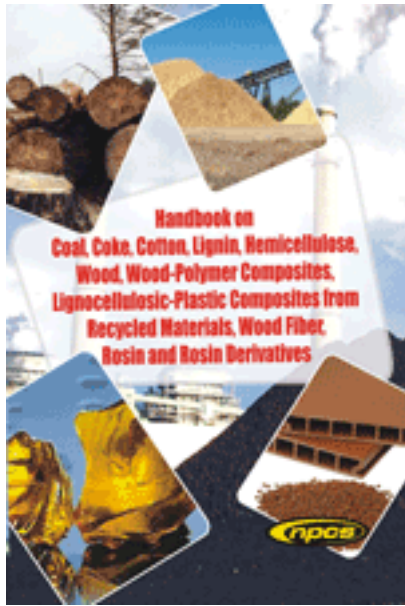
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Handbook on Coal, Coke, Cotton, Lignin,
Hemicellulose, Wood, Wood-Polymer Composites, Lignocellulosic-
Plastic Composites from Recycled Materials, Wood Fiber, Rosin and
Rosin Derivatives



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Handbook on Coal, Coke, Cotton, Lignin, Hemicellulose, Wood, Wood-Polymer Composites, Lignocellulosic-Plastic Composites from Recycled Materials, Wood Fiber, Rosin and Rosin Derivatives

(Also Known as Handbook on Coal, Lignin, Wood and Rosin Processing)

Coal is the product of plants, mainly trees that died tens or hundreds of millions of years ago. Coal is a fossil fuel and is the altered remains of prehistoric vegetation that originally accumulated in swamps and peat bogs. The energy we get from coal today comes from the energy that plants absorbed from the sun millions of years ago. Coal is used primarily as an energy source, either for heat or electricity. It was once heavily used to heat homes and power locomotives and factories. Bituminous coal is also used to produce coke for making steel and other industrial process heating. Lignin is a constituent of the cell walls of almost all dry land plant cell walls. It is the second most abundant natural polymer in the world, surpassed only by cellulose. Lignin is found in all vascular plants, mostly between the cells, but also within the cells, and in the cell walls.

Wood is an aggregate of cells essentially cellulose in composition, which are cemented together by a substance called lignin. The cells are made of three substances called cellulose (about 50 percent), lignin (which makes up a fifth to a quarter of hardwoods but a quarter to a third of softwoods), and hemicellulose. Rosin refers to an extraction process that utilizes a combination of heat and pressure to nearly instantaneously squeeze resinous sap from your initial starting material

In India's energy sector, coal accounts for the majority of primary commercial energy supply. With the economy poised to grow at the rate of 8-10% per annum, energy requirements will also rise at a reasonable level. The Indian coal industry aspires to reach the 1.5 billion tonne (BT) mark by FY 2020. In fore-coming years, the industry will naturally need to focus on building on the success, and be on track for reaching the FY 2020 goal. One of the primary goals of the Government of India is to ensure that it is able to meet the country's power generation needs. Another aim is to lower the country's reliance on coal imports by boosting the coal production quickly.

The Major contents of the book are Coal, Analysis of Coal and Coke, Cotton, Lignin and Hemicelluloses, Degradation of Wood, CCA-Treated Wood, Wood-Polymer Composites, Lignocellulosic-Plastic Composites from Recycled Materials, Chemical Modification of Wood Fiber, Delignification of Wood with Pernitric Acid, Rosin and Rosin Derivatives, Polymerizable Half Esters of Rosin and Photographs of Plant & Machinery with Supplier's Contact Details.

It will be a standard reference book for professionals, entrepreneurs, those studying and researching in this important area and others interested in the field of these industries.

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Sample Chapter:

Coal

Coal carbonization byproducts (coal tar and coke-oven gas) were the main sources for the production of organic chemicals till the Second World War. However, the abundant availability of cheap petroleum and natural gas caused a major shift from coal to these raw materials. After the Second World War, there was a consistent increase in the consumption of petrochemicals. In the last 10 years, with the continuing rise in oil prices, and scarcity and uncertainty regarding assured supplies of natural gas and petroleum oils, attention towards achieving self-sufficiency in chemicals and production of fuels has been focussed on exploring alternative feedstocks like coal and biomass. In this context, there is a need for reassessing the possibilities of obtaining organic chemicals from coal. It is anticipated that it will be cheaper to make liquid and gaseous fuels from coal than from oil before the end of this century.

The use of coal as a source of chemicals is at present confined mainly to high temperature carbonization (HTC) through the recovery of by products. Apart from the traditional coking route, concerted efforts are being made to obtain various chemicals by other coal conversion processes, such as direct hydrogenation or solvent extraction of coal followed by cracking, hydrotreating or hydrocracking of the products and by synthesis of hydrocarbons via synthesis gas produced by coal gasification.

Ethylene

Ethylene is an important basic building block of the petrochemical industry. The production and recovery of large quantities of olefins from petroleum refinery off-gases first started with the advent of catalytic cracking. Rapid growth in the demand for petrochemicals necessitated the setting up of plants to produce ethylene and other olefin monomers by thermal cracking of a wide range of petroleum feedstocks.

The routes considered for the production of ethylene from coal include: (i) Fischer-Tropsch synthesis, (ii) direct conversion of synthesis gas, (iii) conversion of coal-derived methanol, (iv) homologation of methanol to ethanol followed by dehydration, (v) cracking of dimethyl ether which again is derived from synthesis gas or methanol, and (vi) cracking of synthetic liquids produced in direct liquefaction processes.

Fischer – Tropsch Synthesis for Olefins

Fischer – Tropsch (FT) synthesis for the production of fuels from coal has been in operation on a commercial scale since 1955 in Sasolburg, South Africa. It is known that through proper choice of reactor, catalyst and operating conditions, the product pattern can be changed in FT synthesis. The dilute fluid bed or Kellogg type of reactor (Synthol) shifts the product spectrum to lower hydrocarbons. It gives an ethylene yield of 4.4% and also C₃ and C₄ olefins. Ethane produced in the process can also be converted to ethylene. The cost of ethylene from the recovery process is about 30 cents/lb compared to 18-19 cents/lb from the conventional gas oil cracking. In the steam cracking of FT product, the cost of ethylene is estimated at 30 - 50cents/lb. In the Sasol 2 plant in South Africa, the annual production of 1.5 million tonnes of automotive fuels, 1,60,000 tonnes of ethylene and 50,000 tonnes of chemicals, 1,00,000 tonnes of ammonia, 90,000 tonnes of sulphur and 2,00,000 tonnes of tar products, including tar acids, is envisaged.

Direct Conversion of Synthesis Gas to Ethylene

Direct conversion of synthesis gas from coal to ethylene and ethanol is now attracting attention. Efforts to get ethylene by passing synthesis gas (CO: H₂ ratio, 74:24:8) in a copper tube at 550°C resulted in 5.6% ethylene in the product gas, whereas when synthesis gas containing 0.6% ethylene was passed over a CuO (3%) – Al₂O₃ catalyst at 250°C and 20 – 40 atm pressure, the ethylene content increased to 7.6%. On the other hand, Peters used a four-component catalyst system to convert synthesis gas (46.4% CO, 42.5% H₂ and 11.1% inert) to ethylene. Several iron and cobalt-based FT catalysts have been evaluated for the conversion of synthesis gas to C₂ – C₄ olefins. As the copper and the alkali contents were increased in iron-copper-kieselguhr-K₂O catalysts, the product distribution shifted towards lower molecular weight hydrocarbons.

The activity and selectivity of Ni- or Co-based bimetallic catalysts containing several other metals as promoters have been evaluated. The bimetallic catalysts give a somewhat different product distribution compared to Ni or Co catalysts. The addition of Re to Ni favours the formation of ethane (22% at 185°C), that of Ru favours the long chain hydrocarbons, while addition of Ir favours the formation of dimethyl ether at 210°C (40% at 190°C). Co - Mn gives products containing a higher proportion of olefins which is higher at lower temperatures and lower H₂ - CO ratios.

The favourable olefin selectivity obtained on the addition of basic promoters to the conventional iron catalysts suggests that metal interactions with basic or electron-donor sites in zeolites may have an important influence on selectivity. A marked increase in the olefin selectivity of ruthenium is observed as sodium ions in the zeolite are replaced by potassium or caesium ions.

The work done at Pittsburgh Energy Research Center indicated that a fused iron catalyst is particularly effective in giving high yields of olefins. Experiments were conducted in a microreactor with temperature range 250 - 350°C, pressure range 20 - 68 atm, synthesis gas having composition of 1:1, 2:1 and 3:1 of H₂:CO and also mixtures containing CO₂ and hourly space velocities of 500-5000.

Ethanol from Synthesis Gas

Synthesis gas has been converted to ethanol at 250-290°C, 50 atm and a space velocity of 1000-4000 hr⁻¹ in a bench scale unit using a special rhodium cluster catalyst. The conversion of CO was 10% and the reaction product contained 75-80% ethanol. The activity of the catalyst during one month period of operation (8 hr-a-day) remained almost constant. Work done at the Union Carbide Corporation showed that addition of Fe to Rh increased the yield of ethanol at 68 atm. On the other hand, large proportions of ethane and dimethyl ether were obtained with alumina-supported platinum.

Olefins from Methanol

Conversion of coal-based methanol to ethylene and propylene offers an attractive route to the use of coal as a basic raw material. The formation of C₂ - C₅ olefins (1.6 mole%) was noticed by Mattox during methanol dehydration over NaX zeolites. Similar results have been reported by several investigators using various catalysts. The product distribution suggests that an α-elimination process (H-CH₂-OH → H₂O + CH₂) is occurring in the methanol adsorbed on the zeolite surface. The carbene methylene species so formed can polymerize to form simple low molecular weight olefins.

Methanol cannot dehydrate to form an olefin unless recombination of one-carbon fragments takes place.

Aromatics are produced by dimerization and cyclization of C₃, C₄ and C₅ olefins.

Laboratory scale experiments were conducted using tungstic acid impregnated on zeolites, MgO or Al₂O₃. Zeolites exchanged with rare earths gave higher yields ranging from 16 to 30% ethylene and 29 to 30% propylene with methanol conversion of 80 - 90%. Dimethyl ether formed in the process can also be converted to olefins using the same catalyst. The reaction mechanism involves three consecutive surface reactions. Adsorbed methanol is dehydrogenated to formaldehyde followed by dimerization of formaldehyde and dehydration of the dimer to give adsorbed ethylene.

The possibilities of producing ethylene and propylene from coal-based methanol on a laboratory scale have been explored by BASF. In 1979, BASF constructed a pilot plant with 15 tonnes per month capacity at a cost of \$ 1.5-1.6 million at Ludwigshafen, West Germany to produce olefins from methanol. In this process, 3-4 lb of methanol is catalytically converted (catalyst, ZSM-5 zeolite) to give 1 lb of olefins. Methanol is first converted to dimethyl ether, which, in turn, gives ethylene by dehydration. Propylene and C₄ olefins are also produced in varying amounts, depending on the reaction conditions.

Methanol Homologation

The best potential approach to the production of ethylene from synthesis gas appears to be through its reaction with methanol to form ethanol and subsequent dehydration of ethanol to ethylene. Wender showed that methanol reacts with synthesis gas in the presence of dicobalt octacarbonyl [Co₂(CO)₈] catalyst to

give ethanol, but higher alcohols, including ethanol, are relatively unreactive in this system. The reaction was carried out in batch autoclaves at 183 – 185°C and 275 atm at 75% conversion to give about 40% of ethanol in the product. About 4% propanol was formed together with 0.3% butanols.

The methanol homologation reaction as catalysed by $\text{Co}_2(\text{CO})_8$ is a very complex one, highly dependent on a variety of reaction parameters and variables. The initial carbonylation product, acetaldehyde, is obtained in high selectivity by proper ligand modification. A selectivity of 62.3% was obtained at 200°C and 270 atm for 3 hr process time using a cobalt-iodine catalyst. High iodine/cobalt ratios lead to undesirable reaction by products and catalyst deactivation. The active form of Co in the iodine – promoted system is $\text{Co}(\text{CO})_4^-$, as indicated by high pressure IR spectroscopy.

Methanol to Acetic Acid

Liquid phase carbonylation of methanol has become an important industrial process which uses iodide or carbonyl of cobalt as a catalyst and an organic or inorganic iodide, such as methyl iodide, hydrogen iodide or potassium iodide, as promoter.

Nickel carbonyl and some other nickel compounds are also effective at low pressures of about 50 atm in the presence of iodide in the liquid reaction media of some organic amines or phosphines.

In the process developed by Monsanto, a new iodide-promoted rhodium catalyst which exhibits high activity for methanol carbonylation even at atmospheric pressure is used. The yield of acetic acid is 99% based on methanol and 90% based on carbon monoxide. A plant with a current annual capacity of 143 million kilograms is now operating. About 40% of the world's capacity for acetic acid is based on Monsanto process.

Ethylene Glycol

The most promising route to ethylene glycol involves direct conversion of synthesis gas using rhodium catalyst.

High yields of ethylene glycol were reported. The reaction takes place at about 2000°C and 1400 - 3000 atm over a rhodium carbonyl catalyst, but comparatively lower pressures of the order of 400 atm may be sufficient to achieve a reasonable degree of conversion. Such a low pressure process using a more specific catalyst promises to be a commercial success. In the work carried out by Union Carbide, a solvent having a high dielectric constant to ensure ion separation and/or complex the cations to prevent pairing with an anionic centers has been used.

Vinyl Acetate

Halcon International has nearly completed the development of a methanol carbonylation route to vinyl acetate. In this process, methanol is reacted with recycled acetic acid to make methyl acetate; the methyl acetate is reacted with synthesis gas to produce ethylidene diacetate, which is subjected to cracking to produce vinyl acetate and acetic acid for recycle.

Other Chemicals

Monsanto reported a method for the alkylation of toluene with methanol over modified zeolite catalyst to produce a mixture of ethylbenzene and styrene. At present, the product concentrations are very low (5 mol% of styrene and ethylbenzene) and frequent catalyst regeneration is necessary. Both BASF and Rohm and Haas have been investigating the base catalysed addition of formaldehyde (as acetal) to methyl propionate to form methyl methacrylate.

Coal Pyrolysis Processes

Coal tar is an inevitable byproduct in the production of metallurgical coke. Important chemicals, such as benzene, toluene and xylenes (BTX), can be produced from the benzole recovered from coke oven gas as well as from the light oil obtained by the distillation of coal tar. The other main constituents of high temperature coal tar are naphthalene (10%), anthracene (1.8%), phenanthrene (5.0%), fluorine (2.0%), fluoranthene (3.3%), phenol (0.4%) and pyridine (0.02%). Bulk products, such as creosotes and pitches,

are also produced from coal tar.

