Part III.
Products From Nontraditional Crops
How Crops Can Provide Raw Materials for the Chemical Industry

Nature has produced an estimated 300,000 different plant species, of which we use only a few hundred in organized agriculture. In 1957, USDA initiated a program that collected plants worldwide from a number of sources. The idea was to take a close look at these plants chemically and see if any new and different materials in them could be useful to humanity.

About 8,000 different species were collected, most of which had never been examined before. Their chemical compositions were analyzed for potential sources of starch, protein, oil, fiber, gum, and medicinal components, as well as for any special individual characteristics. For example, researchers found over 100 different, never-before-discovered oils.

This effort to utilize new species, as well as to develop new uses for traditional crops, is possible because nature offers renewable, reliable “living factories” for an incredible array of chemical materials.

Agriculture in the United States is accustomed to identifying crops as specific commodities (corn, soybeans, cotton, etc.) in relation to the traditional food, feed, and fiber markets. To fully explore potential uses of a crop, we must view it not simply as a commodity but as a complex raw material that has specific functional groups suitable for producing industrial products. The utility of a given crop as a resource for the chemical industry depends upon the chemical composition and structure of the materials found in that crop.

All crops are made up of many types of materials. For example, the corn plant has starches, oil, zein (protein), and a number of lesser components in each kernel. The cobs and stalks contain cellulose (a long chain, or polymer, of sugar molecules containing six carbon atoms), hemicellulose (a polymer of sugar molecules containing five carbons), and lignin (a polymer made up of six-member carbon-hydrogen rings). Each of these materials contains chemically distinct structural units that can react with other chemical structures to form new...
materials. These reactive chemical units are referred to as the "chemical functionality" of the material.

Its specific chemical functionality is the basis for each material's use as an industrial resource. For this reason, when we consider industrial uses for both traditional and nontraditional agricultural products, we group crop resources in terms of their primary materials: starches, oils, proteins, lignocellulosics, and other natural products such as naturally derived chemicals. We will examine in more detail the functionalities and uses for three of these materials: oils, starches, and lignocellulosics.

**Vegetable Oils**
A major ingredient in many plants is the oil that can be extracted from their fruits or seeds. Seed oils have been used for millenia as an energy component of food—and almost as long in nonfood applications. The ancient Egyptians used castor oil in their paints and as a lubricant, and Biblical passages refer to olive oil as a source of fuel in lamps.

Seed oils from traditional crops such as soybeans, corn, cotton, coconuts, and flax provide raw materials for many of the products that we use every day. From the soap we wash with, to the grease we use to lubricate our automobiles, combines, and military equipment, vegetable oils are a prime ingredient. In addition, a number of new crops, such as crambe, rapeseed, lesquerella, and others, produce oils with unique compositions. The oil from these new crops is used

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New crops, such as lesquerella, produce oils with unique compositions that are opening up new applications as raw materials for products from lubricants to cosmetics.

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for products ranging from lubricants to plastics and from cosmetics to industrial chemicals.

Seed oils consist primarily of a chemical form called a triglyceride. These triglycerides are liquids at room temperatures and insoluble in water. Some triglycerides are stable at high temperatures because they are either saturated (nonreactive) or partially unsaturated (somewhat reactive). These oils, used in cooking, include corn oil, peanut oil, safflower oil, olive oil, and sunflower oil. Others, with high levels of chemical unsaturation, are valuable either because they are chemically reactive or because they contain unusual chemical structures.

Vegetable oils can react with other materials to form either a much thicker liquid (a lubricant) or solids. The oils can be used directly for dust control or as carriers for pesticides. Alcohols such as methanol or ethanol can react with the oil’s triglyceride to give what is called a fatty acid ester, which is useful, among other things, as a substitute diesel fuel. Vegetable oils can be converted to glycerol (used in cosmetics, synthetic fibers, explosives, etc.) and fatty acids through the chemical addition of water to the triglyceride.

The fatty acids of soybean oil and tall oil (from wood, primarily pine) are used to make materials included in hot-melt glues and in the curing component of epoxy glues, while the fatty acids in coconut oil are the major ingredient in soaps and detergents. Other uses for fatty acids include fabric softeners, cosmetics, plastics,
paints, coatings, inks, antifoaming agents, minerals processing agents, and mold release agents in foundries. In short, whether we realize it or not, we use vegetable oils in our everyday life for many things we would be hard pressed to do without.

