Non-Food/Feed Uses of Rendering Products: Identification of New Opportunities and Assessment of Major Barriers to Their Exploitation

Draft Final Report

Fats and Proteins Research Foundation
Research Project 01-B6

Submitted by

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I. Project Objectives:

a) Evaluate the opportunities for industrial uses of rendered products as raw materials on the basis of their intrinsic chemistry (lipid, protein, mineral). The new uses may come from substituting for another source of a similar material, by taking advantage of inherent properties of the material, or by new derivatives of the material. This evaluation will be based upon the existing patent and technical literature.

b) Perform a preliminary assessment of market size, price structure and growth trends for those segments that appear to offer the greatest opportunities for penetration of derivatives from rendered products.

c) Identify the most attractive potential applications, determine the major barriers to entrance of rendered products into the market, and recommend strategies to overcome those barriers. Examples of barriers include needed enabling technologies, technology demonstration, product certification, or regulatory issues.

II. Resource Evaluation

The strategy used to identify potential raw material streams for value-added products was to examine the overall material balance for existing rendering operations. This balance includes quantification of all materials input into the plant and identification and quantification of the effluent streams from the plant. The terms "quantification" of the "effluents" are important in the identification of opportunities for new products.

Renderers have been characterized as the "Original Recyclers". This clearly is true. The norm for the industry, however, is identifying products as they relate to entrants into the food chain or into the traditional oleochemical industry. The approach in this project is to reassess the same "effluents" as sources for industrial products.

A. Visits to Rendering Operations

An essential element of the work plan was visiting a number of different rendering operations, representing a sample of the categories of renderers. The categories that have been identified include:

- Beef rendered products
- Pork rendered products
- Poultry rendered products
- Beef slaughter/rendering
- Pork slaughter/rendering
- Others as recommended by the advisory committee

The visits completed to date have been to a pork renderer, a poultry renderer, a beef slaughter/rendering operation and a grease renderer. The material balance information has been normalized on the basis of effluent type per 100 pounds of raw material. The material balances must be reviewed by the plants visited before they are incorporated into the final reported results. The visits have helped identify some opportunities for diversion of effluent materials into non-food uses.

B. Candidate Effluents for Non-Food Product Uses

The non-food raw materials identified thus far include hard bone, "fugitive" protein (DAF float, waste water), keratin materials, and fats and greases. While none of these materials may be novel, they all can be diverted from the current product streams for other uses, some of which are novel.

The discussion for each material is organized in terms of the chemistry of the material, current and new uses for the material, and the enabling product development needed to determine the feasibility and potential value for the new uses identified.

III. Potential Product Identification

A. Hard Bone

Bone material is primarily a mixture of calcium phosphate and calcium carbonate, with a number of other minerals present. The calcium occurs as a mixture of hydroxyapatite (HAP) crystals and amorphous calcium phosphate. Hard bones have a larger fraction of HAP, which is the material of most interest in this study.

The largest fraction of hard bone is found in pork and beef leg bones. Poultry bones are essentially all soft bones. The typical disappearance of the hard bones is by grinding into bone/protein meal as a source of calcium and as a means of controlling the protein percentage.

The separation of the hard bone sources could take place at the slaughter facility or at the rendering plant. Hard bone processing could take place on-site or at a second-party facility.

Chemistry: HAP is a crystalline mineral that has the nominal formula $Ca_{10}(PO_4)_6(OH)_2$, with a stoichiometric (Ca/P) ratio of 1.67. There is considerable natural variation in the (Ca/P) ratio, ranging from 1.37 to 1.71. The calcium in HAP can be partially replaced by other metals, including lead, strontium, copper, barium, cobalt, iron, nickel, and platinum. It is not clear from the literature reviewed what the naturally occurring non-calcium metals are in pork or cattle hard bone. The literature reviewed to date makes it clear that an effective methodology needs to be developed to separate the hydroxyapatite fraction from the calcium phosphate fraction of hard bone.

Uses for Hydroxyapatite and Calcium Phosphate: HAP is a water insoluble, crystalline material. Its physical structure and its chemical properties make HAP useful as a catalyst, catalyst support, chromatographic packing material, enzyme immobilization substrate, and as a component for artificial bone reconstruction. Calcium phosphate is an important feed component for poultry, but is also used in artificial tooth and bone restoration and as a catalyst.

1. Catalyst Applications for Hydroxyapatite

The intrinsic properties of HAP that affect its catalytic performance are the Ca/P ratio and the ability to substitute other metals for part of the calcium without significantly changing the crystalline structure and properties. HAPs with a Ca/P ratio ≤ 1.67 act as acidic catalysts, while HAP with a Ca/P ratio > 1.67 behaves as a basic catalyst.

The literature reports a number of catalysts based on HAP with partial substitution of the calcium by platinum, copper, lead, strontium, barium, cobalt, nickel, and iron. The applications of HAP and substituted HAP as catalysts include:
- HAP and acidic HAP – partial oxidation of methane to CO and H_2 (e.g. for fuel cells); dehydrogenation of methanol to formaldehyde
- HAP with Pt, Cu, Co, Ni, or Fe – exhaust gas catalyst to remove NO_x, CO, and hydrocarbons
- HAP and metal basic catalyst (Ca/P > 1.67) – amination of alcohols
- HAP with Sr or Ba – dehydrogenation of propane to propylene
- HAP with Pb – production of ethylene from methane
- HAP as catalyst support for zinc, nickel, or copper chloride – conversion of aromatics to alkyl aromatics (reformulated gasoline and polymers)

Catalysts are at the heart of the petrochemical industry. Catalyst sales in refining are about $ 2.4 billion per year, with a 2 percent growth rate. There are only a few catalyst manufacturers, and they tend to do part of their own development, and to work with a number of university laboratories for the rest of their research.

Most of the functionalities noted above are applicable to the catalyst needs of the petroleum refining industry. In addition, the opportunity to offer a non-noble metal exhaust gas catalyst is

highly significant. The caveat with this application is that most of the technology has been developed in Japan, and there is a considerable patented prior art. However, the exhaust catalyst market is about $ 2.5 billion per year. Further development of HAP catalyst applications is a moderately risky, high payoff activity that should be pursued.

2. Column Packing and Support Applications for Hydroxyapatite

The availability of stable hydroxyl groups as a part of the HAP crystal structure makes it an ideal packing material for various chromatographic and immobilization applications. Among the applications noted in the literature are:
- Immobilization of enzymes
- Protein enrichment/recovery by column chromatography
- Ion exchange substrate

3. Biological Implant Applications for Hydroxyapatite

One approach used to make ceramics for restoration of teeth and bones is to use a mixture of whitlockite (crystalline calcium phosphate) and HAP. The use of hard bone as a raw material, in this case would be to separate the HAP and calcium phosphate fractions, then make the whitlockite, and then make the prosthetic ceramic.

Another method for using HAP is to create a polymer – mineral composite by precipitating the HAP onto polymer fibers. While polystyrene-co-acrylic acid polymer has been reported for this application, the most common polymer used is poly(L-lactic acid) fibers. In either case, the application is to use the polymer to create the shape needed for the prosthesis, precipitate the HAP onto the polymer fibers, and insert the prosthesis. Over time the polymer is absorbed and the HAP provides a matrix for the natural bone to grow into.

4. Enabling Technologies for Expanding the Use of Hydroxyapatite

Catalytic HAP is currently applied in the laboratory. The HAP is prepared by reacting $Ca(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2HPO_4$, dried at 120 C for 18 hr, and then heated at 500 C for 3 hr. The resulting solids are then ground to the desired size for the catalyst application. This is not a process that lends itself to extensive, commercial application.