With the exception of limited quantities produced in USA through dealkylation of aromatic petroleum fractions, naphthalene is almost exclusively obtained from coal tar. Methyl naphthalene and dimethyl naphthalenes are present in the heavier coal tar fractions (250 – 3500C). The dealkylation of these methyl naphthalenes can yield further quantities of naphthalene. -

The Coalite and Chemicals Products Ltd, UK, are processing the tar from LTC into valuable chemicals (pure phenols, chlorinated phenols) and chemical intermediates for plasticizers, pharmaceuticals and adhesives. A phenol-free middle oil fraction was processed into diesel oil till 1965.

The pyrolysis of tars or vapours from LTC of coal is considered as a possible route for producing olefins. Laboratory scale investigations were conducted on cracking of vapour and tars obtained by LTC of Texas and North Dakota lignites. When Texas lignite was carbonized at 5500C and the tar vapours were cracked at 8000C, the yields of ethylene, propylene and benzene were 40, 7.6 and 6 lb respectively per tonne of lignite. However, the process was not considered economically viable. LTC of cannel coals from West Virginia in the presence of superheated steam followed by cracking of the vapours at 800 – 9000C gave 191-245 lb of ethylene, 20-41 lb of propylene and 21-47 lb of benzene per tonne of coal (MAF).

Acetylene

Acetylene is an important chemical intermediate for the production of acetaldehyde, vinyl acetate, vinyl chloride, acrylonitrile, etc. It is generally obtained by high temperature pyrolysis of natural gas or naphtha fractions in addition to the conventional calcium carbide route. A process to make acetylene by pyrolysing coal in an electric arc has been developed by Avco Everett Research Laboratory, Everett, Mass. In this process, pulverized coal is injected into a stabilized arc, the pyrolysis products are quenched and acetylene is separated from the product. Pyrolysis is conducted in hydrogen atmosphere, which increases the yield of acetylene. The process has been tested in a unit that operates at 75-100 kW producing 0.15-0.20 lb/min of acetylene. A pilot plant to process 10 tonnes/day of coal that would yield 3-3.35 tonnes/day of acetylene has been proposed.

Production of Chemicals by Coal Liquefaction Processes

Several investigations have been made to study the possibilities of producing chemicals from coal liquefaction products. Dow Chemical Company studied the feasibility of producing chemical feedstocks from coal-derived liquids from COED, Synthoil, H-Coal and Solvent Refined Coal (SRC) processes. In the Exxon Donor Solvent (EDS) process, which provides a technically feasible route to the production of liquid products from various types of coal, the byproducts form a potential source of petrochemical feedstock. The major source of ethylene and propylene is derived by cracking the light gas product blend containing ethane, propane and mixed butanes.

Analysis of Coal and Coke

Coal is a readily combustible rock containing more than 50% by weight and more than 70% by volume of carbonaceous material, formed from compaction or induration of variously altered plant remains similar to those of peaty deposits. Differences in the kinds of plant materials (type), in degree of metamorphosis (rank), and range in impurity (grade) are characteristic of the varieties of coal. In lump form, coal appears to be black or brownish black. The luster, fracture, and texture vary according to type, rank, and grade. Chemically, coal consists mainly of carbon, hydrogen, and oxygen, with minor amounts of nitrogen, sulfur, silica, alumina, iron, and trace amounts of fifty-three other elements. The composition varies to such an extent that Hendricks states that no two coals are absolutely the same. Some of the elements are inherent in the original plants; others have been incorporated during the coalification process; and others have been picked up as extraneous matter in mining, preparation, and transportation.

That types, ranks, and grades of coal are dependent on the characteristics of the original plants and the chemical, biological, and physical processes involved in metamorphosis. Variations in the combination of

processes and the materials processed produce end products varying in chemical and physical properties. Analytical techniques that will consistently show numerical differences between these products provide data with which the types, ranks, and grades can be determined.

Each of the principal coal producing countries in the world has a series of procedures or national standards. The Technical Committee 27 on Solid Mineral Fuels of the International Standards Organisation (ISO) consists of representatives of Australia, Austria, Belgium, Canada, Denmark, Spain, France, Germany, India, Italy, Netherlands, Poland, Romania, Switzerland, Czechoslovakia, Turkey, United Arab Republic, United Kingdom, United States, Soviet Union, and Yugoslavia collaborating on the international standardization for coal and coke.

Even though the coke was produced and used by metallurgical plants, the specifications were maintained by chemical and physical tests. Uniformity is very essential in the various Processes.

Methods of Analysis

In this section, the methods for coal are discussed in detail. Testing methods for coke are the same as for coal except the procedures for stability, porosity, and density. More detailed information on the testing methods can be found in the publications of the U.S. Bureau of Mines, British Standards Institution, and the American Society for Testing and Materials.

Sampling

Preliminary to any chemical or physical testing of coal in the laboratory it is essential that a representative sample be provided. The most carefully conducted analysis is meaningless unless the sample be truly representative of the lot. This means that increments are specified in number, weight, frequency, and method of extraction. The properly collected gross sample must be reduced in particle size and mass to laboratory size by a method that retains the representativeness without gain or loss of such fleeting substances as moisture.

Determination of Constitution and Physical Properties

Knowledge of the constitution and physical properties of coal is of great value in combustion, carbonization, gasification, and in the utilization of coal in making nonsolid fuels and in chemical syntheses. A number of techniques have been developed and other are in development status to provide this vital information.

Functional Group Analysis

Essentially all of the functional groups recognized as being present in coal are associated with oxygen. Both the nitrogen and organic sulfur are considered to be present primarily as parts of heterocyclic systems since there is no satisfactory evidence for any functional groups containing either element.

Carboxyl groups, both free and as salts, are present in lignites and brown coals and may represent as much as 14wt % of the dry lignite. Determination of free carboxyl group generally has been carried out by ion exchange between coal and barium or calcium acetate, followed by titration of the liberated acetic acid. Methoxyl groups also are present only in low-rank coals. Zeisel determination of methoxyl contents of lignites and brown coals indicates a maximum of 2% for lowest-rank coals. The number of carbonyl groups also decreases with increasing rank, although no satisfactory procedures have been developed for quantitative determination of this functional group in coal. Some oxygen is also present in heterocyclic rings. Acetylation. Several different acetylation procedures have been used on coal. The one which is most widely used utilizes acetic anhydride in pyridine

Procedure

Add a weighed sample (500-800mg) of dried coal to 10 ml of a 1:2 mixture of acetic anhydride and pyridine in a 200-ml flask. Reflux the mixture for 24 hr, cool, and dilute with 100 ml of water. Filter the mixture and wash the residue until free of acid. Boil the acetylated coal for 5hr in a 150-ml flask with 2 g of barium hydroxide in 40 ml of water and keep on a steamplate overnight. Add 2 ml of 85% phosphoric acid, and distill 24 ml into a titration flask. Titrate the acetic acid in the distillate with sodium hydroxide. Add

increments of water to the residue and distill into the titration flask until no more acid is observed upon titration.

Trimethylsilylation. A second method for determining the hydroxyl content of coal involves treatment of the coal with hexamethyldisilazane, and trimethylchlorosilane in pyridine. This results in the conversion of the hydroxyl groups to trimethylsilyl ethers. Silicon analysis of the resultant coal ethers affords a quantitative value from which the hydroxyl content can be calculated. Alternatively, the trimethylsilyl ether content can be estimated from the extinction coefficient of the trimethylsilyl group measured at $8.0\mu\text{m}$.

Spectroscopy

Various spectral techniques are now applied to the study of coal. The methods discussed here include infrared, ultraviolet and visible absorption, mass, nuclear magnetic resonance, and electron paramagnetic resonance spectroscopy. A good general reference is that of Silverstein and Bassler. Although considerable coal research work is done by spectral methods there are as yet not many analytical applications of spectroscopy in the coal industry.

Infrared Spectroscopy. Infrared spectroscopy is the most universally applicable spectral method. With the exception of monatomic gases, all substances have infrared spectra. Historically, infrared has been applied principally to organic materials, but it is being used increasingly on inorganic substances. Of all spectral methods infrared has most earned the right to the title of "fingerprint method".

Ultraviolet and Visible Absorption Spectroscopy. The principal use of ultraviolet and visible spectroscopy is the study of aromatic compounds particularly polynuclear condensed aromatic compounds. Because of the prolific and characteristic spectral fine structure that results from the electronic excitation of polynuclear condensed aromatics, ultraviolet and visible spectroscopy is the best spectral method for establishing identification of these compounds. Similar aromatic compounds have radically different characteristic spectra---- for example, anthracene and phenanthrene, chrysene and benz-phenanthrene, pyrene and fluoranthene. Also the derivatives of the parent compounds display.

Mass Spectroscopy. Since the first mass spectral studies of coal a considerable amount of work has been done, principally at the Pittsburgh Energy Research Center of the U.S. Bureau of Mines. Mass spectra of pyridine extracts of bituminous coal have shown the presence of thirteen types of aromatic compounds having molecular weights from 78 to 400.

Research investigations of various oils and pitches from coal tar have been carried out. Many aromatic hydrocarbon types were identified along with several nitrogen and a few oxygen compounds. Also, average molecular weights, aromaticities, and mean size of aromatic nuclei of these samples were calculated from the mass spectra of oils and pitches.

Nuclear Magnetic and Electron Paramagnetic Resonance Spectroscopy. The application of NMR or EPR in the coal utilization industries is limited. One development appears to be approaching the application stage; the analysis of water in coal is being carried out on moving conveyor belts. Belt speeds are low and throughput is small as yet but the method has promise.

Free radicals exist in coals in relatively large amounts and are easily detected by EPR. Unfortunately, no fine structure has been detected in coal spectra it is therefore difficult to characterize structures. However, considerable characterizing information is obtainable from free radical concentrations, line widths, and spectral g-values.

Petrographic Analysis

Coal petrography deals with descriptions of different physical parts of coals that can be distinguished best by microscopic observation. These small parts of coals look different because they are of different size and shape and they modify in different ways the light that they reflect or transmit to the eyes. Coal petrography relates these different parts to the plants or plant parts from which they were derived and deduces something about the changes that have occurred from plant to coal.

Another physical component of coals that may be observed microscopically is inorganic mineral matter. These mineral constituents may have been present in the original plants, may have deposited as the peat beds formed, or crystallized from waters percolating through the coal bed. The principal ones are quartz, kaolinite, calcite, and pyrite. Traces of many mineral elements are present.

Some attempts have been made to separate or concentrate different coal components on a commercial basis to take advantage of properties favorable to various uses. These usually depend upon differences in resistance to breakage or differences in density.

Thin-Section Analysis. Petrographic thin-section analysis is usually made on specimens obtained from column samples cut out of a coal bed from top to bottom. The specimens are small blocks measuring approximately 1×0.8×0.5 in. The 0.8-in. dimension is in the vertical direction of the column or bed, so that the total of the 1×0.8-in./faces represents a ribbon area over the entire height of the bed, excluding the material lost in cutting between the blocks.

Microscope analysis of thin coal sections is conducted with a biological microscope equipped with binocular eyepieces. A pair of 15× eyepieces is used with 16 and 32 mm objectives to attain magnifications of 60× and 150×. Anthraxylon is measured at 150× and opaque attritus, fusain, and mineral at 60×. Translucent attritus is determined by difference. Measurements are made by means of a Whipple micrometer disc inserted in one of the eyepieces. This is a glass disc on which is centered a 7 mm square field divided into one hundred 0.7 mm squares with the central one subdivided into twenty-five 0.14 mm squares. The effective sizes of these squares under different magnification conditions are determined by comparison with a stage micrometer.

A detailed study of the errors involved in this type of thin-section analysis showed that the percentages of components in a column sample of a coal bed as determined by this technique usually should not be in error by more than 2%.

Figure 1 illustrates the results of thin-section analysis on a complete vertical column of a coal bed. **Polished surface analysis.** Petrographic polished surface analysis is usually made on briquets of granular coal molded with a binder. The granular sample, usually of -20 mesh size, is representative of much larger lots of broken coal.

A variety of grinding and polishing steps may be used. A detailed grinding plan would include the use of 240, 400, and 600 grit papers in succession. Similarly, a careful polishing procedure might involve successive use of 3 mm alumina on chemotextile cloth, 1 mm on chemotextile, and 0.05 mm on two or three layers of cloth, the top being silk or cotton. Some of these steps may be omitted, depending on experience or the desired quality of the polish. After polishing most coal briquets should be dried in a desiccator for a period of about 15 hr. More details or variations in specimen preparation procedures can be found in References 54 and 55.

Reflectance Measurement. This measurement is important in petrographic analysis and permits the determination of optical constants. Various assemblages of equipment have been used for this purpose. A brief description of one of these will serve to illustrate the general principles of the measurement.

It has been found that, for accurate reflectance measurements, the polished specimen surface must be precisely perpendicular to the optic axis of the microscope. A commonly used hand-leveling press cannot be relied on to attain this positioning. A reliable method involves observation of focus preservation with an objective of at least a 60× magnification as the specimen surface is traversed over about 1 in. in two perpendicular directions. Mounting the specimen on a device capable of controlled tilt in two directions permits adjustment of the surface plane until the specimen remains in focus through all possible displacements.

In this method, absolute reflectance is obtained by reference to a standard of known refractive index and negligible absorption. The reference to a standard should be in the range of those of coal components.

Some investigators have used a series of glasses of different reflectances in this range, although some surface changes by oxidation have been encountered. Synthetic ruby and particularly sapphire have proven satisfactory. The standard should be cut in a form so that reflectance from the back face is not allowed to interfere with the measurement. Measurements on several minerals of known refractive index, in different media, provide an excellent means of checking the accuracy of the method. If the indices calculated from the reflectance measurements agree within an acceptable limit with the indices provided by other means, the operation of the equipment is satisfactory.

Determination of Vol % of Macerals. Macerals commonly determined are vitrinite, exinite, resinite, micrinite, semifusinite, and fusinite. The equipment used is essentially that described for reflectance measurement with the addition of devices for scanning the specimen and for selection of areas to be identified and summed. The additional devices are a Whipple ocular disc or a crosshair disc, a mechanical stage, and a counter. The stage maybe operated manually or electrically. In the latter case it maybe coupled to an electrically actuated counter. The mechanical stage stage should be of such type that the specimen can be advanced quickly by definite fixed increments in two perpendicular directions. If an electrically operted stage is used, increment steps in one direction across the specimen may be actuated by the counter switches. The counter should be capable of totalizing counts in at least six channels.