Many new uses of seed oils are now being developed to take advantage of their natural functionalities. Soybean oil has been modified to replace petroleum in inks for newspaper printing. (The 1991 and 1992 Yearbooks of Agriculture were printed with soy ink.) A number of nylos based on oils from other crops, particularly nylon-11 and nylon-13,13, are being evaluated for use as engineering plastics in the automotive industry. New, flexible coatings and paints can be made from rapeseed and crambe oils.

The functionality of each oil is unique. The fatty acids in each oil are different, and therefore each oil’s ability to react is different. The unsaturated bonds in the fatty acids that make up the triglycerides are reactive; that is, they can combine with other chemicals easily. So, when we deliberately add oxygen, sulfur, or phosphorus to the unsaturated bonds in a triglyceride, we can make a lubricant, a rubber additive, or a wax. The reactivity of unsaturated bonds in fatty acids also leads to the production of raw materials necessary in the manufacture of nylos, polyesters, waxes, and other products.

The natural structure of seed oils allows us to create unique products for use in all facets of our daily lives. In some of the chapters of this yearbook, you can find more complete descriptions of how scientists are searching for new oil crops while, at the same time, pursuing new uses for several of the seed oils.

**Starches**

Traditionally, we view corn, potatoes, tapioca, rice, and wheat as foods for human and animal consumption, not as sources of a naturally occurring starch. But these food items are important sources of industrially useful starch, a polysaccharide (“many sugars”) consisting of a long chain of individual glucose (sugar) units.

Today starch is an important raw material for the chemical industry. For instance, the paint and coatings industry has utilized starch and its derivatives as stabilizers and flow modifiers for latex paints and other water-dispersed coatings. Starch is also used as a binder in explosives, for example for fireworks and industrial applications. Starches can be acidified, dried, heated, and cooled to produce either British gums or white and yellow dextrins, which are used as adhesives. The specific nature of the product is controlled by the processing.

Unmodified starch has been used for many years to size textiles. Sizing consists of passing a yarn through a solution of starch to deposit a coating of starch over the surface of the yarn to bind individual fibers into a smooth strand. After heating to dry the sizing agent, the coated or sized yarn is ready for weaving. During weaving, a yarn is exposed to abrasion and tension, and sizing provides abrasion resistance and strength for the fibers.

Starch is commonly used in a wide
variety of adhesives, particularly those designed to bond paper to itself, glass, or other materials. It is also useful for binding mineral wool in ceiling tiles and for binding clay in ceramics. The overwhelming majority of all starch used for adhesives is used in the production of corrugated board. Other applications are in the manufacture of paper bags, bottle labels, gummed tapes, envelopes, and a variety of poster pastes or billboard-type applications. Starch-based adhesives are the materials of choice for wallpaper and other pasting operations requiring the alignment of patterns and edges.

The structure of starch can be modified or changed by a number of chemical reactions. Among them is the reaction of starch with dithiocarbonic acid to make what is called xanthated starch. Applications for xanthated starch include wastewater treatment, slow release of volatile chemicals such as pesticides, fillers for powdered rubber, and papermaking.

Modified starches are used extensively in the paper industry. The starch acts as a binder for paper to enhance its dry strength and imparts desirable water retention properties that prevent excessive dewatering during the papermaking process. Modified starch is also used to thicken coatings used on paper so that they are smooth and nonsagging. This application is similar to using starch as a thickener in cooking a stew. Starch also is the “carbon” in carbonless paper.

Starch modified with monochloroacetate is called carboxymethyl starch and is used as an absorbent in adhesives, medical poultices, papermaking, coatings, dentifrice powders, and pulp refining and for making tablets, binders, and disintegrants. Carboxymethyl starch is also used for textile printing and as a component in film-forming mixtures. Other applications of carboxymethyl starch are as a thickening agent, flocculant (to enhance settling of suspended solids), antisoil-deposition agent (to help surfaces repel dirt), and chelating agent (to combine with dissolved metals).

Modification of starch to cyanooethyl-starch provides water dispersability, resistance to swelling, excellent adhesive properties, and increased fiber absorbency. Methyl starches are used as thickeners, protective colloids, soil-suspending agents, and detergent compounds. Ethyl starches are used primarily in the paper industry as a component of sizing formulations, a pigment adhesive, and for other specialty coatings.