The enabling steps that are needed to determine the potential for using hard bone as an industrial source of HAP catalysts are:
- Develop a method for separating HAP and amorphous calcium phosphate that can be economical at a large scale. This will probably be a selective solubilization of the calcium phosphate.
- Demonstrate equivalency of performance between chemically prepared HAP and recovered HAP in various catalytic and column packing applications. The most attractive application is as an exhaust catalyst, if a way to avoid a number of Japanese patents can be devised.

- Collaborate with one of the current catalyst manufacturers to evaluate the market for HAP-based catalysts for selected applications and, if indicated, to enter the market. The economic impetus for this approach is that a few companies control the world catalyst market, but typical catalyst costs are on the order of $ 3.00 to $ 10.00 + per pound. In the applications noted above, the annual volumes can be quite large.
- Collaborate with one of the column packing manufacturers to develop an assessment of the market niches that appear promising. The unit costs for these specialty packings are also rather high.

B.   Fugitive Proteins

The primary products from rendering operations are protein meals and tallows and greases. However, the processing of the feed materials involves large quantities of water that eventually is evaporated or sent to several levels of treatment. The water sent to treatment typically contains 4,000 – 15,000 mg/l of COD (majority protein) and 50 – 1,000 mg/l of grease. Much of the protein can be removed using a DAF system, with various practices employed to recover or recycle the DAF float. Given a value-added use, the "fugitive" protein can become a source of additional products and income to the renderer.

There are several potential application areas for the proteins as non-food products. These include:
- Protein-based adhesives
- Protein surfactants
- Protein films
- Miscellaneous Applications

1.   Protein-Based Adhesives

Chemistry: The key to the use of proteins in adhesive applications is the large number of chemical functionalities (groups that can form bonds) associated with the amino acids that make up the protein chain. Although most proteins are naturally coiled, they can be hydrolyzed or denatured into long-chain configurations that allow the functional groups to interact with other materials. The functional groups can then form both physical (attraction) bonds with the substrate material and/or can form true chemical bonds with functional groups found on the substrate. Mechanisms for using proteins as adhesives include:

- Gel penetration and setting;
- Protein-substrate bonding;
- Thermoset encapsulation; and,
- High-adhesion protein structures.

An example of gel penetration and setting is the use of collagen-based adhesives to bond porous materials together. The protein is suspended in warm water to form a gel. The gel penetrates the pores of the substrates, dries, and binds them together. The disadvantage of this adhesive

mechanism is that water resistance is typically poor. Casein and blood-based adhesives also depend on the gel-set mechanism to varying degrees. Hydrazine and/or formaldehyde can be used as a stabilizer to add water resistance (U.S. Patents 1,994,050; 2,668,154). Sales of animal (gel) based glues in 1948 were 168 million pounds, but the introduction of petroleum-based adhesives rapidly eroded their market.

Proteins such as casein and soy protein isolate can, after denaturation, form bonds with the functional groups available on substrates like paper or wood, bonding the wood or paper together. These materials have been in use since the 1800's and before. The adhesion, however, is not extremely strong and is subject to water degradation. A number of pretreatments, including alkali, heating, and trypsin modification have been used to improve the protein-substrate bonding. Modified protein systems have been employed for making coated paper for color printing of magazines, etc. (U.S. Patent 5,766,331, with patent citations back to 1871). In this application the ability to form a clear binding layer the hold the whitening agents to the paper is more important than high adhesion.

Another mechanism for forming adhesive bonds is to use an additional reactive agent that reacts with the adhesive (protein) to form a network polymer that encapsulates the material that is being bonded together. The result is an adhesive with greater strength and, typically, greater water resistance. Common co-polymerization reactants include di-isocyanates, oxiranes (di-epoxides), and urea-formaldehyde (U.S. Patents 4,282,119; 5,506,285; and 6,231,985).

A common product is wood composites, such as particleboard. Particleboard is made up of a very large polymer network that encloses the wood particles. This network is formed by first mixing a paste or solution of the protein and co-polymer mixture with the wood or pre-treated straw material. Then the total mix is subjected to high temperature and pressure to carry out the curing (polymerization) reaction. The resulting board typically performs comparably to urea-formaldehyde or phenol-formaldehyde boards, without the formaldehyde out-gassing.

A specialty chemistry unique to protein polymers is based on the Maillard reaction. This is a reaction between a protein and a sugar or a polysaccharide such as starch or cellulose to form a condensation polymer (U.S. Patent 5,371,194 [1994]). Sugar molecules have a number of hydroxyl groups that can form bonds with other reactive groups. The protein has a large number of reactive groups available. The Maillard reaction occurs naturally when bananas or apples are bruised and turn brown. When this reaction is applied to a wood or paper substrate, the resulting product is a very strongly bonded, network polymer that is water resistant. The composites have strength and weight properties similar to the phenolic resins used to mount electronic circuit boards.

Uses for Protein Adhesives: The largest adhesive market is for the production of wood products such as plywood or particleboard. Currently this market is dominated by urea – formaldehyde and phenol – formaldehyde resins. The phenol-formaldehyde resins are used primarily for outdoor applications, because of their water resistance. This same water resistance minimizes the emission of formaldehyde (a suspected carcinogen) from the composite.

Urea-formaldehyde (UF) resins are less expensive and are less water-resistant. Their primary use is as adhesives for indoor wood composite products. About 1 million metric tons of UF resins are produced annually in the U.S., with 61% used for particle board, 27% for medium density fiberboard (MDF), 5% for hardwood plywood and 7% for laminating adhesives. The market for particleboard is projected to grow 2.2% per year through 2006 to a total volume of 5.2 billion square feet. The market for MDF is expected to be relatively flat, with an expected output of 3.2 billion square feet by 2006.

The market opportunity for protein-based adhesives is the result of increasingly stringent restrictions on formaldehyde emissions from composite materials used indoors. The target market is the replacement of urea-formaldehyde resins with protein-based adhesive resins.

Much of the recent protein-based adhesive work has been done using soybean protein. The forms of the soybean protein that have been used include the crude protein, hydrolyzed soy protein, and soy protein isolate (SPI). The materials have been used neat, in conjunction with other linking compounds (methylene diphenyl diisocyanate (MDI), formaldehyde, etc.), and with saccharides.

The literature on soybean protein adhesives is extensive. However, important for this work is the fact that the literature, both conventional and patent, is silent with respect to the use of protein materials from sources such as stickwater or DAF float. In other words, the basic technology is available, but it needs to be demonstrated using "fugitive" rendering plant proteins. The clear competitive advantage is the opportunity for replacement of the expensive soy protein and soy protein isolate with denatured and hydrolyzed "fugitive" protein from the rendering facility. Replacement of 1 million metric tons of urea-formaldehyde adhesive resin with a current waste material is a compelling opportunity.

Enabling Technologies for the Use of "Fugitive" Proteins as Adhesives

The factors suggesting the recovery and use of "fugitive" proteins as adhesives are:

- In most cases the materials contribute a net operating cost to the plant;
- They constitute a relatively large stream; and,
- They are already isolated from the rest of the plant operation.

The steps needed to further determine the value of these materials as adhesives include:

- Work with one or more of the research groups with experience in soybean protein adhesive chemistries to perform a performance evaluation of rendered-based products with conventional adhesives in representative applications.
- Develop an economic estimation of the cost of using rendered-based adhesives and compare with conventional urea-formaldehyde and phenol-formaldehyde products.
- Develop data on comparative emissions between rendered adhesives and conventional adhesives in the same application.

- Develop partnerships with producers of particleboard products to develop market opportunities for the rendered adhesives.