The specimens for automatic scanning microscopy are prepared in a way very similar to those previously described for visual studies in reflected light. However, because there is no element of human judgment involved, the surfaces should be more carefully polished to attain the least possible relief, pits, and scratches. This objective may require modifications to the grinding and polishing steps, depending, for one factor, on the relative importance of the results for the softer organic components or the harder mineral, especially pyrite.

Determination of Optical Constants

Optical constants are of interest because they are the basis of the optical descriptions of the petrographic components and because they are related to structural atomic arrangements in coals.

One of the simplest methods of determining these optical constants involves only the microscopic measurement of reflectance in two different media. The measurements are made using objectives corrected for air, oil or water immersion, preferably the first two.

The simple equation for transmission is the equation given above for defining k . However, in practical measurements on thin sections of coals and carbons, corrections must be made for reflections at interfaces between the various media. The thin section usually is supported on a transparent substrate and the radiation enters the system on the substrate side. Reference light (I_0) is usually measured after transmission through the substrate. An equation governing transmission through a system consisting of an absorbing medium on a transparent substrate has been given by Born and Wolf.

Electron Microscopy

The principal procedure involved in the study of coal with an electron microscope is the preparation of suitable specimens. At first, powdered coal mounts were observed, but these supplied little useful information. Replicas of polished or etched coal surfaces were later tried with some interesting results, but these have been little used recently. The most productive type of specimen for electron microscopy is the ultrathin section, prepared as described previously. Preparation of electron micrographs and electron diffraction patterns of coal specimens involves no differences in procedure from those commonly used.

Density

The true density of a somewhat porous material such as coal cannot be determined in a simple way. Any satisfactory medium for displacement should consist of molecules small enough to penetrate the pores but should not react chemically with the coal. It has been found that helium most satisfactorily meets these requirements. An approximation for the density can be derived by measuring the displacement of water by

the coal, usually in granular form. However, it is questionable whether the water molecules can penetrate into the minute pores of the coal sufficiently to result in the determination of true density.

A blank run without a sample in a sample frame will give the scattering due to air and background. Air scattering is appreciable only at low angles. A few scans of the blank run are sufficient. The readings to be subtracted must be normalized to the number of scans used in obtaining the intensity with sample in place. An idea about the instrumental broadening can be obtained by preparing a sample of 2.5mm diamond powder and obtaining the scattered intensity for the diamond powder under the same conditions. The widths of the diamond lines are largely due to instrumental factors. If they are excessive, the observed intensities with the coal sample can be corrected by unfolding them with those of diamond.

Consider an x-ray beam traversing a distance in the sample before reaching a differential element of volume dV in the interior of the sample and further consider the scattered beam traversing a distance y in the sample before leaving it. The incident beam will undergo a reduction in intensity by a factor $\exp(-mx)$. Where m is the linear absorption coefficient, and the scattered intensity will be reduced by a factor $\exp(-my)$. The overall loss of intensity due to absorption depends upon the scattering angle as well as the sample diffractometer geometry, thus corrections must be made. Further, the scattered intensity is polarized to a different degree at each scattering angle, and correction must be made for polarization. Finally, the observed intensities are in arbitrary units, they must be converted or normalized into Thomson or atomic units.

This form of the Warren-Bodenstein equation also can be modified to consider an assembly of stacks each containing different layers.

X-Ray Fluorescence Analysis. X-ray fluorescence analysis of elements of relatively high atomic number is well developed. Presently the method is practical for element down to, perhaps, fluorine, of atomic number 9. It has not yet been shown to be reliable for oxygen, nitrogen, and carbon, although research in to these applications is progressing well. Therefore, fluorescence analysis may now be used for virtually all the mineral elements in coal, but cannot yet determine the composition of the organic components.

The sample required for fluorescence analysis is about 2g. It must be ground to an extremely fine particle size approximately 2 mm or less, in order to minimize and to render less variable the absorption of the fluorescence x rays by the mineral matter in the coal sample. This extreme pulverization can be accomplished in a tungsten carbide pestle by vibration for 5 min on a device similar to a Crescent Wig-L-Bug, available from the Crescent Dental Manufacturing Co. Chicago. The sample is then pressed into a frame with typical dimensions of 4cm. x 2.5 cm x 2.5 mm, under an applied pressure of about 150Kg/cm². For the analysis, a standard sample containing proportions of each of the elements to be analyzed similar to those to be expected in the unknown samples is necessary. For coal analysis, this could be a typical coal sample or a synthetic mixture of the various coal mineral elements in carbon black. This sample is kept in one of the spectrometer chambers. Reading on the standard sample are taken at regular intervals so that those on unknown samples may be normalized to minimize errors due to variations in conditions.

Specification Tests

The American National Standards Institute, Inc. (ANSI) represents the United States at the international standards level and corresponds in part to the British Standards Institute (BSI) in the United Kingdom. The ANSI is unlike the BSI in that it does not develop standards but recognizes the work of some independent organization. For coal, the American Society for Testing and Materials has been recognized as the developing body. The committee for coal consists of approximately seventy five experts equally divided in interest as producers, consumers and general interest

The tests constituting coal analysis have been divided into three groups – Proximate, ultimate, and miscellaneous analysis. Some of the tests are empirical and strict adherence to the specified conditions is required in order to obtain meaningful results.

Proximate Analysis

Proximate analysis is the quantitative separation of the components of a mixture. In the proximate analysis of coal, the amounts of moisture, volatile matter, and ash are determined. The sum of the percentages of these components is subtracted from 100 to calculate the amount of fixed carbon present.

Moisture. The determination of the moisture content of coal is probably the most important test. It is also one of the most difficult components to determine accurately because of its several forms, its fleeting nature during the collection and preparation of the gross sample, and its strong affinity for the coal during the last stages of drying.

Usually, three moisture values are required in the analysis of coal. First, if the coal is too wet to crush and sieve without losing moisture, it must be air-dried, which results in the value of *air-dry moisture*. The air-dried coal is then crushed and prepared for the laboratory where the *residual moisture* is determined. This laboratory sample is used to prepare the analysis sample which is used for most of the tests. The knowledge of the *total moisture* content of this sample is necessary in order to express all items on a dry basis. The total moisture is calculated from the air-dry and residual moisture values and is used to convert the various dry analyses to the as-received basis.

Residual Moisture. Two methods are given; the first is used for coals known to be resistant to oxidation and the second is applicable to coals subject to oxidation or to coals of unknown origin.

Procedures

oxidation-resistant coals. Transfer one of the air dried sample to a shallow, weighed, noncorrodible metal pan to a depth of about 10 mm, weigh, and heat in a forced air circulation oven at 105-110°C to constant weight. Calculate the % of residual moisture from the loss on heating and weight of the air-dried sample.

other coals. Mix the air-dried sample well and place approximately 10 g into a weighed capsule made of glass or noncorrodible metal with close-fitting covers with a diameter of 60mm, cover, and weight to the nearest mg. Place the cover in desiccator containing magnesium perchlorate desiccant, and the capsule in an oven with a minimum free space, capable of maintaining a temperature of 105-1100C and having facilities for introducing nitrogen at a flow rate of three oven changes per minute. Use a nitrogen containing less than 10 ppm of oxygen. Heat the sample in the oven to constant weight; approximately 2 hr are required. Remove the capsule, cover and put on a metal plate for 10min. Transfer to desiccator until cooled to room temperature, then weigh. Calculate the % residual moisture from the loss in weight and weight of the air-dried sample.

Total Moisture. The % total moisture is calculated from the percentage of air-dry and residual moistures, as follows:

$$\% \text{ total moisture} = \% \text{ air-dry} + \% \text{ residual}$$

Moisture of Analysis Sample. This moisture value is used to calculate other analyses made to a dry basis, using the analysis sample of 250mm size coal.

Volatile Matter. Volatile matter refers to loss of weight, corrected for moisture, that results when coal is heated in specified equipment and under standard conditions. It is one of the more important items in purchase specifications of coal; it is valuable for the fuel engineer in setting up and maintaining burning rates, and is used with other parameters in almost all coal classification systems.

The test given below is empirical and easily performed. However, it can lead to erroneous results if all the vital factors are not observed strictly. If carried out properly, duplicate tests by the same operator and equipment should agree within 0.3% for anthracite, 0.5% for semianthracite and bituminous coals, 0.7% for subbituminous coals, and 1.0% for lignite. For the test, special high-form crucibles made of platinum, 31 mm high, with a 25.4 mm diameter at the top and 16 mm diameter at the bottom, are used. The crucibles are equipped with platinum covers, 10 mm high, with a 25.5 mm diameter at the top and 25.3 mm diameter at the bottom. The total weight of the crucible and capsule is between 14 and 15g. The heating of the

sample is to be performed in an electrically heated vertical tube or muffle furnace. The tube furnace heating zone should be approximately 38 mm ID by 100 mm long. The crucible is suspended in the heating zone by a platinum or nichrome wire cradle. The size of the muffle furnace should be large enough to insert and remove the crucible conveniently. It is essential that the heating zone of the furnace be maintained as close as possible to 9500 C , but must not vary more than 200C.

Ash. Coal ash is the residue remaining after the combustion of coal under specified conditions. Ash should not be confused with mineral matter. The ash can be more than, equal to, or less than the take place during combustion.

The quantity of ash in coal is of prime importance in purchase specifications, utilization, and classification. Ash represents an impurity, adds to the cost of transportation of the coal, and is costly to dispose to after utilization. In certain methods of utilization, ash contributes to air pollution as well as corrosion of the burning equipment.

Fixed Carbon. The fixed carbon is calculated by subtracting the sum of moisture, volatile matter, and ash from 100. It consists mainly of carbon but, also contains small amounts of hydrogen, sulfur, nitrogen, and oxygen.

Ultimate Analysis

The ultimate analysis of coal expresses the elemental composition in terms of the determined percentages of carbon, hydrogen, nitrogen, sulfur, and the calculated value for oxygen. The five items are generally calculated on moisture and ash free basis. A slight more accurate value for oxygen is obtained if the analysis computed on a moisture and mineral-matter-free basis.

Carbon and Hydrogen. These two elements contribute virtually all the energy derived from coal. The carbon and hydrogen contents of coal are utilized in certain classification systems and also permit an estimate of the calorific values of coals.

All methods employ the same basic principle of burning the sample in oxygen in a closed system and collecting and determining quantitatively the combustion products. The standard U.S. method carries out the combustion at 800-850oC. A high temperature (1350oC) combustion method has been used successfully in a number of European laboratories.

The oxygen to the combustion tube flows through the other area of the T connection by passing the above described pressure-safety device, and passes through a U-tube. The first arm contains soda-lime, the bottom contains a glass-wool plug , and the second arm is filled with magnesium perchlorate. A one-hole rubber stopper is used to seal the open end of the combustion tube. Metal or glass tubing is used to connect this U-tube with the tee and the combustion tube. The joints are sealed with flexible tubing. Repeat this procedure using an accurately weighed sample of standard sucrose or benzoic acid. Several tests may have to be made before the determined values for hydrogen and carbon are in satisfactory agreement with the theoretical values. Repeat the procedure with an accurately weighed sample of coal. Duplicate determinations by the same operator using the same equipment and the same analysis sample should not differ more than 0.07% for hydrogen and 0.30% for carbon.

Nitrogen. Nitrogen occurs almost exclusively in the organic matter of coal. The amount is rather constant and in most bituminous coals it varies from 1.0 to 1.5 % in anthracite and low-rank coals.

The kjeldahl method is most commonly used, and consists of destructive digestion of the coal with a mixture of concentrated sulfuric acid, potassium sulfate, and mercury catalyst. The nitrogen is distilled from alkaline solution as ammonia into a standard acid solution and quantitatively determined titrimetrically.

Total Sulfur. Sulfur occurs in coal as the sulfide of iron and in combination with the organic matter. In some weathered coals small amounts of sulfate sulfur may also be found. Two chemical methods are used for the determination of total sulfur. In the method given , the coal is oxidized in an Eschka mixture. The resulting oxides of sulfur are retained by an alkaline mixture, extracted with water, precipitated high-temperature

combustion in a closed system with oxygen, the sulfur oxides are absorbed in aqueous hydrogen peroxide, and the sulfuric acid formed is treated with a standard alkali. It is particularly applicable where results are required in a very short time.

Oxygen. The oxygen content of coal can be used to estimate the degree of oxidation of a weathered bituminous coal, and it is an indicator of the lowest rank in the bituminous group that can be used for making a satisfactory metallurgical coke.

Oxygen can be determined directly by a semimicro combustion method. For most purposes it is estimated by subtracting from 100 the sum of the percentage hydrogen, carbon, nitrogen, sulfur, moisture and ash. A more accurate estimate can be made by converting the analysis to a mineral-matter-free basis.

Colorific Value

The test consists of burning a weighed amount of the material in a closed vessel under a pressure of oxygen. Heat is released and absorbed in a fixed mass of water. The increase in temperature of the water is directly related to the calorific value of the material. The manner of absorbing this indicates the two principal types of calorimeters commonly used *in the isothermal calorimeter*, the temperature of the water bath surrounding the calorimeter is maintained at a constant temperature. Since the temperature of the water surrounding the combustion vessel or bomb varies, there is heat exchange between the two systems, and the amount of heat gained or lost must be determined between the two systems, and the amount of heat gained or lost must be determined. *Adiabatic calorimeters* have the facilities to adjust or raise the temperature of the outer water bath to the same temperature of the water surrounding the combustion vessel.

Remove the bomb and release the pressure at a uniform rate in about 1 min. Inspect the interior of the bomb for unburned carbon, and if it is present discard the results and repeat the test. Wash the interior of the bomb with water containing methyl orange indicator until all acid is removed, collect the washings and titrate with a sodium carbonate solution containing 20.90g/liter, 1 ml of this solution corresponds to 10.0 Btu. If a combustible firing wire is used, determine the weight of the unburned wire.

Fusibility of Coal Ash

This test gives an approximation of the temperatures at which the ash remaining after the combustion of coal will sinter, melt and flow. The correlation of the laboratory and utilization results is only approximate, because of the homogeneity of the laboratory test piece and the heterogeneity of the residue or ash from utilization. The fusibility data are of value in the procurement of coals that most likely will perform satisfactorily.

The procedure given below consists of heating a molded trilateral pyramid of the ash in a mildly reducing or oxidizing atmosphere and observing the changes in shape and the temperatures at which the changes occur. Four such temperatures are defined below.