Plastic is so widely used in all facets of everyday life that its disposal after use has become a serious problem. Many applications—food packaging, disposable plates and utensils, and medical items such as syringes—have a fairly short useful life and are not, or cannot be, recycled. Starch-derived materials that are truly biodegradable are leading candidates to replace nondegradable petroleum-derived plastics. The chemical functionalities of starch allow it to be used in the preparation of polymers that can be formed into films or solid shapes and that can retain their properties throughout the useful life of the products. When the starch-based products
must be disposed of, they can be consumed by microorganisms, for example in composting systems.

**Lignocellulosics**

By weight, the largest component of plant matter is lignocellulosic material—a mixture of cellulose, hemicellulose, and lignin. The relative amounts of the three lignocellulosic components depend on the type of plant and, to some extent, the age of the plant.

Traditional uses of lignocellulosic materials have taken advantage of their fibrous nature, which is a result of the long polymer chains of cellulose and hemicellulose. Common lignocellulosic materials are wood and paper pulp. In fact, paper is almost pure cellulose.

Cellulose and hemicellulose polymer chains can be hydrolyzed (a chemical process in which water is added, breaking the chains) into individual sugar molecules. These sugars can then be fermented into a number of commercially important chemicals through the action of yeasts and bacteria.

Because cellulose is a stable natural polymer, it is much more difficult to hydrolyze than hemicellulose, and its hydroxyl groups (bonded hydrogen and oxygen) react easily with other chemicals without destroying the basic polymer. This can be an advantage in making a number of important cellulose derivatives: cellulose acetate, which is used in photographic film and various coatings; rayon, which is used in textiles; and cellulose nitrates, which are used in explosives and Ping-Pong balls.

The least utilized component of lignocellulosic materials is lignin.

Lignins are highly complex polymers that consist of phenolic rings (six carbons in a ring with a hydroxyl group attached) that are connected by combinations of carbon and oxygen linkages. Lignins can react with sulfuric acid to produce a group of compounds called lignosulfonates, which are used as binders (in wallboard) and dispersing agents (in pigments).

Most of the commercially available lignin is a byproduct of paper production, which uses sulfur compounds to separate the lignin from the cellulose pulp. The lignin coproduct, called “black liquor,” is used as the primary source of carbon disulfide (a chemical intermediate in making other sulfur compounds) and dimethyl sulfoxide (an organic solvent). Sadly, though there is an oversupply of lignin, the most valuable structure within the lignin, the phenol ring, continues to be little utilized. Essentially all of the phenolic compounds in industry, including most synthetic dyes, are made from petroleum or coal, not lignin.

Finally, lignocellulosic materials can be viewed as the most abundant source of carbon-hydrogen-oxygen (C-H-O) compounds that we have. Through the processes of pyrolysis/gasification (thermal degradation in the absence of oxygen for combustion) and liquefaction (depolymerization into a variety of smaller compounds), it is possible to produce the equivalent of synthetic crude oil,
synthesis gas (a mixture of carbon monoxide and hydrogen), and synthetic natural gas. These materials, in turn, provide raw materials identical to those used in the existing petrochemical industry.

In summary, lignocellulosic materials are a resource that will always be produced at the same time that we are producing crops for food, feed, fiber, or chemicals. Wood wastes, harvestable field residues, and most food-processing wastes can be collected as sources of lignocellulosics. The chemical functions of lignocellulosics permit their use either directly as chemical derivatives or indirectly as a source of C-H-O compounds for further chemical synthesis. As a category of materials, lignocellulosics are one of the cheapest per unit weight as well as one of the most abundant renewable resources that we have.

Summary
Plants contain a host of compounds that are chemically useful in making industrial products. To develop industrial products, we need to think of plants not just as commodities but as "living factories" for chemical raw materials. The major materials present in all plants are the three described here—oils, starches, and lignocellulosics—and protein and naturally derived chemicals. Together, these materials are the source of a broad range of products from medicines to newsprint, from jet engine lubricants to lipstick.

Kenaf: Annual Fiber Crop Products Generate a Growing Response From Industry

"Don't put shade on it."
That is the only general crop management recommendation for the steadily increasing number of kenaf growers in areas of south Texas and southern Louisiana. They—along with newer groups of interested farmers in the Mississippi Delta, the plains of Oklahoma, the tidewaters of the Carolinas, and the valleys of California—are quickly learning that growing this annual hibiscus fiber crop is compara-