2.   Protein-Based Surfactants

Chemistry: "Surfactant" is a contraction of the term "surface active agent". A surface active agent is a chemical that, as a result of its structure, is attracted to the interface between two phases of matter. For example, wax on the finish of a car presents a surface that repels water because there are no functional groups in the wax that will interact with the water. As a result, the water interacts with itself and forms droplets that tend to accumulate and run off of the surface. The albumin in an egg serves as a surfactant in making mayonnaise because it has functional groups that can interact both with the water and with the vegetable oil, keeping small droplets of both materials in a single phase.
Surfactants are characterized by their amphipathic structures, one part of the molecule will be lypophobic (not attracted to the solvent) and the other part of the molecule will be lypophillic (strongly attracted to the solvent). Since the predominant solvent in our world is water, we use the terms hydrophyllic and hydrophobic.

Proteins are macromolecular polymers of a number of amino acids. Each of the amino acids have a number of functional groups that can interact directly with two sides of an interface, or that can be derivatized with another compound to form an ampipathic structure. Often the derivatization of proteins or specific amino acids to make a surfactant is done with a lipid compound.

Surfactant Uses: Surfactants are used as wetting agents, foaming and anti-foaming agents, emulsifiers, and dispersion and aggregation agents. Detergents are specially designed surfactants used to separate oily or solid soiling materials from fabrics, solid surfaces and the skin. The total value of the surfactant market in the U.S. is $ 6 billion per year. It is growing at about 2.4% per year.

Surfactant production is dominated by synthetic surfactants made from petroleum. Surfactant production in the oleochemical industry is a distant second in magnitude. There has been significant consolidation in the industry through mergers and acquisitions and now there are nine global companies that dominate the market.

Protein-based surfactants are primarily used in the cosmetic and personal care industry. Most of the products use one or two specific proteins as components in the creation of a surfactant compound. The use of protein surfactants in cosmetics and personal care applications is well covered in **Protein-Based Surfactants**, by Nnanna and Xia (Dekker, 2001). Vegetable derived proteins are almost exclusively preferred in the personal care market

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Enabling Technologies for the Use of "Fugitive" Proteins for Surfactants

The surfactant industry is searching for "greener" surfactant materials and the overall market is very large. However, there is no impetus at this time to pursue development of uses for rendering "fugitive" proteins in these applications.

An extensive search of the patent literature resulted in a single citation relevant to this study. Lochhead, *et al.* (U.S. Patent 5,985,840) discloses a process for recovering precipitated proteins from menhaden processing stickwater. They indicate that the "protein preferentially absorbs at the oil/water interface", but offer no uses for the product.

3. Protein-Based Films

Chemistry: Films can be created from most thermoplastic (meltable) polymers either by blowing, casting, or molding. A blown film is made using a ring like that used for soap bubbles, but larger. Molten polymer is injected onto the ring, while air, or another agent, is blown through the ring. The result is a long cylinder of film that can easily be cut and sealed into bags, or made into a single film layer.

A cast film is made by laying a solution of the polymer dissolved in a volatile solvent on a flat surface. When the solvent evaporates, the polymer film is left. A variation of film casting is film molding, where the polymer or polymer solution is placed in a heated mold and formed into a desired shape.

Uses for Protein-based Films: There is a long history of natural protein films being used as meat casings. Other commercial uses include gelatin capsules, collagen casings, wound dressings and microcapsules. More recently, the search for biodegradable polymers for utensils, packaging and food wraps has generated considerable research and development activity.

Centers for development of protein film technology include Clemson University, Iowa State University and the University of Nebraska-Lincoln. The book **Protein-Based Films and Coatings** by Gennadios (Culinary and Hospitality Industry Publications Services, 2001) Reviews the state of the art for vegetable and animal protein film applications. Essentially all of these applications are in the food industry.

There is a growing body of technology related to the production and use of protein films made from soy protein. However, the likelihood of penetrating a primarily food market with "fugitive" proteins from the rendering industry seems remote. The animal-derived entries noted by Gennadios are based on collagen, keratin (wool), gelatin, and egg whites.
The patent search located two patents calling for the use of hydrolyzed protein as an ingredient for care of fingernails. Hydrolyzed animal protein is used in a fingernail rehydration device (U.S. Patent 4,943,462), while hydrolyzed soy protein is used as a humectant in a nail polish remover (U.S. Patent 4,824,662).

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One skin care formulation calls for hydrolyzed animal protein in an after bath "splash" (U.S. Patent 4,482,537). Soy protein isolate is used as a humectant/protectant in an aftershave formula (U.S. Patent 5,194,252). In both applications, the film casting ability of the proteins is used to create a protective, temporary protein barrier on the skin. Oxybutylated gelatin can be used as a protectant component in skin and hair detergent formulas (U.S. Patent 4,115,548).

Enabling Technologies for "Fugitive" Protein-based Films

There is a sizable body to information for soy-based protein films. It would be rather easy to apply the methods and information to rendering waste proteins. However, essentially all of the proposed applications are for food packaging and it is unlikely that the raw materials would be accepted. No research or development effort is recommended in this area.

4. Miscellaneous Protein Applications

Proteins and fluorinated proteins have been used to produce foams that can suppress vapor formation of non-polar hydrocarbons (U.S. Patents 5,824,238; 5,218,021; 4,460,480). These materials can be used in spill mitigation and fire suppression.

In an unrelated area of application, milk casein is an effective replacement for polyphosphate compounds in several detergent applications, including stain removal, conventional laundering, and preparation of cotton for dying (U.S. Patent 4,761,161). Polyphosphate replacement is a very large potential market, and there may be some opportunity for other animal proteins to enter this application.

There are also patents for the use of waste proteins for liquid plant food (U. S. Patents 6,080,222; 5,271,912; 5,904,946). Also disclosed is a methodology to convert leather tanning wastes into compressed composite materials through the incubation of the wastes with transglutaminase to create crosslinking bonds (U.S. Patent 6,200,789).

No patents or literature citations were found for utilization of meat and bone meal. Sadly, the two articles found that dealt with meat and bone meal were evaluations of the properties of the material in fluidized bed combustion. In essence, seeking to recover the fuel value of the products.

No specific areas for application development appear to be indicated in this area.

C.   Collagen and Keratin Proteins

1. Collagen and Gelatin Uses

Collagen is a fibrous protein that is abundant in all animals. Although there about twelve types of collagen, the most common is Type I, which is found in skin and tendon materials. Collagen

and gelatin have a number of industrial uses. The collagen market is about $ 300 million annually and the gelatin market is approximately $ 1.3 billion.

Collagen and gelatin have long been used as the emulsion substrate for the image-forming layer in photographic films. Similarly, collagen and gelatin products are used in the food processing industry as casings and wraps. Innovation in this area continues with new materials like collagen membranes from pig skins being used to make a wrapping film for hams and other food products (U.S. Patent 6,482,240).

The medical uses for collagen and gelatin are rapidly increasing in sophistication. Collagen sponge materials are being used for wound dressings, anti-microbial dressings and sealants. Collagen materials can be cast into three-dimensional structures to provide a matrix for tissue re-growth and for the repair or creation of internal organs (U.S. Patent 6,479,072). Specially prepared bone powder, when mixed with a collagen gel, forms bone putty that is used to repair bone defects and to promote new bone growth (U.S. Patents 6,458,375; 6,326,018). Unfortunately, concerns about interspecies allergens and, more recently BSE, appear to have eliminated ruminant derived collagens from medical applications. The medical collagens come from specialty sources, such as rat skin, or from recombinant mammalian cell production as represented by FibroGen, Inc.

There are a number of possibilities for broader industrial uses for collagen materials. For example, hydrolyzed collagen salts are active foaming agents. A recent use for a collagen foaming agent is as a component in a foamed cleaning solution used to clean the turbine blades in combustion turbine engines (U.S. Patent 6,478,033). The recent exploratory research project approved by FPRF noted potential applications collagen dispersions include flocculation and filtration aids, extraction agents, and aerogel insulation.