Behavior on Heating

Some of the phenomena exhibited by coal on heating have been assigned names that refer to essentially the same behavior; they differ only in the rate of heating. These slight differences of operation become of great importance when they are used in the classification of coals. The various terms may be defined as follows:

Caking refers to the behavior of the coal when it is heated rapidly in measuring the free-swelling index and Roga index or as the combustion of coal. The agglomerating index refers to the behavior of coal when heated rapidly in the volatile matter test.

Coking refers to the behavior of the coal when it is heated slowly in the Audibert-Arnu dilatometer and Gray-King coke-type tests or as in carbonization.

Plasticity, dilation, contraction, and agglutinating value are other terms also used to describe the behavior of coal on heating.

Below, some of the tests used to investigate the behavior of coal during heating are discussed more detail. Free-Swelling Index or Crucible Swelling Number. The free-swelling index is quite important in differentiating between groups in the classification of coals; it also gives considerable information on the combustion characteristics of coal. The test consists of heating the coal under prescribed conditions and comparing the residue or button with standard profiles as shown in Figure 5. Since the test is empirical, the special apparatus is specified exactly.

Roga Index. The Roga index is an alternate procedure for measuring the caking properties of coals. It requires a special drum tumbler and an anthracite with specified properties to mix with the coal before carbonizing. Because of the limited use of the Roga index and the difficulty of getting the specific anthracite or suitable substitute, the details of the test will not be given.

Agglomerating Index. The agglomerating index is required in the ASTM classification of coals in order to differentiate between the anthracitic and bituminous classes and between the bituminous and subbituminous classes of coals.

The test is made by examining the residue from the platinum crucible in the standard volatile matter determination. If the agglomerate button shows a cell structure or swelling or supports a 500-g weight without pulverizing, it is considered as agglomerating.

Gray-King Coke-Type Test. This test and the Audibert-Arnu dilatometer are used alternatively for assessing the coking phenomena of coal in the International Classification of Hard Coal by Type. The equipment for the Gray-King coke test is more easily acquired and the technique of operation less exacting than for the Audibert-Arnu dilatometer. Consequently, only the procedure for the Gray-King test is given.

The test consists of heating pulverized coal out of contact with air in a horizontal tube retort at a uniform and slow rate.

Plasticity of Coal Measured by the Gieseler Plastometer. The test is a semiquantitative measurement of the plastic property or apparent melting of coal on heating in the absence of air. The plasticity phenomena have been quite closely related to carbonization and many researchers have attempted to relate the Gieseler plasticity values with the quality of coke produced from a particular coal or more often a blend of coals. The detailed specifications of the testing equipment and procedure of operation make this a very empiric test. The slightest variation in equipmental detail or deviation in operation can result in erroneous results.

At present, two types of equipment are in use, one utilizing a constant torque of 40g-in. by suspended weight on the stirrer imbedded in coal, and another which produces an equal torque by a magnetic clutch between a constant speed motor and the stirrer. For more detailed information on the procedures, the instruction manuals supplied with the equipment should be consulted.

Equilibrium Moisture of Coal at 96-97% Relative Humidity and 300C

This test is used to restore wet coal and partially dried coal to the moisture content it contained in the bed. The test results are used to measure the degree of drying and excess moisture, and in the classification of coals by rank. It is applicable to all coals from metaanthracite to lignite. The measurement is carried out in a moisture oven maintained at 105°C and with provision in dry air or dry nitrogen at a rate of two oven changes per minute. Air is used only with coals known to be slowly oxidized.

Determination of Hardgrove Grindability Index of Coal

The Hardgrove grindability index (HI) of coal is a relative measure of the ease of pulverizing. The test consists of grinding a specially prepared sample in a laboratory mill of standardized design. The Hardgrove grindability machine is available from Babcock & Wilcox Co. Alliance, Ohio. An index is derived from a sieve analysis of the ground product. For comparison, a standard coal sample with an index of 100 is used.

Special Constituents

In addition to the determination of the carbon, hydrogen, nitrogen, sulfur, and oxygen content of the coal, sometimes investigations are carried out to determine the amount of sulfur present in various forms, and

the chlorine and mineral carbonate content of coal.

Forms of Sulfur. Sulfur occurs in coal as sulfate, pyrite, and in combination with the organic material.

Sulfate sulfur is usually less than 0.1% except for weathered coal containing appreciable FeS₂. The pyritic sulfur content varies considerably more than the organic sulfur, and is of more interest because it is the only form that can be removed from coal by current preparation practices.

Chlorine. A considerable amount of the chlorine in coal is present as sodium chloride and therefore the amount of chlorine present has been used as an estimate of the sodium content. Sodium is suspected of contributing to operational difficulties caused by deposits on the heating surfaces. Coals containing less than 0.15% chlorine are considered as potentially trouble free. The chlorine content is used in some system for the estimation of the amount of mineral matter from the determined ash content.

In the method given, a muffle furnace, heated to 675± 250C and ventilated at three to four air changes per minute, is used. The coal sample is oxidized with an Eschka mixture, and the chlorine content retained as chloride. The resulting mixture is dissolved in diluted nitrate acid, the chloride is precipitated with silver nitrate, and the excess of silver is titrated with potassium thiocyanate.

Mineral Carbonates. Infrequently, a coal contains mineral carbonates in sufficient quantity to affect its carbon content, mineral matter, and classification. The carbon dioxide of the mineral carbonates is determined by heating the coal with dilute hydrochloric acid, absorbing the evolved carbon dioxide in a suitable absorbent, and determining the weight increase. Duplicate determinations by the same operator using the same equipment and sample should not differ more than 0.05%

The second hole of the stopper in the Erlenmeyer flask is fitted with the small end of a coil-type condenser, 300mm long. The open top end of the condenser is connected with an approximately 300 mm long, 7 mm OD glass tube. The top of a Stetser- Norton bulb is filled with 15 mm glass-wool in the bottom and anhydrous calcium chloride on top. The bottom connection of this bulb is connected with a short section of rubber tubing to the bottom connection of a second Stetser-Norton bulb filled two thirds full with granular pumice impregnated with anhydrous copper sulfate; the remainder of this bulb is filled with anhydrous calcium chloride.

Coal Classification

The wide variation in chemical and physical characteristics shown by the several testing methods, methods, provides an opportunity to devise numerous systems for the classification of coals. Some of the systems have received only limited acceptance possibly because of little practical applicability.

Three of the more widely known and used systems are briefly described below. The *British National Coal Board Coal Classification System* is based on the dry, mineral-matter-free, volatile matter and the Gray-King coke-type test.

Cotton

Cotton is one of the plants utilized by mankind at the dawn of civilization archeological evidence indicates that cotton was used in the Indus Valley, in about 3000 BC, for making cloth. Cotton was brought from India to Egypt by Alexander the Great in the fourth century bc, and from there it spread to other countries around the; Mediterranean Sea. Cotton was introduced from India to China during the seventh century ad, first as a garden plant, and about 1000 ad for use as a fiber. In America, remains of cotton bolls dating back to about 5000 bchave been found in Mexico, and discoveries indicate that it was used for textile purposes about 2500 bc.

All wild and cultivated species of cotton plants belong to the botanical genus *Gossypium*. Most of the cultivated cotton belongs to four species: *Gossypium herbaceum* and *G. arboreum*, which probably originated in southern Arabia or northeastern Africa and were introduced into India, *G. hirsutum*, which originated in southern Mexico and Guatemala, and *G. barbadense*, which was found in the northern part of South America but is also cultivated in Egypt and Sudan.

Chemical Properties. Cotton fiber, like most vegetable fibers, is essentially cellulosic; however, the percentage of cellulose which it contains is higher than in most other materials and may be as high as 96% of the dry weight of the unpurified fiber.

Methods of Analysis

Methods related to the identification and analysis of the nature of cottons modified with organic reagents and organic finishings, as well as the determination of trace inorganic elements present either as contaminants or as additives, are discussed below.

Modified Cottons

As mentioned, superficial or partial reactions of the hydroxyl groups of cotton cellulose produce valuable permanent finishes on cotton products. These reactions include esterification and etherification, further reaction with double or multiple bonds, and replacement reactions resulting in specifically modified cottons. Infrared Spectroscopy. The identification of the organic groups introduced into the cellulose molecule, as well as the determination of the degree of substitution, can be carried out by the use of infrared spectroscopy.

The fact that infrared absorption spectra can be obtained without modifying the crystallinity of even highly crystalline native cotton because grinding of the sample is not required is a major advantage of this procedure. O'Connor et al. showed that satisfactory spectra could be obtained with very large pieces of native cotton cellulose, and cutting 20 mesh was recommended in order to provide a reproducible technique.

Two special methods are also of interest in the infrared investigation of modified cotton products. The first developed by McCall, Miles, and O'Connor utilizes the frustrated multiple internal reflectance (FMIR) technique; the technique of Knight and co-workers permits the measurement of cotton fibers without any cutting, grinding, sifting or mixing with extraneous material.

The technique of direct pressing into parallel fibers was demonstrated to give satisfactory spectra, and had the advantage that the cotton fiber was subjected to no treatment other than mechanical pressing and the highly oriented manner in which the fibers are aligned should be helpful in polarization studies. This technique is the only satisfactory manner in which the study of crystallinity by means of deuterium and infrared measurements can be extended to include crystallinities of short, staple cellulosic fibers of native or modified cottons.

Finishing Agents

There are a great variety of substances which are being used in the chemical finishing of cotton fabric. Included in this list are chemicals used to produce water repellency, fire resistance, resistance to mildew, or protection from actinic radiation, lubricants, plasticizers, softeners, antibacterial agents, deodorants, fungicides, germicides, rot resistant agents, and resins used to obtain durable-press or wash-and-wear characteristics. It is almost impossible to establish a single coordinated procedure for the analysis of cotton for any chemical finishing agent; however, two systematic methods approach this goal.

Separation and Identification

The first systematic approach to separate and identify the chemical agents used in cotton fabrics was developed by Skinkle in 1946. The sample is successively extracted with five solvents, each selected to remove by solubilizing certain classes of substances. Subsequent evaporation of the solvent reveals the presence of the entire group. Individual components of each group are subsequently identified either by further separations, by application of additional solvents, or by applying chemical tests which are valid in the presence of some or all of the other substances within the specific group.

Spectroscopic Methods

Ultraviolet, visible, and infrared spectroscopy permit the identification and quantitative analysis of a number of chemical finishing agents used for cotton and cotton fabrics.

Ultraviolet and Visible Spectroscopy. The end points in the analysis of several of the chemical finishes, after extraction and separation, as by the scheme described above or by one of the many modifications of this scheme, have been achieved through the production of a characteristic color produced by reaction of the finishes in a single group with a reagent which would produce a specific color with only one constituent of the group. Often interfering colors, by reaction of the selected reagent with other materials in the group or through a reaction with the solvent, would necessitate further pre-separations before the color test could be applied.

Total Formaldehyde. An accurate quantitative method for the determination of the total formaldehyde content of cotton fabrics treated with a formaldehyde-containing resin is often of considerable aid in the elucidation of the resin reactions involved. However, the usual procedure involving distillation with dilute acid and estimation of the formaldehyde in the distillate is not entirely satisfactory, as it is difficult to distill formaldehyde completely from solution.

Melamine-Formaldehyde Resin. Hirt, described a method for the determination of melamine resins used to impart wet strength to paper. The method, which is applicable to extracted melamine resin from cotton cellulose fabric, is based on the strong ultraviolet absorption of melamine near 235 nm.

Cationic Surfactants. The method of Scott depends upon the chloroform extraction of dye salt formed quaternary ammonium surfactant and excess Orange II (*p*-(2-hydroxy-1-naphthylazo) benzenesulfonate) in aqueous solution. Advantage is taken of this last fact to establish a standardization factor, related to molar absorptivity, obtained from purified surfactants for the analysis of commercial surfactants.

Infrared Spectroscopy. Although the infrared absorption technique was completely successful for the identification and quantitative determination of the extent of chemical modification by reactions with the active hydroxyl groups of cotton cellulose, its application for the analysis of the chemical finishes encountered several difficulties. These difficulties led to the development of complex methods. In one such method, differential infrared spectroscopy accompanied by linear scale expansion is utilized. The frustrated multiple internal reflectance (FMIR) technique of McCall et al. already discussed for chemically modified cotton fabrics also be applied for the investigation of the cotton fabrics with chemical finishes.

Differential IR Spectroscopy. McCall, Miles, Tripp, and O'Connor investigated cottons with chemical finish by comparing their spectra with those obtained from untreated cotton. This method is only practical if some estimate of the actual amount of the modifying reagent (the so-called add-on) can be made.

The analytic scheme starts with the conventional potassium bromide disc procedure. If this technique permits satisfactory detection, identification, and quantitative determination of the resin finish, the analysis is completed with minimum effort. If, however, sensitivity problems are encountered, the same prepared sample is remeasured using the differential and/or linear scale expansion techniques. If the resin finish still cannot be identified or quantitatively determined, resort is made to the acid hydrolysis procedure.

Inorganic Constituents

Because it is an agricultural product, cotton may contain a number of metallic or nonmetallic elements or anions. These substances may also contaminate the original native product during processing. Besides this, a number of elements may be added in small amounts as inorganic salts or oxides or as organometallic compounds to the cotton during processing to produce a specific property not native to cotton.

Chemical Methods

The various elements (either metallic or nonmetallic) in cotton samples may be identified by the chemical spot test methods developed originally by Feigl.

These spot tests have one major disadvantage; a separate test is required for the identification of each element. A second disadvantage is that spot tests do not yield any real quantitative data regarding the concentration of the specific element in the sample. For chemical methods for the quantitative

determination of the major inorganic constituents, see Cellulose.

Spot tests have one advantage over spectroscopic techniques: they permit distinguishing between various anion groups. Thus, tests can be made to differentiate among sulfite, sulfate, or sulfide, between nitrate and nitrite, chloride or chlorate, etc. The atomic spectroscopic methods in current use permit only the identification (and determination) of total elemental content. Thus, sulfur is identified and measured as differentiation of the oxidation state of a specific element as by induced electron emission are not impossible, they have not been developed to the point where they can be said to be tools for the use of the analytical chemist engaged in the analysis of cotton and cellulose.

Spectroscopic Methods

Although there are about a dozen spectroscopic techniques which are of potential application to the determination of elements, both metals and nonmetals, only three, electronic emission, x-ray fluorescence, and atomic absorption spectroscopy, have been used in the analysis of cotton cellulose. It is of some importance, therefore, to consider the respective merits and disadvantages of each of these three techniques.

The advantage of emission spectroscopy in cotton analysis is primarily its ability to permit, with a single scan, a complete qualitative analysis of a considerable portion of the entire spectrum. If the photographic technique is being employed, such a spectrogram permits the operator to investigate in detail the presence or absence of almost all specific metals. In many large spectroscopic laboratories, the use of emission spectroscopy is confined to such qualitative surveys, and x-ray fluorescence or atomic absorption is used (often subsequent to the qualitative survey) when quantitative values are required.

A limitation of x-ray fluorescence analysis is that light elements may escape detection or accurate measurement. However, techniques and selection of accessories such as x-ray tube, analyzing crystal, and detector have pushed these analyses down to magnesium and, with special vacuum spectrophotometers and specially designed analyzing crystals, such as lead stearate, analyses are being made down to boron, leaving very few elements which cannot be detected and determined by this technique. These latter determinations, between magnesium and boron, can be made, however, only by a significant increase in instrumental sophistication and expense.

Another disadvantage of x-ray fluorescence is the sophistication and the cost of the initial equipment, which is higher than the cost of the equipment used in the other techniques.

Emission Spectroscopy. Emission spectroscopy consists of three more or less independent steps. First, the proper preparation of the sample; second, the technique for obtaining the raw data, the emitted atomic lines of the desired constituents; and third, the evaluation of these data to properly identify and quantitatively determine the element or elements of interest.

In the original paper of O'Connor and Heinzelman, describing the general method for the spectrochemical analysis of plant products, two procedures were recommended, one for samples with an ash content of less than 1% (where there could be no matrix effect from the composition of the ash), and another for samples with ash content of sample over 1% (where the composition of the ash might effect the condition for constant matrix). In later works the second procedure was used, mainly because the cotton samples being analyzed were fabrics chemically modified by the introduction of metal-containing substances to produce specifically desired effects. The two procedures are given below.

Procedures

ash-content of sample less than 1%. Accurately weigh 16.67 of the sample into a Vycor dish with 90-mm diameter, and add 2 ml of a solution of 250 g of magnesium nitrate hexahydrate in 1 liter of 95% ethanol. The ratio of sample weight to the magnesium nitrate buffer is arbitrary and can be varied for different samples depending upon the sensitivity required, if the ratio actually used is considered in obtaining and using the working curves. The ratio suggested here will permit analysis with a sensitivity of about 1 part of

metal in 10,000,000 parts of sample for the more sensitive metals, copper and iron, for most types of samples.

ash content of sample over 1%. Ash exactly 5 g of sample in a tared Vycor dish as described in the earlier procedure, but without addition of the magnesium nitrate solution. After removal from the furnace, cool the dish and reweigh to determine the ash content of the sample. Add a volume of a very dilute aqueous solution of germanium dioxide so as to introduce a quantity of the dioxide equal to 4.14% of the ash. Grind and thoroughly mix the ash prior to analysis.

Prepare a mixture of salts representing the major constituents of a typical ash. A suggested composition is as follows: 65.18% potassium carbonate, 0.95% sodium chloride, 11.02% calcium carbonate, 18.70% magnesium carbonate, and 4.14% germanium oxide. Prepare working curves by adding graduated amounts of elements to portions of this salt mixture.

X-ray Fluorescence Analysis. When x rays strike any material, as any analytical sample, one usually considers their penetration, as it is their dominant characteristic. However, if the beam of x rays is measured before and after striking the sample, a decrease in intensity will be found. Some of the x rays have been absorbed by the material, the amount, of course, depending upon the nature, particularly the density of the material, and the thickness of the sample. These absorbed x rays can be used as a successful method of spectroscopic analysis in a manner essentially analogous to the use of the absorption of photons, except that absorption of x rays is an atomic process, and absorption by a given element is independent of the chemical combination in which the particular element occurs. Thus, x-ray absorption is a technique for elemental analysis.

An x-ray spectrometer consists of an x-ray tube capable of emitting an intense x-ray beam that impinges upon the sample to be analyzed. Fluorescent rays, which appear as secondary emission, are dispersed by utilizing crystal with a known lattice constant, frequently a bent mica crystal, to act as a diffraction grating. The diffracted fluorescent x rays are detected by a Geiger counter goniometer, and their intensities may be automatically recorded as a function of the goniometer angle which is proportional to the wavelength or frequency of the x rays.

Sections of such a tabulation are reproduced in Table 11 for the five elements, calcium, chromium, potassium, manganese, and zirconium. All the lines in Table 11 involve the innermost orbit, as indicated by the letter K in column 3, although in more complete tables the L and occasionally M and N lines may occur. ABS indicates the absorption line or edge.

For the purpose of determination by x-ray fluorescence methods, the elements introduced into cotton through chemical and additive modification (which are the major purposes for such analyses) fall into two broad categories; those of atomic number 22 and higher, and the lighter elements. The heavier elements are used to impart protection against degradation by outdoor exposure or microorganisms (copper, mercury, lead, cadmium, selenium, zirconium), and to impart flame resistance (tinbromine); they are also used in certain classes of dyes and pigments (chromium, iron, titanium) and for miscellaneous purposes, such as catalysts.

Count rates of equivalent discs usually show a maximum difference of 2%. The relationship of percentage composition to counting rate is found to be linear over a range of 0.01 to about 3% for most of the elements examined. In all cases, a loss in counting rate was noted at concentrations above 3% indicating self-absorption. This loss of counts becomes marked at concentrations of about 10% and dilution with pure cellulose should be employed.

Lignin and Hemicellulose

The compositions and percentages of lignin and hemicellulose vary from one plant species to another so it is difficult to arrive at generalizations concerning structure and abundance of these polymers. Moreover, composition varies within a single plant (roots, stems, leaves), with age (heartwood versus sapwood), stage

of growth (early wood versus late wood in annual rings) and with the conditions under which the plant grows. Study over many decades has elucidated the major structural features of wood hemicelluloses and lignin's along with the biochemical mechanisms for their degradation. Most recently attention has turned to the molecular characteristics of these enzymes. It is beyond the scope of the present review to recapitulate these findings in detail. Rather, the focus will be on specialized or recently revealed aspects.

II. Hemicellulose

Softwoods (gymnosperms), hardwoods (angiosperms), and grasses (graminaceous plants) have evolved separately, and they contain different lignin and hemicellulose constituents. Moreover their specialized tissues have varying proportions of cellulose, hemicellulose, lignin, pectins, proteins, and extractives. Lignin is deposited during maturation of cell walls, and some carbohydrates become cross linked to it. Because the lignin and hemicellulose constituents differ, the crosslinks between these polymers differ from plant to plant and from tissue to tissue.

A. Assay systems

Hemicellulases are most commonly assayed by measuring the rate of reducing group formation under optimum conditions. A suitable polysaccharide substrate is suspended in buffer and mixed with an enzyme solution that is appropriately diluted to yield a linear response over time. Alternately, several successive two-fold dilutions are assayed for a single fixed time (10 to 30 min), and the enzyme titer is calculated from the average of several successive dilutions that exhibit a consistent enzyme activity. This approach is necessary because at very low dilutions (or long assay times) the substrate is exhausted, and the calculated activity is not representative of the actual value.

B. Classification

Hemicellulases are classified according to the substrates they act upon, by the bonds they cleave and by their patterns of product formation, Table 1, but greater variety exists among the endo-xylanases and β -glucosidases than is reflected in this simple classification system. One notable distinction is made between endo-1,4- β -xylanase (EC 3.2.1.8) and xylan 1,4- β -xylosidase (EC 3.2.1.37). While the former produces oligosaccharides from random cleavage of xylan, the latter acts principally on xylan oligosaccharides producing xylose. Some endo-xylanases appear to have greater specificity for straight chain substrates, and others appear to be able to accommodate more frequent side chains of branching.

Deacetylation makes native xylans much less soluble in water, which is an observation that causes some consternation to trained organic chemists. Even though acetylation makes the xylan polymer more hydrophobic, it also blocks extensive intrachain hydrogen bonding. When the acetyl groups are removed, hydrogen bonding leads to xylan precipitation. Even though the substrate is less soluble, deacetylation generally increases susceptibility of the substrate to enzyme attack. Some acetyl esterases, however, show specificity for the native acetylated substrate.

C. Thermophilic hemicellulases

Thermostable enzymes are often of interest for biotechnological applications, and hemicellulases are no exception. Thermophilic xylanases have been recognized for several years. Ristoph described an extra cellular xylanase produced by the thermophilic actinomycete *Thermonospora* that was stable for approximately 1 month at 55 °C and could withstand up to 80°C in a 10 min assay. Gruninger described a highly thermostable xylanase from a thermophilic bacillus that has a catalytic optimum of 78° and a half life of 15 h at 75°. Both enzymes were predominantly endo in activity and produced only trace quantities of xylose after long periods of incubation. The thermophilic fungus *Thermoascus aurantiacus* produces an extra cellular endo-xylanase that has a temperature optimum of 80°C. At that temperature, the half life is 54 min. These characteristics are fairly similar to thermostable xylanases from *Talaromyces emersonii*, another thermophilic fungus that grows on straws and pulps.

D. Alkaline active xylanases

An alkaline active enzyme was also purified and characterized from an alkalophilic actinomycete. Tsujibo et al. purified three endo-xylanases from the culture filtrate of *Nocardopsis dassonvillei* subsp. *alba* OPC- 18. The molecular weights were 23,000, 23,000 and 37,000 for X-1, X-11, and X-111, respectively.

E. β -Xylosidase

Endo-xylanases are much more common than β -xylosidases, but the latter are necessary in order to produce xylose. Most β -xylosidases are cell bound, and the enzymes are large relative to endo-xylanases. The β -xylosidase of *Bacillus sterothermophilus* has a molecular weight of about 150,000 and is stable at up to 70°C. Utt described a novel bifunctional β -xylosidase from the ruminal bacterium *Butyrivibrio fibrisolvens* was cloned in *E. coli* and shown to consist of a 60,000Mr protein with dual glycosidase activity.

F. Mannanases and galactanases

Mannanases and galactanases are described far less frequently than xylanases. It is not known whether this is attributable to their lower prevalence in nature or simply because they are sought less often. Bacterial species known to produce mannanases include *Aeromonas hydrophila*, *Cellulomonas* sp. and *Streptomyces olivochromogenus*. Multiple endo – β -mannanases are found in the extra cellular broth of *Polyporus versicolor*.

G. Accessory enzymes for hemicellulose utilization

A number of enzymes appear to be critical in the early steps of hemicellulose utilization. These include acetyl xylan esterases, ferulic and *p*-coumaric esterases, α -L rabinofuranosidases, and α -4-O-methyl glucuronosidases.

Acetyl xylan esterase was first described by Biely in several species of fungi known to degrade lignocellulose and most especially in *A. pullulans*. Acetyl xylan esterase was subsequently described in a number of different microbes including (*Schizophyllum commune*, *Aspergillus niger* and *Trichoderma reesei*, *Rhodotorula mucilaginosa* and *Fibrobacter succinogenes*. Acetyl xylan esterase acts in a cooperative manner with endoxylanase to degrade xylans. This enzyme is not involved in breaking LC bonds because the acetyl esters are terminal groups.

The ferulic acid esterase of *S. commune* exhibits specificity for its substrate, and it has been separated from other enzymes. Borneman et al. assayed feruloyl and *p*-coumaroyl esterase activities from culture filtrates of anaerobic fungi using dried cell walls of Bermuda grass as a substrate. The enzyme preparations released ferulic acid more readily than they released *p*-coumaric acid from plant cell walls. Assays using methyl ferulate or methyl *p*-coumarate as substrates in place of dried cell walls showed the presence of about five times as much enzyme activity. McDermid employed ethyl esters of *p*-coumarate and ferulate as substrates for these activities.

111. Lignin

Lignin is an aromatic polymer with the substituents connected by both ether and carbon-carbon linkages. It is composed of three principal building blocks: *p*-coumaryl alcohol (*p*-hydroxyphenyl propanol), coniferyl alcohol (guaiacyl propanol), and sinapyl alcohol (syringyl propanol)

A. Lignin-degrading enzymes

Recent years have witnessed an increasing interest in the enzymatic mineralization and depolymerization of lignin. No doubt this stemmed in part from the description of a family of peroxidase-like enzymes from active lignin-degrading cultures of *Phanerochaete chrysosporium*. These enzymes, termed lignin peroxidases (LiP) are capable of degrading a number of lignin model compounds- including the *p*-aryl ether model- and are closely associated with the mineralization of ¹⁴C- labelled lignin to CO₂. Of particular note is the ability of enzyme preparations from *p. chrysosporium* to depolymerize methylated spruce lignin.

B. Lignin degradation in whole cell cultures

There are essentially two approaches to understanding the roles of these various enzymes in lignin degradation. One approach is to reconstitute a lignin- degrading system in vitro using crude, purified, or

cloned enzyme constituents. The other is to regulate the cellular metabolism of lignin- degrading fungi in vivo so as to produce either LiP or MnP, and then to observe the cultures for depolymerization and mineralization.

Studies by Perez showed that both the appearance of lignin- degrading enzymes and mineralization of lignin are affected by the presence of manganese. The effects, however, vary with the organisms and test systems employed. In *p.chrysosporium*, elevated Mn concentrations represses LiP while inducing MnP, and in *phlebia brevispora*, Mn represses LiP while inducing both MnP and laccase. In both cases, high rates of mineralization correlate with the appearance of LiP at low Mn concentrations and not with the appearance of MnP or laccase. *D. squalens* produces only MnP and laccase, and in this organism, mineralization correlates with the appearance of MnP.

C. Degradation by cell-free enzyme systems

Complete catalytic depolymerization of lignin has not been demonstrated in vitro with a cell-free enzyme system. Extracellular proteins from *p.chrysosporium*, *Coriolis versicolor*, and *phlebia radiata* were reported to increase the number of hydroxyl groups, decrease the mean molecular weight, or otherwise chemically alter various lignin preparations. Kern investigated the action of crude and partially purified LiP from *p. chrysosporium* on the molecular size distribution of ¹⁴C – labelled lignins, and he further used pyrolysis GC mass spectrometry to investigate changes in substrate characteristics.

The mechanism of lignin depolymerization may not be the same in all organisms. Galliano studied lignin degradation (solubilization) by *Rigidoporous lignosu*, an organism that does not produce LiP, but rather synthesizes MnP and laccase. When the two enzymes were purified and their properties studied *in vitro*, neither enzyme was able to solubilize radioactive lignins. When both enzymes were added to the reaction, mixture at the same time, lignin solubilization was extensive; the MnP and the laccase acted synergistically. In addition, glucose oxidase enhanced lignin solubilization by preventing repolymerization of the radicals formed by the two oxidative enzymes.