2. Keratin and Feathers

Keratin Chemistry: Keratin is any one of a class of fibrous proteins that serve as structural units for living tissues. Keratin proteins are major components of hair, wool, nails, hoofs and the quills of feathers. Keratin molecules are helical and twist around each other to form elongated strands. Cysteine is a major component of keratin proteins. The sulfur molecules in the cysteine amino acid easily form cross-linking bonds with adjoining protein chains, making a rigid aggregate that is difficult to hydrolyze.

The high cysteine content of keratin makes it an attractive material for the absorption of heavy metals from aqueous solution. In particular, waste wool from a carpet processor has been used to remove mercury from the wastewater produced by a chlor-alkalai plant. Other heavy metals are similarly attracted to the thiol functionalities in keratines. It is not clear from the literature that the heavy metal adsorption property of keratins has been exploited commercially.

Keratin materials can be partially hydrolyzed and/or derivatized to form a number of useful materials. Keraplast Technologies, Ltd. of San Antonio, TX, has disclosed a process to partially oxidize the disulfide bonds in keratin, forming water-soluble peptides. When these peptides are

neutralized and precipitated with a solvent such as methanol, the resulting solids are useful as a wound-healing agent (U.S. Patent 6,270,791).

The Keraplast process was then modified by directly neutralizing the sulfonic acid residues with a monovalent base. The suspension of oxidized keratin salts is dried and powdered. The resulting material is a hydratable, highly absorbent powder. The patent (U.S. Patent 6,316,598) notes that the keratin absorbent can take up from 10 to 13 times its own weight in water. This appears to be an effective water absorbent material. Keraplast has three additional patents disclosing medical applications for the absorbent keratin derivative (U.S, Patents 6,270,793; 6,274,155; 6,461,628). However, it does not appear that they have considered broader industrial applications of their process and product.

Feathers: There are about 4 billion pounds of feathers produced in the U.S. each year. Much of this production is converted into feather meal. Feather meal is partially hydrolyzed to make animal feed supplements and for use as a fertilizer (nitrogen source). Feather meal is also a significant export commodity.

There are numerous uses for feathers and feather derivatives. A patent search for the topic "feathers AND uses" for the period 1976 to the present returned 648 patents. A small listing of these patents and their topics is given in Table 1.

3. Enabling Technologies for Collagen and Keratin Proteins

The current FPRF research project is an appropriate investment in exploring new collagen uses. Keraplast Technologies should be approached to develop broader applications for the super-absorbent keratin derivatives, The superabsorbent industry is a $ 2 billion per year industry.

Table 1. Sample Uses for Feathers in Industrial Applications

Patent Title	Patent Number
Insulating composition	4,248,927
Method of improving the contaminant resistance of smectite clay by rewetting and impregnating the clay with a water-soluble polymer-impregnated clay	5,578,219
Fiber and fiber products produced from feathers	5,705,030
Oil coagulant products and methods for use therefor	5,837,147
Oil drip mat apparatus	5,957,241
Two part, reinforced, room temperature curable thermosetting epoxy resin compositions with improved adhesive strength and fracture toughness	6,248,204
Pest repellent compositions and articles and a method for preparing the same	6,475,504
Low density cellular concrete with accelerators for rapid hardening	6,487,545
Agents and method for producing temporary colorations of keratin fibers	6,494,923

D.   Fats, Oils and Greases

The fats, oils and grease (FOG) products from rendering constitute about 24 percent of the lipid, or triglyceride, resources used in the world. The primary use of these triglycerides continues to be for human and animal nutrition, but the use of these materials in industrial applications is growing, both in terms of volume and the diversity of applications. Non-food uses of triglycerides include applications in the following industrial sectors (total sector size – 1994):

- Plastics and Plasticizers   11.2 billion pounds
- Solvents   5.9 billion pounds
- Adhesives   7.5 billion pounds
- Surfactants   6.0 million pounds
- Agrochemicals   1.2 billion pounds
- Industrial Chemicals   4.8 billion pounds
- Lubricants   3.5 billion pounds

The primary raw material for the products in all of these categories is petroleum. However, there is a significant and growing utilization of vegetable oils and FOG materials in all segments of the industrial market.

The competitive advantages for rendered products in general, and animal fats and oils in particular for industrial applications include:

- Generally lower cost;
- Primary source for stearic acid, and major source for oleic acid; and
- Greater oxidative stability due to low polyunsaturate content.

The paper "Fats and Vegetable Oils: Feedstocks for the Renewable Biorefinery," included as Appendix A, summarizes a number of the derivative chemistries available for producing industrial products from these materials.

Nearly all of the examples represent uses based on soybean oil. However, many of the applications, particularly for lubricants, may well be enhanced by the simpler chemistry of tallows and lards. The need is for demonstration of these applications using animal triglycerides. There has been a very successful program at the University of Northern Iowa in developing soy oil based lubricants. Perhaps there is an opportunity to approach them to evaluate animal tallows or yellow grease materials in the same applications

Biodiesel: The industrial application for FOG resources that is drawing the greatest attention at this time is the production of biodiesel fuel, in the form of methyl esters. This application will not be reviewed here. However, it is essential to the industry to note that while biodiesel may

well be the largest potential market for FOG materials, it is the least valuable market for methyl esters.

The National Biodiesel Board sponsored a study of the non-fuel industrial uses of soybean oil methyl esters in 1997/97. The final report "Non-Fuel Industrial Uses of Soybean Oil-Based Esters," (Ahmed, Clements and Van Dyne, www.biodiesel.org/resources/reportsdatabase /default.asp All of the current and potential uses noted in the report are equally applicable to animal derived esters. The ester application areas described in the report are summarized in Table 2.

Enabling Technologies for Fats, Oils and Greases

It appears at this time that the most underutilized rendered FOG materials are poultry fats and greases. Tallows, along with palm oil, are the materials of choice for the oleochemical industry. Poultry fats do not appear in the end use market, and feed uses or yellow grease is threatened.

The opportunity exists for the rendering industry to build upon the extensive research investment made in soy oil industrial uses. This can be done by demonstrating comparable finished product quality for soy oil and yellow grease feedstocks.

Areas of opportunity include lubricants, solvents, and agricultural chemicals. In most of these cases the end product is a fatty acid derivative that does not depend on the origin of the acid. Clearly, this is the case for fatty acid ester applications as fuels and solvents.

More penetration of yellow grease materials into chemical applications will require tighter quality control of the grease product, or more robust pre-treatment processes to make the feed materials easier to handle in most conventional oleochemical processes. There will need to be close cooperation between the renderer and the end user. It may become more common for the renderer to be the end user in a more integrated process facility.

E.   Recommendations

This study is a survey of opportunities for expanding the industrial uses of the products and the current waste streams for rendering process plants. Moreover, the study is a starting point for developing a research plan for industrial uses for the Fats and Proteins Research Foundation. It is in the spirit of research planning that the following potential development directions are recommended for consideration.

High Impact – Moderate Risk Programs
- "Fugitive" Proteins for Wood Adhesive Applications
- Lubricants from Yellow Grease

High Impact – High Risk Programs
- Hydroxyapatite Catalyst Applications
- Superabsorbent keratin derivatives
- Polyphosphate replacement

Table 2. Opportunities for Industrial Applications of Fatty Acid Methyl Esters

Segment	Application	Segment	Application
Solvents		Ag Chemicals	
	Oil well drilling mud		Adjuvants
	Paint removers		Product enhancement
Surfactants		Industrial Chemicals	
	Fabric treatments		Printing inks
	Mineral and ore processing		Pharmaceuticals and cosmetics
	Slurry forming surfactants		Magnetic recording media
	Pipeline friction reducers		Miscellaneous fine chemical uses
	Specialty product applications		
	Enhanced oil recovery		

Appendix A

Fats and Vegetable Oils:
Feedstocks for the Renewable Biorefinery
(Paper Presented at the AIChE Annual Meeting, 1995)

Introduction

Oils and fats constitute one of the largest volume agricultural products traded in the world today. The world commerce in vegetable oils for the period 1993 - 1997 is an estimated 70.6 million metric tons, with an additional 19.9 million metric tons of animal fats and oils marketed (Anon., 1994). Although certain regions dominate in production of specific materials, the overall sources of production for fats and oils are distributed globally. The dispersion of resources, along with an established distribution and marketing system, makes the supply and pricing of oils and fats relatively stable. The predominant sources of fats and oils and their disappearance over the 1993 - 1997 period are shown in Table 1.