D. Role of glycosides in lignin degradation

One of the first enzymes implicated in lignin biodegradation was cellobiose: quinone oxidoreductase (CBQase). This enzyme catalyzes the reduction of a quinone and the simultaneous oxidation of cellobiose. The discovery of this enzyme and the proposal that its role might be to prevent repolymerization of lignin during degradation. Recent studies have not borne this out, but the enzyme may be important nonetheless. The CBQase of *P.chrysosporium* binds very tightly to microcrystalline cellulose, but such binding does not block its ability to oxidize cellobiose, indicating that the binding and catalytic sites are in two different domains.

An essential feature of lignin biodegradation is that degradation products resulting from the activity of extracellular enzymes must be taken up by the mycelium; glycosylation by β -glucosidase seems to be an important part of this process. Whether or not sugars attached to lignin in the native substrate by nonglycosidic linkages play a similar role has not been addressed.

1V. Lignin-carbohydrate complexes

Lignin-carbohydrate complexes (LCCs) are heterogeneous, poorly defined structures that are found in many plant species. Lignin is directly or indirectly bound covalently to carbohydrate, and the resulting complexes present a barrier to biological degradation. LCCs have proven to be highly intractable materials that are in large part responsible for limiting the biodegradation rate of plant materials.

A. Fractionation of lignin and carbohydrate in wood

The existence and character of LC bonds have long been studied and debated. In 1956, Bjorkman published techniques for liberating MWL from finely ground wood. He also obtained an LCC by exhaustive milling and extraction. Aqueous dioxane was used to extract MWL, and dimethylformamide, dimethylsulfoxide, and aqueous acetic acid were used to extract LCC. The lignin contents of LCCs are

similar to that of the MWLs except that the latter contain less carbohydrate. Despite many attempts Bjorkman could not separate carbohydrates from LCC without resorting to chemical degradation.

B. Isolation of LCCs

The LCCs are highly heterogeneous and difficult to study. Many conventional chemical treatments, such as alkali, readily disrupt some of the most prevalent LC bonds. The best approaches employ neutral solvents and purified enzyme preparations. Most research has focused on the isolation of water-soluble LCCs, because they can be fractionated, sized, and subjected to spectroscopic study. Larger, insoluble LCCs exist and may even account for the bulk of LC bonds in the substrate, but less is known about them. Most evidence suggests that the chemical linkages are similar to those of the soluble LCCs.

C. Chemical characteristics of LC bonds

Existence of chemical bonds between lignin and carbohydrate has been questioned because of the intimate physical integration between the lignin and carbohydrate constituents, the possibility of entrapment or adsorption, and lability of many linkages. Several different types of LC bonds have been proposed based on knowledge about changes in sugar composition following digestion and about hemicellulose structures. The proposed LC bonds include bonds to xylan, glucomannan, cellulose, various other hemicellulosic sugars, and pectin.

D. Ferulic and *p*-coumaric ester side chains

Grass and bamboo lignins differ from those of hardwoods and softwoods in that they are formed not only from guaiacyl and syringyl units, but also from *p*-hydroxyphenyl units. Esterified *p*-coumaric acid can comprise 5% to 10% of the total weight of isolated lignin. The participation of *p*-hydroxyphenyl glycerol- β -aryl ether structures is of minor importance. Based on methanolysis and spectral studies, Shimada proposed that the majority of *p*-coumaric acid molecules in bamboo and grass lignin are ester-linked to the terminal *g* carbon of the side chain of the lignin molecule Fig. 11. Ferulic acid is also present in small amounts. The *p*-coumaric ester linkages are extremely stable as they are not removed by methanolysis, thioglycolic acid treatment, or catalytic hydrogenolysis.

E. Frequency and stability of LC bonds

The amount of carbohydrate remaining on the lignin can be measured by sugar analysis following acid hydrolysis. Obst found 10.8% carbohydrate in a MWEL from loblolly pine. A fraction of this amount (11%) was removed by dilute alkali.

F. Residual lignin in kraft pulp

Kraft pulping removes large quantities of hemicellulose and lignin and disrupts ester linkages between lignin and carbohydrate and between hemicellulose chains. Even so, significant amounts of carbohydrates remain bound to the residual lignin after kraft pulping. As the reaction progresses, however, residual lignin becomes harder to remove. Lignin remaining in the kraft pulp cannot be removed without unacceptable large yield losses.

to the O-6 of galactoglucomannan. Although this structure is in accord with what is known about native LC bonds, the bonds in kraft pulp can be very different. The nature of the covalent linkages in kraft pulp have not been fully characterized because (1) many rearrangements occur during pulping (2) difficulties are encountered in isolating the residual lignin, and (3) reliable degradation and characterization methods are lacking. At least some changes appear to result from the formation of alkali- and acid-stable carbon-carbon bonds between lignin and carbohydrates. Several rearrangements are possible. Particularly, primary hydroxyls of glucose and mannose can react with the *a*, *b* or *g* carbons of phenylpropane units to form ether linkages. The reducing -end groups can also react. Glucose is the most prevalent sugar bound to residual lignins from kraft pulps, and it seems probable that this results from the reaction of cellulose with lignin during the pulping process. This conclusion is supported, but not proven, by the observation that the glucose content of lignins from wood. Reactions with the *b* and *g* hydroxyls of the phenyl propane are

particularly acid and alkali- stable and may escape detection in methylation analysis.

Minor used methylation analysis to determine the characteristics of polysaccharides attached to residual lignin in loblolly pine kraft pulps. The total carbohydrate content of the residual MWEL was only about 8%. As compared to the 12% obtained with MWEL from native wood, but methylation data indicated that the carbohydrate bonding was similar in kraft and native wood. The primary O-6 position was most frequently found for hexans and the primary O-5 for arabinan. Xylan was bonded to lignin at O-3, with a small amount at O-2. The predominant methylated derivatives obtained from galactose and arabinose indicated 1 \rightarrow 4 and 1 \rightarrow 5 linkages, respectively. The apparent DP ranged from 4 for xylan to almost 13 for galactan. Because of the small differences in methylation patterns between carbohydrates from MWELs of pine and pine kraft pulp. Minor was not able to confirm the possible formation of LC bonds during pulping.

G. Biodegradation of LCCs

Most carbohydrate chains or side groups appear to be attached to lignin through the nonreducing moieties. Because *exo*-splitting enzymes generally attack a substrate from the nonreducing end of a polysaccharide, removing substituents progressively toward the reducing end of the molecule, complete degradation is not possible. Even when carbohydrates are attached to the lignin by the O-1 hydroxyl, a single sugar residue could remain attached even after complete attack by *exo*-splitting glycosidases.

I. Residual LC structures after exhaustive enzymatic digestion

The presence of lignin, aromatic acid, and other modifications of hemicellulose clearly retards digestion of cellulose and hemicellulose by ruminants. Phenolic acids associated with forage fibre are known to decrease fibre digestion when they are in the free state. *p*- Coumaric, ferulic, and sinapic acids inhibit the activity of rumen bacteria and anaerobic fungi.

The influence of LCCs on ruminant digestion was studied by examining the solubilization of LCCs using cell-free hemicellulase complexes from the rumen. LCCs from grasses of increasing maturity were isolated and treated with cell-free rumen hemicellulases. As the lignin content increased, the extent of degradation declined, indicating that the lignin content of the LC was the overriding factor in determining its digestibility.

2. Solubilization of LCC by microbial activity

In recent years, studies on the solubilization of lignin from grasses or wood labelled with ¹⁴C phenylalanine have proliferated. The bulk of the radioactive label is incorporated into the lignin rather than into carbohydrate or protein of the plant, but it is clear that lignin purified from the labelled plant tissue contains significant amounts of carbohydrate. This material is probably closer to the structure of native lignin than is synthetic lignin prepared by *in vitro* dehydrogenative polymerization of coniferyl alcohol.

In summary, research on the solubilization of LCC by microbial activity has periodically shown that cellulases, hemicellulases, esterases, and perhaps peroxidases all correlate with lignin solubilization. The mineralization rates and extents reported for streptomyces are relatively low, and the solubilized lignin is not extensively modified. Lignin mineralization and solubilization could, therefore be attributable to two (or more) different enzymes. These studies require additional rigorous clarification.

V. Enzymatic treatments of pulps

For many applications, residual lignin in kraft pulp must be removed by bleaching. Successive chlorination and alkali extraction remove the remaining lignin to leave a bright, strong pulp suitable for printing papers and other consumer products. Although chlorine bleaching solves the immediate problem of residual lignin, the chlorinated aromatic hydrocarbons produced in the bleaching step are are recalcitrant and toxic. These chlorinated products are hard to remove from waste streams, and trace quantities are left in the paper, so other bleaching processes were devised. One approach is to use hemicellulases to facilitate bleaching.

V1. Conclusions

Lignin and hemicellulose are complex polymers occurring in plant materials. Either polymer alone presents a

formidable challenge to microbial degradation. In native substrates, however, lignin and hemicellulose are intermeshed and chemically bonded through covalent cross-linkages. As such they are even more resistant. Covalent lignin – carbohydrate linkages can be divided into two types: ester linkages through the free carboxy terminus of uronic and aromatic acids and ether linkages through sugar hydroxyls.

Degradation of Wood

Introduction

Microbial degradation of wood should be considered on two levels. From an organismic point of view degradation concerns the interaction of the cell with its microenvironment. At this level, degradation is strongly affected by diffusion of the degradative agents and the uptake of the oligomeric products. From a biochemical perspective, degradation concerns the molecular architecture of the biopolymers, the capacities of the enzymatic catalysts to bind to them and the catalytic turnover rates. Lignin reactivity is limited by the accessibility, heterogeneity, and stability of the polymeric linkages; cellulose reactivity is limited mostly by accessibility and crystallinity; and hemicellulose reactivity is limited by substitution.

Distribution of Wall Components

The three principal components of wood are found throughout the wall. Cellulose is organized into laminar crystallites which are bundled into the microfibrils. Each micro-fibril contains regions of amorphous cellulose interspersed and intertwined with hemi-cellulose, Fig. 1. The latter is in turn crosslinked to lignin. Most of the cellulose is in the secondary wall layers. Its concentration depends on the relative portions of hemicellulose and lignin.

Component Chemistries

Lignin is a stable, highly cross-linked aromatic macromolecule arising through dehydrogenative free radical polymerization of *p*-coumaryl, coniferyl; and sinapyl alcohols. Gymnosperm lignin is made up principally of coniferyl alcohol (guaiacyl lignin) whereas angiosperm lignin is made up from approximately equal amounts of coniferyl and sinapyl alcohols (syringyl/guaiacyl lignin). *p*-Coumaryl alcohol is found principally as a precursor to the lignin of grasses and in reaction wood. Cellulose microfibrils are the most conspicuous element of the plant cell wall. The β -(1,4)-D-glucose chains which make up the cellulose polymer can be arranged in both parallel and antiparallel crystallites; but based on what we now know about the biosynthetic and biodegradative mechanisms and x-ray crystallographic studies, the parallel arrangement is almost certainly the form found in nature.

Microstructure and Porosity

Porosity and microstructure are critical in determining accessibility of enzymes to their polymeric substrates. The relationship between enzyme diffusion and substrate accessibility has been shown in the number of ways. For example, reducing particle size greatly increases surface area and speeds up the enzymatic hydrolysis of cellulose. Grinding or cutting wood to open all the lumina to attack will expose considerably more surface than is available in whole wood. The total surface area reaches about 1 m² g⁻¹. Once the lumina are accessible, however, relatively little further increase in surface area occurs following further grinding, because the cell wall thickness is very small compared to its length. Particle size is not the only factor important in enzymatic depolymerization. Enzymatic accessibility depends on the structure of the wall itself.

Degradation of whole wood

Microbial degradation of whole wood occurs principally by fungi. Although bacteria apparently possess much of the biochemical machinery necessary for biodegradation of the wood components, they do not form mycelia, and hence, cannot propagate through the tissue structure or translocate nutrients into the wood or from one region to another as decay progresses.

Biodegradation of Lignin

Biodegradation of lignin has been studied for more than 80 years with only incremental progress over much of the time. Early assays employed the disappearance of acid-insoluble Klason lignin. The development of Synthetic ¹⁴C-labelled lignins enabled rapid radiorespirometric determination of lignin degradation under controlled conditions, and a series of experiments using this assay led to improved understanding of the cultural and nutritional conditions under which lignin biodegradation occurs.

Other aspects of lignin biodegradation such as the roles of oxidative species details of biochemical mechanisms, regulation and bacterial lignin degradation have been reviewed elsewhere.

Biodegradation of Cellulose

The biodegradation of cellulose has probably attracted more attention world-wide than any other single biochemical event outside the field of medicine, yet the mechanism of cellulose hydrolysis is still imperfectly understood. The cellulase complex from *Trichoderma reesei* has been studied most thoroughly, but it is not yet clear exactly how this complex works to depolymerize cellulose. The focus here is placed on the biochemical mechanisms involved in hydrolysis.

When all of the cellulases are present, *Valonia* crystals undergo a delamination to form bundles of microcrystallite fibrils. A similar delamination has been observed with the purified bacterial cellulose from *Acetobacter xylinum*. Although no direct evidence is available, the delamination probably occurs between the sheets adjacent van der Waals-bonded sheets rather than between adjacent hydrogen bonded chains.

The distinction between CBH I and II is not confined to *T. reesei*. CBH I and II are also found in the cellulase complex of *Penicillium pinophilum* and in *Fusarium lini*. In the later instance, CBH I was found to be active against D-xylan, whereas CBH II was not. Given the apparent importance of the C6 carbon in forcing the half-chair conformation during the hydrolysis of the glycosidic bond by lysozyme, it is apparent that substrates lacking this substituent may not be appropriate for some cellulases.

Biodegradation of Hemicellulose

Because of the diversity of hemicelluloses, it is not possible to survey here all of the different types known. Dekker have provided an extensive, useful compilation of this sort. Likewise have recently reviewed the literature on microbial xylanases. Mannanases have been studied to a lesser extent, hence, the emphasis here is placed on xylanases.

The characterization of hemicellulase mechanisms presents numerous difficulties not encountered with cellulase because the substrate employed is heterogeneous and branched. Moreover, the literature is not definitive because substrates such as larch arabino – glucuronoxylan commonly used for hemicellulose assays – presumably because of their easy solubility – but they are not really representative of the bulk of hemicellulose found in wood. Selection of an appropriate substrate is critical because the apparent specific activity of a xylanase can vary greatly depending on the xylan preparation used for assay. Substrate variability is not confined to the type of xylan employed, because different batches of xylan from the same supplier can lead to apparent changes of as much as two-fold. Native xylans tend to be highly acetylated. Acetyl groups increase solubility but decrease the rate of enzymatic depolymerization so the method of substrate preparation can have a profound effect on the apparent activity.