Oils and fats share the triglyceride structure shown in Figure 1. The figure indicates that each triglyceride molecule has three fatty acids connected to the glycerol backbone through ester linkages, although some oils have fatty wax esters instead. The hydrolysis of the ester bonds yields glycerol and free fatty acids or a wax made up of fatty acids and fatty alcohol esters.

$$
\begin{array}{ll}
\text{H} & \text{H} \\
\text{H - C - OOC - R}_1 & \text{HC - OH} \; + \; \text{HOOC - R}_1 \\
\quad | & \quad | \\
\text{H - C - OOC - R}_2 \; + \; 3\,\text{H}_2\text{O} \; \longrightarrow & \text{HC - OH} \; + \; \text{HOOC - R}_2 \\
\quad | & \quad | \\
\text{H - C - OOC - R}_3 & \text{HC - OH} \; + \; \text{HOOC - R}_3 \\
\quad \text{H} & \quad \text{H} \\
\\
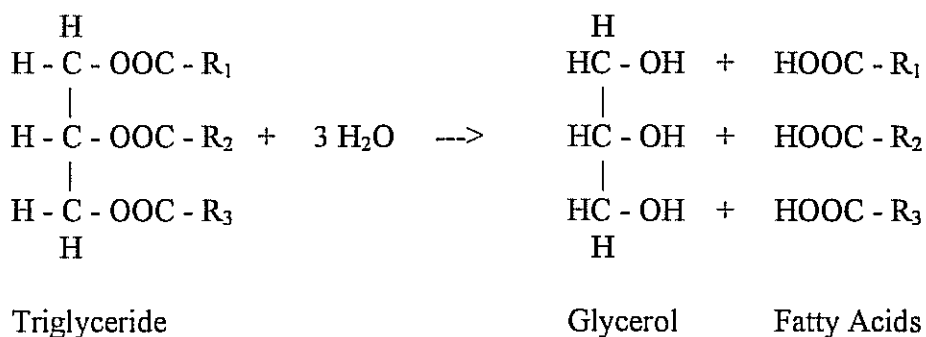\text{Triglyceride} & \text{Glycerol} \qquad \text{Fatty Acids}
\end{array}
$$

Figure 1. Triglyceride Structure and Hydrolysis Products

The sources of triglycerides are relatively interchangeable because of the limited number of fatty acids abundant in nature and the similarity in the relative fatty acid composition among the sources. This fact is illustrated in Table 2, with the comparison of the relative amounts of the most abundant fatty acids among major types of oils and fats. Important to the robustness of supply is the fact that there is only minor variation in fatty acid composition between the same fat or oil source from different points of origin.

The fatty acids noted in Table 2 offer a rich range of possible derivatives for applications ranging from solvents to surfactants to lubricants to polymers and coatings. This is due to the chemical functionality offered by the organic acid group and the unsaturated bonds present. However, it is important to note that there are several additional naturally occurring functionalities available in certain fats and oils. These include hydroxy fatty acids, epoxy fatty acids, fatty alcohols, and fatty wax esters.

This paper describes a number of chemical pathways for the modification and utilization of fatty acids for the production of industrial chemicals and polymers. The pathways encompass conventional derivative organic chemistry and both inorganic and enzymatic catalysis. The paper is organized by derivative families: triglycerides, fatty acid esters, and ester derivatives. Johnson and Fritz (1991) have already presented a comprehensive review of traditional fatty acid derivatives. The applications of these materials lie in several categories, which are noted along with the chemistry.

Table 1. Major Sources of Oils and Fats and Global Disappearance

Source	Annual Disappearance 1993 – 1997 (million metric tons)	Primary Production Regions
Palm	15.4	Malaysia, Indonesia
Soybean	17.9	United States, Latin America
Rapeseed	10.1	Europe, China, India
Sunflower	8.4	Argentina, Russia, India, Europe
Tallow, grease, lard, butter fat	18.7	United States, Argentina, Europe, Australia, Russia
Cottonseed	4.2	India, China, United States, Pakistan, Brazil
Groundnut (Peanut)	4.2	India, China, Senegal, Nigeria, United States
Linseed	0.6	India, Russia, Argentina, Canada

Table 2. Comparison of Fatty Acid Composition Among Major Oil and Fat Types

Oil Source	14:0	16:0	16:1	18:0	18:1	18:2	18:3	22:0	22:1
Palm	1.5	42.0	--	4.0	43.0	9.5	--	--	--
Soybean	--	11.5	--	4.0	24.5	53.0	7.0	--	--
Rapeseed	--	1.7	--	4.0	24.5	12.7	7.6	0.9	59.4
Canola	--	4.0	0.5	1.4	23.8	10.1	0.3	--	--
Sunflower	--	3.8	--	2.6	14.7	73.0	7.6	--	--
Tallow	3.1	25.2	4.3	20.1	38.8	2.0	--	--	--
Cottonseed	1.0	26.0	--	3.0	17.5	51.5	--	--	--
Groundnut	--	9.5	--	2.6	56.6	24.2	--	2.8	--
Linseed	*	*	**	10.1	20.5	23.1	45.9	--	--

* 18:0 value is sum of 14:0, 16:0, 18:0, and 20:0
** 18:1 value is sum of 16:1, 18:1, and 20:1

Triglyceride Derivatives

The largest application of fats and oils in the triglyceride form is for cooking, either as a heat transfer medium, or as a consumable. Fats and oils are an essential part of the human diet, and are used as an energy source in animal feeds. The original basis for the production of most oilseed crops is for their food use, but 28 percent of all fats and oils used in 1992 in the United States were used for non-food applications (USDA-ERS, 1993).

Some direct applications of fats and oils include spraying on grain to reduce the dust created by abrasion during conveying and the use of oils as a carrier solvent for herbicides (Kapusta, 1985). The rather high melting temperature of tallow (beef fat) allows it to be sprayed onto hay rolls, where it forms a water repellent layer that protects the hay from winter weather.

Fats and oils have been used for centuries as fuels, primarily for lighting. More recently, the fuel used in the first diesel engine was peanut oil. Indeed, it apparently was Otto Diesel's expectation that diesel engines would always be vegetable oil powered. Modern compression ignited engines can be fueled by whole vegetable oils, but they experience operating problems after extended operation (Ryan, et al., 1982; LePori, et al., 1992 a,b). One approach to permit the use of whole oils as a diesel fuel is the formation of microemulsions stabilized by mixtures of a fatty alcohol and a 1-alkanol (Dunn and Bagby, 1994).

The unsaturated bonds found in a number of fatty acids in common fats and oils are generally in the *cis-* conformation, although heating at temperatures in excess of 220 C for more than 2 hours can lead to as much as 50 to 60 percent di-*trans* isomerization of linolenic acid in linseed oil (Wolff, 1993). Similarly, there are a number of fatty wax esters found in nature that contain mono-unsaturates in the *cis-* configuration that can yield of up to 56 percent *trans-*

21

mono-unsaturates using selenium and NO_2 catalysts (Wisniak and Alfandary, 1977). Isomerization of the fatty wax esters in jojoba oil leads to a significant performance improvement of lubricants formulated with them, even in comparison with an improved lubricant that includes natural jojoba oil (Arndt, 1987).