Many xylanases are not able to remove glucuronic acid residues from the xylan chain probably because of the 30-fold greater stability of glucuronide glycolytic linkages noted earlier. By comparison, the ester linkages connecting acetyl groups to the xylan are exceedingly unstable and most are removed during isolation of the polymer. Although synergism is observed between xylan esterases and endoxylanases during hydrolysis of partially acetylated xylan, it seems unlikely that deacetylation would be a rate-limiting step in the enzymatic hydrolysis of xylan under most practical conditions because of the extreme lability of the ester linkages.

Applications

Technical developments, particularly the discoveries of xylose-fermenting yeasts and lignin-degrading enzymes have paved the way for specific removal of hemicellulose and lignin in order to recover cellulosic fibers and to produce useful chemicals from the hemicellulose and lignin fractions.

An alternative approach to biological pulping which permits more direct control over the degradation activities is to employ isolated enzymes for lignin or hemicellulose removal. Because the lignin is cross-linked mostly into the hemicellulose is more readily depolymerized than lignin, it has been the initial target of treatment. Removing only a small portion of the hemicellulose might be sufficient to open up the polymer and ease solvent removal for the residual lignin. The principal problem in these studies has been in obtaining selective removal of hemicellulose without degrading the cellulose. Selective inhibition of cellulase activity can be realized by the addition of 1 mM HgCl₂. Xylan was specifically removed from delignified cell walls leading to a decrease in energy demand during beating. Removing less than 2% of the initial dry pulp weight gave better fiber bonding due to increased flexibility. Therefore, enzymatic treatments of pulp hold the prospect of both decreased cost and improved fiber qualities.

CCA-Treated Wood

Wood treated with CCA is widely used in outdoor architectural projects such as decks, walkways, gazebos and retaining walls. Although this material was originally marketed as a maintenance-free product, most preservatives manufacturers and end users today recognize the advantages of protecting and beautifying CCA-treated lumber with surface finishes. As a consequence, it frequently becomes a substrate for a variety of coatings products.

Unfortunately, little published information is available on the performance of surface finishes over CCA-treated wood. This has led to some confusion among preservatives manufacturers, coatings companies, the trade, and consumers as to the compatibility of coatings with this material. Not surprisingly, there are a number of misconceptions about the effects of CCA treatment on coatings performance. This project was undertaken to help clarify some of these issues.

All of this suggests that surface finishes applied over CCA-treated lumber would perform better than those applied over untreated wood of the same species.

The objective of this project was to evaluate the performance of a variety of surface finishes over untreated and CCA-treated wood and to determine the extent of the chromium enhancement effect.

Wood-Polymer Composites

Wood is a hygroscopic material that can sorb water as a liquid or as vapor from its surroundings. The sorbed moisture can exist in wood as liquid or vapor in all cavities and as water bound chemically within cell walls. Moisture in the cell walls affects all wood properties, but moisture in voids affects all wood properties, but moisture in voids affects only weight. The amount of moisture held in cell walls varies according the particular piece of wood and is a function of both the relative humidity and temperature of the surrounding air. The fiber saturation point is the point at which cell walls are empty. Wood is subject to dimensional changes when its moisture content fluctuates below the fiber saturation point.

One way wood-polymer composites (WPC) are made is by saturating wood with monomers followed by *in situ* polymerization of the monomers. Many monomers used to make WPC do not penetrate the cell walls and do not completely fill the voids after polymerization, leaving voids in the wood because of shrinkage of the polymer. Solvents can be used to help swell wood and aid the penetration of monomers into cell walls, resulting in moderately high dimensional stability. Methanol has been used to swell the wood; after methanol treatment, the wood is then heated.

The objectives of this research were to identify monomers that swell and penetrate the cell wall without the use of solvents, measure the extent of swelling in individual monomers, polymerize the monomer in the wood, and measure the volumetric swelling and moisture content of the WPC at 90% relative humidity (RH).

Materials and Methods

Monomers

Monomers selected for this study were acrylates and metacrylates, which can be polymerized using the thermal polymerization initiator 2,2'-azobis(2-ethylbutyronitrile). All monomers were used as received without further purification or removal of inhibitors added by the manufacturers.

Wood specimens

Maple (*Acer saccharum*), northern red oak (*Quercus rubra*), and southern pine (*Pinus sp.*) woods were used. The wood was cut into specimens 2.5 by 2.5 by 0.6 cm (radial by tangential by longitudinal). Growth rings were oriented parallel to one side of each specimen to minimize distortion during shrinking and swelling.

Volumetric swelling and moisture content

The WPC specimens and untreated control specimens were conditioned in a humidity chamber at 27 C and 30% relative humidity (RH) for 7 days. The conditioned specimens were weighed, dimensions measured, and volumes calculated. The specimens were then placed in a humidity chamber 27 C and 90% RH. Specimens were weighed and measured after 2, 4, 6, and 24 h, and 2, 3, 4, and 7 days. The percentage of volumetric swelling based on the treated oven-dry volumes was calculated based on the oven-dry untreated weight.

Volumetric swelling of WPC specimens

The rate of swelling of WPC specimens was slow for the first few hours at 90% RH, compared to that of the control specimens Tables 6 to 8 After 6 h in 90% RH, maple red oak, and southern pine control specimens swelled 6.6, 6.1 and 7.0%, respectively. In contrast, all maple WPC specimens swelled less than 3%, red oak WPC specimens less than 3.6%, and the southern pine WPC specimens less than 4.0% during the same period moisture into the wood, which lowered the rate of swelling compared to that of controls during the first few hours at 90% RH.

Moisture content of WPC specimens

The moisture content of WPC specimens was calculated from specimen weight at specified time intervals in 90% RH. The rate of moisture sorption during the first few hours was slower than it was after 24 h in 90%RH. After 7 days at 90% RH, the moisture content calculated on the basis of only the wood in the specimens (untreated oven-dry weight) excluding the weight of polymer, showed that many treated specimens sorbed more moisture than did control specimens.

Conclusions

Certain monomers can swell wood at temperatures above room temperatures. These monomers have low molecular weights and molecular structures that facilitate hydrogen-bonding. For wood-polymer composite (WPC) specimens that displayed some volumetric swelling after polymerization, cell-wall bulking had the potential to reduce the moisture-related swelling, but this potential was counteracted by the hygroscopicity of the polymers. This attraction of moisture to the WPC specimens resulted in some swelling that likely would not have occurred had the polymers not been hygroscopic.

Lignocellulosic—Plastic Composites from Recycled Materials

Use of the word “waste” projects a vision of material with no value or useful purpose. However, technology is evolving that holds promise for using waste or recycled wood and plastics to make an array of high-performance products that are, in themselves, potentially recyclable. Preliminary research at Forest Products Laboratory (FPL), and elsewhere indicates that recycled plastics such as polyethylene, polypropylene, or polyethylene terephthalate can be combined with wood fiber waste to make useful reinforced thermoplastic composites. Advantages associated with these composite products include lighter weight and improved acoustic, impact, and heat reformability properties—all at a cost less than that of comparable products made from plastics alone. In addition, previous research has shown that composite

products can possibly be reclaimed and recycled for the production of second-generation composites.

Thermoformable Composites as Outlets for Waste Paper, Wood, and Plastics

Two general types of thermoformable composites exist, distinguished by their very different manufacturing processes. Both processes allow and require differences in composition and in the lignocellulosic component. The two processes used to produce thermoformable composites are melt blending and air laying or nonwoven mat formation.

Currently, the primary application of the thermoformed composites, both melt blended and air laid, is for interior door panels and trunk liners in automobiles. As noted, additional large-volume, low-to-moderate cost applications are expected in areas such as packaging (trays, cartons), interior building panels, and door skins.

Recent Research on Wood Fiber-Thermoplastic Composites

The following is not intended to be a comprehensive review of recent research on wood fiber-thermoplastic composites. Instead, we simply illustrate the effects of some important composition and processing variables in the composite processes, including preliminary indications of the effects of recycled ingredients.

Composites Made by Melt Blending. The 1980s brought a resurgence of research into various aspects of melt-blended composites made from wood-based flour or fiber in virgin thermoplastic matrices. For example, Kokta and his colleagues have published numerous papers in this area, emphasizing improvements in the filler-matrix bond through coupling agents and grafting of polymers on cellulosic fiber surfaces.

Composites Made by Nonwoven Mat Technology. Numerous articles and technical papers have been written and several patents have been issued on both the manufacture and use of nonwoven fiber webs containing combinations of textile and cellulosic fibers. This technology is particularly well-known in the consumer products industry. For example, Sciaraffa and others have been issued a patent for producing a nonwoven web that has both fused spot bonds and patterned embossments for use as a liner material for disposable diapers. Bither has found that polyolefin pulps can serve as effective binders in nonwoven products, many additional references could be cited in this area.

Research and Development Needs

At the FPL and the UW, we are conducting a program aimed at developing technology to convert recycled wood fiber and plastics into durable products that are themselves recyclable, are environmentally friendly, and will remove the raw materials from the waste stream. This program is being conducted in cooperation with the U.S. Environmental Protection Agency. In support of this goal, we have defined a number of research and development needs.

Chemical Modification of Wood Fiber

The wood composite industry has an opportunity to follow this trend and greatly expand markets for new materials based on blends and alloys with other materials. The research program at the Forest Products Laboratory is focusing on wood fiber/plastic blends and alloys in an attempt to produce materials with consistent, uniform, continuous, predictable, and reproducible properties.

The purpose of this paper, is to present some of the initial results in the area of wood fiber thermoplasticization. The wood fiber is a composite made up of a crystalline, thermoset polymer (cellulose) in a thermoplastic matrix (lignin and the hemicelluloses). The melting point of the thermoplastic matrix is too high to allow this phase to flow at temperatures that do not degrade the wood fiber. If the glass transition temperature of the thermoplastic matrix of wood is reduced through chemical modification, it is possible to plasticize the wood fiber allowing it to become more thermo-formable through thermopressing, extrusion, or injection.

Experimental Procedure

Esterification Procedure

Modification of the fibers using maleic (MA) and succinic (SA) anhydrides was performed using the following procedure. Hot xylene was saturated with each of the anhydrides in a reaction vessel. When reflux temperature was reached, the aspen fiber was added and allowed to react for different lengths of time to give different levels of chemical weight gain. Excess anhydride was removed by Soxhlet extraction of the esterified fiber with xylenes for four hours. Excess xylene was removed by evaporation and then the fiber was oven dried overnight.

Analyses of Esterification Products

FTIR spectroscopy was performed using a Nicolet 6000 Spectrophotometer. Samples of each modification were dried, ground, and mixed with potassium bromide in a ratio of 1 mg; 200 mg and pressed under a vacuum to form pellets. Absorbance was measured over a range from 4000 cm^{-1} to 400 cm^{-1} with air as a reference.

Scanning electron micrographs (SEM) were taken with a Jeol 840 scanning electron microscope. All samples were coated with gold. A magnification of 750x was used.

Acetyl contents were determined by saponifying the acetyl groups and using gas-liquid chromatography (GLC) with propionic acid as a standard. The ester content of the MA and SA modified fibers were calculated from the acid and saponification values using a similar technique to that used by Matsuda. Titration of the free carboxyl groups in the esterified wood fiber and in ester groups saponified from the esterified wood fiber gave determinations of the ester content based on the acid and saponification values and indicated whether the anhydride added as a monoester or diester.

Board Formation

Five percent of a liquid phenol-formaldehyde (PF) dryprocess hardboard resin (GP2341.50% aqueous solution), was sprayed onto the esterified fiber followed by attrition milling to distribute the resin. The fiber was hand formed into a mat approximately 15 by 15 cm and then pressed in a heated Carver press at 190°C for 10 minutes to a predetermined thickness of 6 cm and specific gravity of 0.7. For the no resin boards, controls AA, MA, and SA modified fibers were hand formed into fiber mats and pressed in a heated Carver press at 210°C for 5 minutes at 8.5 MPa (board pressure).

Board Testing

Moisture sorption

Fiberboards were cut into 5 by 5 cm specimens and placed in separate rooms at 27°C and 30, 65, or 90% relative humidity. Each specimen was weighed at the end of 21 days and the equilibrium moisture content determined. Triplicate samples were done and the results averaged.

Esterification of Wood Fiber

Figure 1 shows the extent of modification achieved with the three types of anhydrides based on a molar addition. The reaction with AA results in the splitting out of byproduct acetic acid during wood esterification while the reactions with MA and SA result in 100% anhydride carbon skeleton added to the wood. MA showed a much lower reactivity than SA which has the same structure except for the double bond in MA. A possible explanation for the molecule into the cell wall as well as the instability of the reactivity MA chemical intermediate.

Moisture Sorption of Esterified Fiberboards

Figure 2 shows that the equilibrium moisture content (EMC) of the esterified fiberboards is independent of the type of esterification, but is dependent on the molar gain of reacted ester in the wood fiber. A reduction in EMC was seen for each esterification as the level of modification was increased.

Rate and Extent of Swelling of Fiberboards in Liquid Water

Figure 4 shows the rate of fiberboard swelling in liquid water at equivalent levels of anhydride modification. While control boards swelled almost 25% in thickness in the first 20 minutes, all types of esterified boards

swelled less than 10%. AA reduced the swelling to less than half of the control specimens while MA and SA modifications reduced the swelling further. The reduction in swelling can be attributed to the bulking of the cell wall and the reduction in hygroscopicity of wood especially with the larger MA and SA molecules.

Delignification of Wood with Pernitric Acid

Organic peroxides such as peracetic and performic acids will effectively delignify wood and other lignocellulosics. The use of performic acid as a pulping agent is under active investigation. We recently found that the inorganic peroxide, peroxymonosulfuric acid, will readily delignify these materials. Hydrogen peroxide is quite ineffective, however. On the basis of these findings, it seemed highly likely that other inorganic peroxyacids might also be effective in delignification. Consequently, we initiated an exploratory study on delignification of wood with other inorganic peroxyacids.

On the basis of this consideration, we decided to study the possibility of delignifying wood with pernitric acid. We chose finely divided aspen wood as the substrate for study because it delignifies easily. Success with aspen delignification would suggest further pulping studies.