Telomers

The presence of a significant degree of unsaturation in most vegetable oils may be used in other ways. The unsaturated bonds may be oxidized in the presence of air, either to form rancid oil, or, in the case of a "drying oil" such as linseed oil, a hard, semitransparent coating. Indeed, the use of highly unsaturated drying oils is the basis of oil-based paints.

Unsaturated vegetable oils, when heated under an inert or reducing atmosphere to about 300 C begin to react to saturate the available bonds. The reactions may either be between adjacent fatty acid chains within the triglyceride structure, or among triglycerides, forming a triglyceride polymer such as that depicted in Figure 2.

The polymerization process among triglycerides, called "telomerization", may be catalyzed by traces of water or by a number of other catalysts (Landis, 1993). Erhan and Bagby (1994) have found that the telomers, when allowed to react for extended times, form fluids of high, but controllable, viscosity or can form gels. The high viscosity polymers can be blended to form effective vehicles for the tints in printing ink.

As shown in Figure 2, not all of the available unsaturation is used to form the telomers. Landis (1993) has taken advantage of the reactivity of the remaining unsaturated bonds to introduce sulfur and/or phosphite as additional crosslinking agents. Elemental sulfur, when reacted in a telomer, fatty wax ester or vegetable oil solvent at about 180 C for about two hours forms a new, sulfur containing polymer. Sulfur levels on the order of 10 percent in either a telomer or a natural oil or wax ester give a product with superior lubricating properties (Kamman and Herder, 1983; Kammann and Phillips, 1985; Landis, 1993). Jojoba oil sulfurized to 25 percent of the available bonds gives a rubbery polymer (Kammann and Phillips, 1985). The phosphite adduct has been applied to telomers and to jojoba oil (Erickson, et al., 1990) to make lubricant additives.

Epoxides

The unsaturated bonds present in the fatty acids making up the triglyceride can be derivatized to produce additional functionalities. The most common product is epoxidzed soybean oil, which is used as a plasticizer for polyvinyl chloride. The soybean oil is reacted with peraceitc acid formed *in situ* using acetic acid and hydrogen peroxide in an inert solvent (Swern, 1961). The reaction, depicted in Figure 3, results in the formation of oxirane ring at about 67 percent yield. The kinetics of the formation of epoxidized methyl esters of palm olein using peroxyformic and peroxyacetic acids have been measured (Gan, et al., 1992).

$$CH_3(CH_2)_7 - CH - CH = CH - CH(CH_2)_5 - COOCH_2$$

$$CH_3(CH_2)_7 - CH = CH - CH - CH(CH_2)_5 - COOCH_2$$

$$CH_3(CH_2)_7 - CH - CH = CH - CH(CH_2)_5 - COOCH_2$$

$$CH_3(CH_2)_7 - CH = CH - CH - CH(CH_2)_5 - COOCH_2$$

$$CH_3(CH_2)_7 - CH = CH - CH - CH(CH_2)_5 - COOCH_2$$

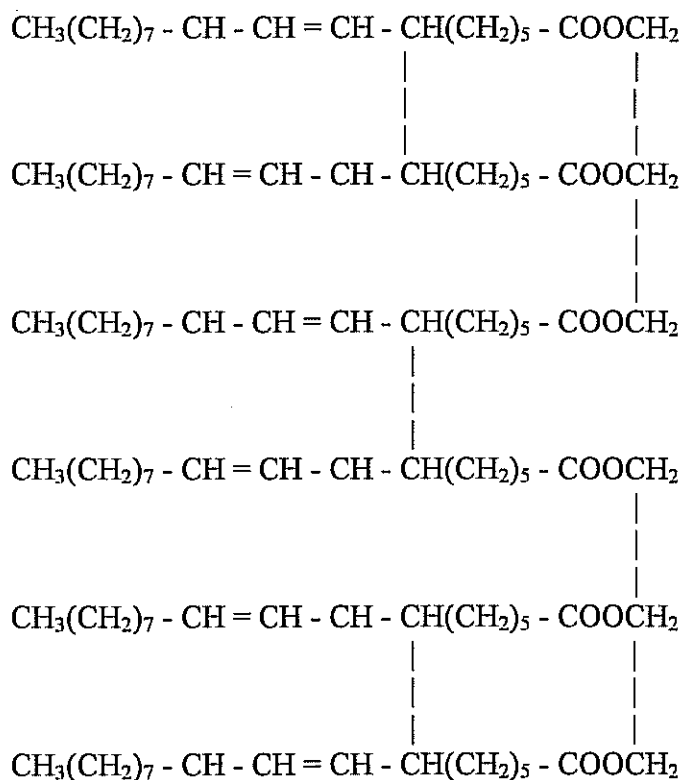$$CH_3(CH_2)_7 - CH - CH = CH - CH(CH_2)_5 - COOCH_2$$

Figure 2. Triglyceride Polymer (Telomer) Structure

The epoxides of unsaturated fatty acids have been shown to have effective rust inhibiting properties in a water dispersible cutting fluid (Watanabe, et al., 1988). As also shown in Figure 3, the oxirane may be further hydrolyzed to form the dihydroxy fatty acid. Also, hydroxy fatty acids have been prepared through hydrolxylation with a selenium dioxide/t-butylhydroperoxide system (Knothe, et al., 1993). Since the dihydroxy materials may not always be desired, kinetic studies (Gan, et al., 1992; Zaher, et al., 1989) have been undertaken to be able to better control the epoxidation and oxirane cleavage process.

The presence of epoxy and hydroxy functionalities in the triglyceride offers the opportunity to prepare interpenetrating polymer networks from triglyceride monomers. While chemically epoxidized or hydroxylated triglycerides may be used, there are a number of naturally occurring hydroxy- and epoxy-fatty acid oils. Hydroxy-oils, depicted in Figure 4, include castor (ricinoleic acid) and lesquerella (lesquerolic acid - not shown). Also shown in Figure 4 is vernolic acid, an epoxy fatty acid obtained from *Vernonia galamensis*.

Barrett, et al.(1993) have presented an extensive review of the use of naturally functionalized oils in the preparation of interpenetrating polymer networks. These oils and their fatty acids are finding applications in urethane foams, paints, and flexible coatings (USDA-CSRS, 1993).
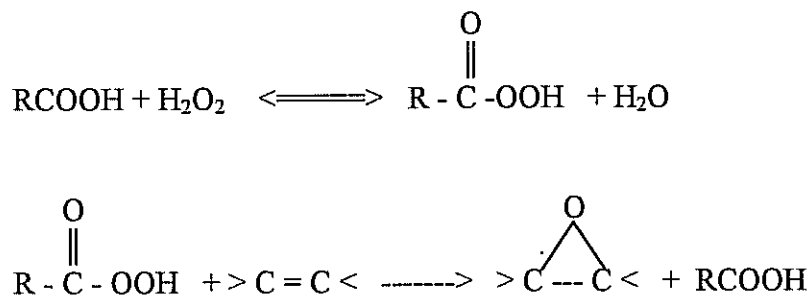
$$RCOOH + H_2O_2 \quad \Longleftrightarrow \quad R\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-OOH} + H_2O$$

$$R\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-OOH} + {>}C=C{<} \quad \longrightarrow \quad {>}\overset{\displaystyle O}{\overset{\triangle}{C}}\text{---}C{<} + RCOOH$$

Figure 3. *In situ* Epoxidation of Monounsaturated Fatty Acids

Intersesterification

Natural triglycerides are made up of a mixture of fatty acids within each molecule. As a first approximation, the specific fatty acids may be assumed to be distributed randomly in proportion to their overall composition (Swern, 1964). The composition of a triglyceride can be adjusted either by direct esterification of glycerol with the desired fatty acid(s) (Hartman, 1966; Grewal, et al., 1993), or by using enzymatic catalysis (Forssell, et al., 1993; Murakami, et al., 1993). Kammann, et al. (1983) used transesterification as a means of making a triglyceride with > 50 percent dibasic fatty acids. The dibasic triglyceride was then sulfurized to make a lubricating oil base stock. Marangoni, et al. (1993) have shown the utility of using enzymatic interesterification (essentially fatty acid exchange among triglycerides) to produce triglycerides with specific physical or rheological properties.