Generation of pernitric acid

There are several methods for preparing pernitric acid. We initially chose the method described by Kenley, Trevor, and Lan that uses only concentrated hydrogen peroxide and concentrated nitric acid. Several attempts at generating pernitric acid by this method were unsuccessful. After adding a drop of peroxide to the chilled nitric acid in an ice bath, a puff of yellowish-brown vapor would occur after a fraction of a second. Apparently, when the drop of peroxide mixed with the acid, some pernitric acid formed and then immediately decomposed to nitric acid and oxygen.

On the basis of the large variability of the data and the ease of obtaining explosive mixtures, it appeared that pernitric acid was quite unstable and would readily decompose, especially at higher concentration. If decomposition of pernitric acid in dilute aqueous was too rapid, it might possess little ability to function as an oxidizing agent. It would therefore lose the ability to degrade the lignin in wood. Because of this consideration, we performed some experiments on the decomposition of pernitric acid in dilute aqueous solutions.

Decomposition of pernitric acid

We generated pernitric acid by adding 1.35 g of chilled (from a refrigerator) 70% hydrogen peroxide to 4.0 g 90% nitric acid in a vial in an ice bath. After 60 min, the mixture was diluted with 24.6 g of distilled water. The solution was then analyzed and was 0.68 *m* (5.4%) in pernitric acid. The total acidity of the solution was 1.93 *m* based on the input of nitric acid. Half the solution remained at room temperature (22°C) and the remaining half at refrigerator temperature (6°C) with periodic analysis of each of the two samples.

Delignification of aspen wood

The generation procedure used in the decomposition work produced a 5.7% solution of pernitric acid. Then 25 g of this solution was added to 1.00 g (o.d. basis) of finely divided aspen wood (passing a 40-mesh screen, 6.0% moisture). The mixture was held at 22°C for 305 min. The liquor was drained from the solid residue. The residue was washed thoroughly with RO water, and air-dried. The residue was dried in a vacuum oven overnight at 60°C and its yield was determined. It was then analyzed for lignin content, and its 0.5% cupriethylenediamine (CED) viscosity was determined. Because the residue was not completely soluble in the CED solution, it was delignified using the chlorite procedure given in the Experimental section.

Rosin and Rosin Derivatives

Rosin is a complex mixture of mainly resin acids and small amount of non-acidic components. Its colour, depending on the source and method of processing, can vary from a water white through dark red to almost black, with a tinge of red. It is generally translucent and brittle at room temperature. The other properties which are of importance in judging the quality of rosin are acid value, saponification value, softening point,

and unsaponification value,. However, entire rosin is sold and purchased on the colour basis, the lightest colour bring the highest price. Opacity in rosin some times degrades its value, Sometimes rosin is upgraded to get better market price.

Composition

Resin acids are monocarboxylic acid having typical molecular formula $C_{20}H_{30}O_2$. The structural formulas of all the known resin acid are shown in Fig.1, which may be divided into abietic and pimaric type. The pimaric type resin acid differs from those of abietic type, in that they have two alkyl groups in the C-7 position in the place of isopropyl group. When double bond occurs in one of these alkyl groups, it can not conjugate with a cyclic double bond. Consequently the double bonds in pimaric and isopimaric acid are not conjugated and so not very reactive.

Reaction and derivatives

The resin acid molecule possesses two chemically reactive centers, the double bonds and the carboxyl group. Through these, many modifications in structure and numerous derivatives are obtainable. Abietic acid is customarily and conveniently used to exemplify the structural and chemical reaction products, constitute the bulk of commercial products. Although the molecular weight of pure acid is 303, for rosin, the value is usually taken as 340 due to the presence of neutral for calculation in involving carboxyl group.

Isomerization

Pure resin acids of the abietic type are isomerized thermally or by treatment with dilute mineral acids. The equilibrium mixture from the mineral acid isomerization of levopimaric acid was 4% palustire, 93% abietic and 3% meoabietic. The equilibrium mixture of a thermally isomerized levopimaric acid was 13% palustric acid, 80% abietic acid and 7% meobietic acid. Methyl abietate isomerised to give the same equilibrium distribution as abietic acid. A major difference between the two was an extensive disproportionation reaction that occurred with the ester.

Photosensitized oxidation

An alcoholic solution of levopimaric acid containing a sensitizing dye, e.g., methylenes blue, readily absorbs one mole of oxygen, when contacted with air, to produce quantitatively a peroxide, 8,12-peroxide-13,14 dihydroabietic acid, by 1-4 addition.

Hydrogenation

Hydrogenation is one of the more satisfactory methods for decreasing the susceptibility of rosin to air oxidation. Because of the structural features of the resin acids, however more vigorous conditions are necessary than with ordinary olefins. Reduction with heavy metals and mineral acids or with sodium amalgam and water, accomplishes only incomplete hydrogenation, even for one double bond. On the other hand molecular hydrogen, in the presence of noble metal catalysts, such as palladium or platinum, will saturate one or both double bonds, depending on the polarity of the solvent employed. By taking advantage of solvent effect, the desired selectivity can be obtained with palladium carbon catalyst.

Hydrogenless Hydrogenation

Resin acids can be hydrogenated by the transfer of hydrogen from sodium formate in the presence of water and a palladium carbon catalyst. The primary product are the dihydro derivatives. Incorporation of a polar solvent (Methyl tertiary butyl in the solvent increases the reaction rate. Although methyl neoabietate hydrogenates faster than abietate, the initial rate of formation of the dihydro compounds is practically the same, same isomerization to methyl abietate (maximum about 25%) and slight dehydrogenation to methyl dehydroabietate occur. The reaction product distribution is essentially the same as for abietate: only trace amounts of 13(15)-abietate are produced.

Polymers of vinyl esters of hydrogenated rosin

Vinyl esters were prepared and homopolymerized in emulsion and copolymerized with vinyl acetate, vinyl chloride, and butadiene and thus compared to vinyl tetrahydroabietate (VTA) and vinyl dehydroabietate

(VDA).

Prehydrogenation

One of the double bonds of rosin acid containing conjugated unsaturation, such as abietic acid, and the exocyclic double bonds of dextropimaric and isodextropimaric acids are easily reduced. The endocyclic double bonds of dihydroabietic acid and pimaric acids are more difficult to hydrogenate, but they can be reduced over a nickel catalyst, under severe conditions. Dehydro abietic acid, which contains a highly hindered aromatic ring, cannot be reduced at a practical rate over conventional catalyst.

Dehydrogenation

The dehydrogenation reaction is the second means of effectively modifying rosins to render them less susceptible to oxidation by atmospheric oxygen. Part of the hydrogen that is removed is readily absorbed by the pimaric type acids, present in rosin, to produce the stable dihydropimaric acid. Because of the absorption of a part of the hydrogen, this reaction frequently has been described as a disproportionation. However, the appearance of only 2-3% of dihydroabietic type acids and the absence of tetrahydro abietic acid, show that the disproportionation of the abietic type acid is not involved.

Thus disproportionated rosin is chemically stable, thermoplastic resin, by the loss of conjugation or aromatization of the molecule. This treatment converts its total oxidation prone AA content to highly stabilised forms of resin acids, predominantly dehydroabietic acid. As a result this DPR has a much greater resistance to discoloration, embrittlement, and other effects of oxidation than do pale grades of ordinary rosin. This improved oxidation resistance, together with a wide compatibility with polymeric thermoplastic and elastomeric materials, makes DPR especially suitable as an ingredient of hot melt applied adhesives and coatings for paper and paper boards substrates, and as a tackifier and processing aid for rubber based adhesives and molding compounds.

Polymerization

In any application only reduction in acid value of rosin does not satisfy the performance requirements of coatings. Rosin (abietic acid) possesses active conjugated dienoic unsaturation, which is very much susceptible to oxidation by atmospheric oxygen. Thus, when exposed to air, rosin and its derivatives undergo discoloration to develop ultimately dark brown colour, On oxidation rosin becomes more brittle and friable and changes its solubility characteristics. Enhanced performance of rosin derivatives with their pale colour and good colour retention properties is obtained by proper nuclear modifications of rosin, such that the oxidation susceptible unsaturation in rosin is reduced to a greater extent or completely eliminated by definite chemical reactions such as polymerization.

Phenolic modification

The phenolic modified rosin is made by adding to the hot rosin either the phenol formaldehyde condensate or the phenol and the formaldehyde separately. The phenols commonly used are bis-phenol, phenol and creasols. The phenolic modified rosins are usually further modified by esterification with glycerol or pentaerythritol.

The condensation reaction is an addition reaction that takes place between the methylol phenol and rosin or rosin esters. These esters are used in oil soluble varnishes.

Salt formation

With unsaturated cyclic and acyclic hydrocarbons

Metal salts of the condensates of resin with unsaturated hydrocarbons, which salts are particularly valuable for use in protective coatings such as varnishes, having excellent bodying and drying characteristics and forming harder films of improved water resistance.

Drier metal salts of this rosin-butadiene condensates were prepared by heating the condensate to 235°C and then gradually adding, with intermittent stirring, during a period of about 40 minutes, the metal salt, while simultaneously increasing the temperature to about 320 °C. The hot, highly viscous resins was then

cooled to room temperature and analysed.

With pentaerythritol and other polyhydric alcohols

Glycols and diethylene glycols are also used to prepare esters by heating rosin at 20-260°C in the presence of zinc, or boric acid catalyst. The unreacted alcohol is removed from the ester at 300°C under reduced pressure. One of the glycol ester is prepared by the reaction with rosin, diglycol and acetic acid. The PVC sandals made from these esters can fully meet the international specifications.

Hydrogenolysis

Rosin has been successfully hydrogenated to produce the hydroabietyl alcohol of commerce. The alcohol may be produced by the hydrogenation of the methyl esters of rosin at 300°C and 5000 psi, in the presence of copper chromite catalyst. With soluble film formers, such as casein and zein, the alcohol is used to impart improved tack, colour and stability. Hydro abietyl alcohol produces esters with a wide range of physical properties, when reacted with organic and inorganic acids.

Polyesterification

Unsaturated polyester modified rosin (UPER) are prepared by reacting first with dibasic acid glycol, maleic anhydride and then with rosin.

The mechanical and physical properties of the castings, prepared by copolymerization with styrene are good to excellent when compared with accepted values of commercial styrenated polyester cast resins. Foams prepared from these polyesters shows promising use in garments as a fabric-foam laminated. This has been due to their ability to be flame taminated directly to the fabric without the use of an adhesive.

Copolyesters

(Copolyesterification) copolysters belongs to broad class of organic high molecular weight compounds, which are formed by repeated esterification reaction. They constitute one of the most important class of plastic material. The great scope lies in the powder coatings, solventless convertible coatings, aqueous coatings etc. The film properties of these polysters have high dimensional stability against change in temperature.

Ammonolysis

The action of ammonia on dehydrogenated rosin at elevated temperatures, yields a nitrile. It is a pale yellow, waxy solid with softening points about 65°C, containing 85-95% of nitrile from which the nitrile of dehydroabietic acid can be crystallized with mp 87-90°C. It is used in the production of Amine D, by catalytic hydrogenation at elevated temperature and pressure. The amine is relatively weak base that forms salts with both mineral and organic acids, at room temperature, in suitable solvents or at elevated temperature.

Preparations

Dehydroabietylamine acetate

To a solution of 2.85 kg. of Amine D dissolved in 4.71 lit. of toluene was added a solution of 654 g. (10.8 mole) of glacial acetic acid in 1.56 lit. of toluene. The solution was stored at 10°C for 2 hour. The crystalline salt was collected, washed with cold toluene and recrystallized from 4.23 lit. of boiling toluene. The colourless crystals were collected, washed several times with n-pentene and air dried to obtain 1.365 kg. (78.5%).

Methods of preparation

Sulfuric acid catalyzed condensation of abietic acid with formaldehyde: Abietic acid, 10 g. (0.033 mole) of formaldehyde (as paraformaldehyde) were suspended in 50 ml. of purified dioxane. On addition of 3 g. of conc. Sulfuric acid, the solution became homogeneous, and the temperature rose spontaneously to 60°C. The darkened solution was maintained at 60°C for 0.5 hr. On addition of 300 ml. of water, a cream coloured precipitate was formed which was thoroughly washed with water and dried in vacuum at 50°C. Experiments similar to that above were run using 2,3 and 5 moles of formaldehyde per mole of abietic acid.

These products showed neutral equivalent values of 357,394, and 419, respectively. The product from condensation of abietic acid with 2 moles of formaldehyde showed no maximum in the region 220-285 μ .

Nitrogenous intermediates

The chlorosulphonyl isocyanate, acrylonitrile, fumaronitrile, benzoquinone, tetracyano ethylene, and many dinitrile and diamine adducts of levopimaric acid are reported here. Diamines and isocyanates from rosin have found many industrial applications, such as polyurethane, ingredients for adhesives and corrosion inhibitors.

The Polymerizable Half Esters of Rosin

This communication is concerned with the partial esters of the polymerizable rosin adducts which have at least two carboxyl group. They are some times referred to as half esters, but in at least one case a trivalent acid is involved. Although they are quite well known, but there is little information published in the literature to coordinate their behaviour and properties.

The specific interest of the partial is that while maintaining acid functionality a wide gradation of properties from hydrophilic to hydrophobic can be obtained and also differential solubilities in various solvents. These properties are transmitted to various copolymers which may be formed from them, dependent on the amount of partial ester included and the nature of the alcohol radical.

Experimental

All the chemical used are of comical type.

Preparation and properties of monomers

The simplest method of preparing the rosin ester is by reacting a stoichiometric quantity of the requisite alcohol with an adduct being by far the most utilized in this respect. The general object is to avoid simultaneous formation of the diester and free acid.

Maleic rosin esters: Maleic rosin is refluxed with absolute alcohols until the conversion to monoester is complete. Rp increases rapidly with temperature till 80oC and is constant to 120oC. Heating above 80oC tends to cause diester formation. Phenol methyl isohexyl alcohol and tert-butanol react slowly. The above experiment was carried out under pressure. Purification of the H rosin esters may be effected by first neutralizing the ester with sodium carbonate solution. In order to remove diesters, the sodium salt is extracted with the solvent. At 25oC, esterification to the half ester in acetone is extremely rapid. Secondary alcohols fail to esterify. Preparations are as flows.

Polymerization & Copolymerization

General and non-aqueous: The dibasic do not, except under special and rather drastic conditions, homopolymer, but they are normally copolymerizable although with rather low reactivities. The anhydride salt, especially maleic rosin, can be made to homopolymerize under drastic condition, but they copolymerize very readily with a strong tendency to alternate, e.g., with vinyl acetate or styrene. The diesters of the dibasic adducts copolymerize readily with vinly esters, e.g., vinly acetate, but the reactivity ratios are somewhat unfavourable for monomers such as styrene.

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