If a "pure" triglyceride such as triolein or tripalmatin is required, an enzyme catalyzed interesterification is used (Ergan, et al., 1990; Trani, et al., 1993). The basis for the selective enzymatic interesterification process is the ability for certain lipases to select for or against a specific fatty acid (Sonnet, 1993; Foglia, et al., 1993). An example of an application of a single acid triglyceride is tribehenin, a non-metabolizable fat substitute.

Triglycerides (TG) are used as reactants in glycerolysis to produce mono- (MG) and diglycerides (DG). As an example, with a molar ratio of 2:1 TG:DG, the reaction

$$2\,TG + DG \longrightarrow 3\,DG$$

gives 85 percent conversion using lipase as a catalyst (Yamane, et al., 1994). Glycerol, and mono- and diglycerides are heavily used, but description of their chemistries and uses is beyond the scope of this work.

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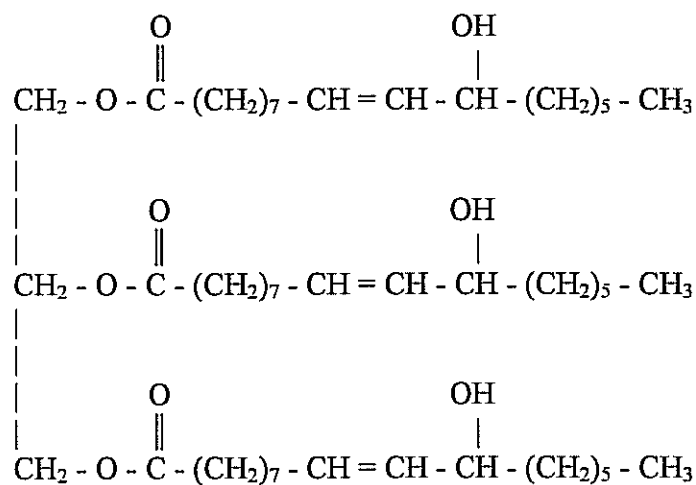
Triricinolein
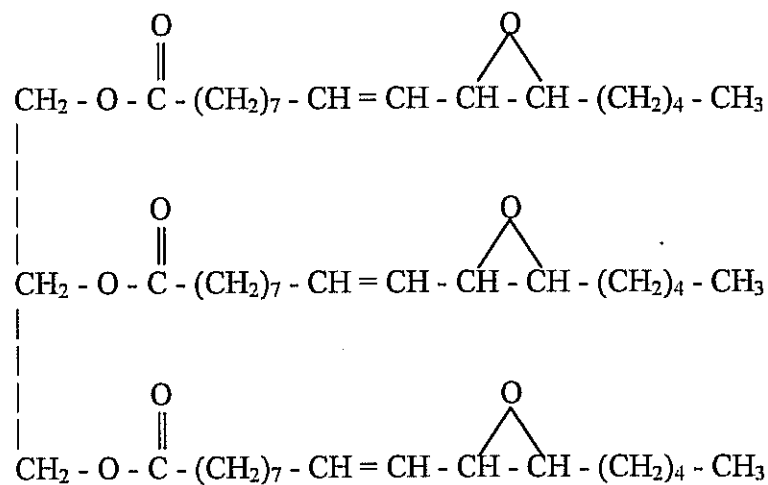
Trivernolin

Figure 4. Naturally Functionalized Fatty Acids

Fat Splitting: Fatty Acids and Soaps

The process of separating the triglyceride into its component glycerol and fatty acids is commonly referred to as "fat spitting". As shown in Figure 1, fat splitting is the result of the hydrolysis of the ester linkages in the triglyceride to form glycerol and free fatty acids. The process can occur naturally in the presence of water, but commercially fat splitting is done at elevated temperature and pressure, with a catalyst such as sodium hydroxide. For example, the Colgate-Emery process operates at temperatures in the range of 150 to 260 C and pressures of 1.2 to 5.1 MPa. Yields of 97 to 98 percent require reaction times of 3 to 24 hours, depending on reactor configuration and mixing (Sonntag, 1989).

The fat splitting reaction is similar to many of the reaction chemistries found in fats and oils processing; it involves reactants in two or more immiscible phases, a catalyst localized in one of the liquid phases, product inhibition, and products that also are immiscible. Rate limiting factors change from mass transfer to reaction kinetics to product inhibition as the reaction progresses. Until recently, most of the reaction engineering has focused on manipulation of reaction conditions, rather than on reactor system design.

Brummond (1991) demonstrated that the fat splitting reaction actually involves at least three different, sequential process steps, as depicted in Figure 5. The initial step of the reaction sequence is the introduction of water to the triglyceride in the presence of the water soluble catalyst. Because the aqueous and oil phases are immiscible, this step is mass transfer limited. The strategy used by Brummond to overcome this limitation includes intense mixing to promote high mass transfer rates and addition of a small excess of free fatty acids, combined with an inert solvent, to promote solubility of water in the oil phase.

Overall Reaction:

$$TG + 3\,W \Longleftrightarrow G + 3\,FA$$
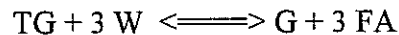
where TG = triglyceride, DG = diglyceride, MG = monoglyceride, W = water and catalyst, G = glycerol, FA = fatty acids

Actual Reactions:

Step 1: $TG + W \Longleftrightarrow DG + FA$ (Solubility Limited)

Step 2: $DG + W \Longleftrightarrow MG + FA$ (Rate Limited)

Step 3: $MG + W \Longleftrightarrow G + FA$ (Product Inhibition)
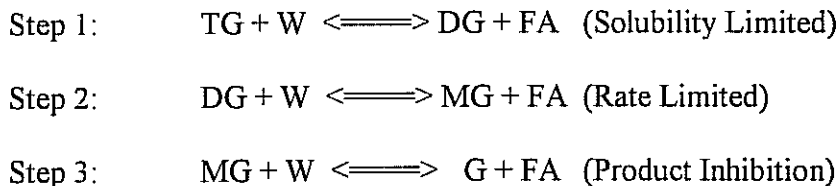
Figure 5. Reaction Steps in Fat Splitting

Once the initial, mass transfer limited triglyceride reaction has progressed somewhat, the reaction exhibits rates consistent with reaction rate limitations. However, as glycerol begins to accumulate in a separate phase, there appears to be product inhibition, and the rate again slows down. In batch runs that included addition of free fatty acids to promote water dispersion in the oil phase, intense mixing, and use of t-butanol as an inert solvent, initially for the water and later for the glycerol, it was possible to achieve hydrolysis yields of 97 + percent in reaction times of 0.5 to 2 hours (Brummond, 1991).

The effect of glycerol product inhibition has also been demonstrated in an enzyme catalyzed membrane reactor system by Molinari, et al. (1994). Lipase from *Candida cylindracea* was immobilized on a membrane pretreated with glutaraldehyde. One series of reactions was run with an olive oil-water emulsion that was continuously recirculated on the lumen side of the capillary membrane reactor. There was no product separation, and there was a definite product inhibition effect. By contrast, when two separated liquid phases were used, with the enzyme membrane in between, there was no product inhibition, since the products were separated during the course of the reaction.

The use of stoichiometric quantities of an alkali metal hydroxide in the splitting reaction leads to a mixture of fatty acid salts, called "soap". Sodium salts are the primary components in bar soap, while potassium salts are used in liquid soaps. Calcium salts of fatty acids are important as antiblock agents (internal lubricants) in the extrusion forming of polymers.

Fatty Acid Splitting: Transesterification (Alcoholysis)

The ester bond between the glycerol backbone and the fatty acids may also be broken by transfer of the hydroxyl group from a primary alcohol, the process of transesterification. The reaction is trans-esterification because the products are glycerol and alcohol esters. This process is also called "alcoholysis".

Transesterification proceeds slowly without some form of catalyst, but the range of materials that are suitable as a catalyst is extraordinary. Mineral acids and bases, lipase enzymes, a number of metal halides and oxides, and several organic compounds have been demonstrated to have some catalytic effects on the reaction. A number of these studies are summarized in Table 3.

The conversion of a fat or oil to alcohol esters is used extensively as a means of rapid analysis of fatty acid content and for the separation of fatty acids because of the esters greater volatility (for example, Chapman, 1979; Ayorinde, et al., 1988; Schuchardt and Lopes, 1988; and Bryant, et al., 1992). The greater volatility of the methyl esters, compared with the volatility of the fatty acids, is the basis for the preparation of technical grade fatty acids. The fat or oil is transesterified with methanol and the mixed esters are fractionated by vacuum distillation. The fractionated methyl esters are then easily hydrolyzed to free fatty acids and methanol.

A potentially massive use for fatty acid methyl and/or ethyl esters is as an alternative diesel fuel. The esters of soybean, rapeseed, sunflower, palm and other oils and of beef tallow have been shown to perform similarly to diesel fuel, but with fewer emissions of all regulated materials except NOx (Quick, 1982; Klopfenstein and Walker, 1983, Cundiff, 1992; Masjuki, 1993). The esters, designated "biodiesel", can be used as a neat fuel, or in blends with conventional diesel fuel. The most common blend is 20 percent biodiesel and 80 percent petroleum diesel, designated as B-20.

The alcohol transesterification reaction exhibits the same mass transfer limitations as the fat splitting reaction. However, Muniyappa (1994) has demonstrated that above a threshold intensity of mixing, mass transfer limitations are eliminated and the transesterification can be complete in less than 5 - 10 minutes at a modest (70 C) temperature. The overall process is straight forward. The capital investment for equipment for the production of biodiesel ranges from $ 0.75 to $ 2.00 per installed annual gallon, depending upon capacity and technology. The cost of the triglyceride constitutes about 70 to 85 percent of the cost of the final product.

Ester Derivatives Based on Fatty Acids

Polyol - Fatty Acids

A wide range of water-in-oil emulsifiers are based upon the esterification reaction between a fatty acid and a polyol. The polyol can be a glycerol or a mono-, di-, or polysaccharide. As depicted in Figure 6, the reaction may be a direct esterification with the fatty acid, transesterification of a fatty acid ester, or transesterification of a triglyceride. The reactions are often enzyme catalyzed, and are usually in an organic solvent (Shaw and Lo, 1994). The polyol and the lipid (fatty acid) are typically poorly miscible and as a result the reaction rate is low.

There are various approaches to producing the polyol-fatty acid ester materials (micellar reactions, derivatization, solubilization), but the goal is a solvent-free system, perhaps such as that reported by Charlemagne and Lo (1995). Their approach uses a silica gel absorbent for the polyol, the methyl ester of the lipid, and lypozyme as the catalyst. As the transesterification progresses, the methanol product is evaporated at reaction temperature (60 C) and the polyol-fatty acid esters are recovered.
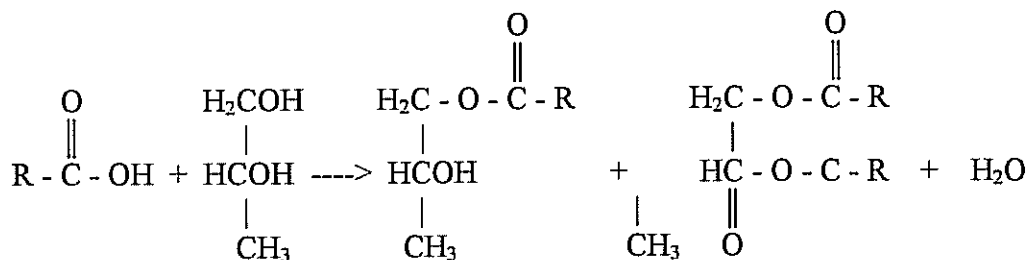
$$
\begin{array}{c}
& & & \overset{O}{\underset{\parallel}{C}} & & \overset{O}{\underset{\parallel}{C}} \\
O & H_2COH & H_2C - O - C - R & & H_2C - O - C - R \\
\parallel & | & | & & | \\
R - C - OH + HCOH \longrightarrow HCOH & + & HC - O - C - R & + & H_2O \\
| & | & & | & \parallel \\
CH_3 & CH_3 & & CH_3 & O
\end{array}
$$

Figure 6. Esterification of 1,2-propanediol and Fatty Acid

Table 3. Transesterification Catalysts

Authors	Catalysts
Many Authors	NaOH at 0.5 to 1.5 % w/w
Peterson and Scarrah, 1984	Metals, metal oxides, metal carbonates
Klopfenstein and Walker, 1983	H_2SO_4 at 2 % w/w
Harrington and D'Arcy-Evans, 1985	H_2SO_4
Ramamurthy and McCurdy, 1994	*Candida antarctica* lipase
Vieville, *et al.*, 1993	*p*-toluenesulfonic acid/ cation exchange resins K2411 and K1481 in supercritical CO_2
Chapman, 1979	BCl_3 at 10 %; BF_3 at 14 %
Ayorinde, *et al.*, 1988	CH_3ONa at 3.33M in CH_3OH
Fourie and Basson, 1990	Tetramethyl ammonium hydroxide in methanol
Schuchardt and Lopes, 1988	Tetramethylguanidine: 4 parts methanol (v/v)

Polysaccharide - Fatty Acids

Mono- and polysaccharides also have hydroxyl groups that can form ester linkages with fatty acids. Current methods for producing sugar fatty acid esters are based on high-temperature transesterification in the presence of an alkaline catalyst. Fregapane, et al. (1994) used monosaccharide acetals and fatty acid mixtures in a lipase catalyzed reaction to form monosaccharide fatty esters. A similar approach has been used for the preparation of disaccharide esters (Sarney, et al., 1994). An alternative approach to production of saccharide-fatty acid esters is the use of organic solvents such as isooctane or benzene with immobilized lipase and an acetylated saccharide (Akoh, 1994).

Saccharide-fatty acid esters may also be produced directly through fermentation. As an example, Zhou and Kosaric (1995) used glucose and lactose as the carbon source and canola oil as the lipid source for a fermentation with *Candida bombicola*. Yields of sophorose liquids ranged from 70 to 160 gm/liter. The liquids are being evaluated as biosurfactants.

The interest in biodegradable polymers has led to renewed interest in the production of fatty acid cellulose esters (FACE). Malm, et al. (1951) used the pyridine-acid chloride reaction to produce FACE for a series of fatty acids. Recently Kwatra, et al. (1992) used a novel vacuum-acid chloride process to achieve 90 percent yields in the production of palmitoyl FACE.

The utility of bacterial polyesters such as polyhydroxy butyrate-valerate (PHBV) as a biodegradable polymer has been demonstrated in ICI's introduction of the polymer "Biopol" to

the market. The possibility exists that analogs of PHBV may be possible using fatty acid raw materials and synthetic chemistry.

Fatty Acids and Glycerol Esters

Although much of the current work in esterification employs enzymatic catalysts, some work continues on the use of inorganic catalysts. For example Erdem-Sentalar, et al. (1994) have investigated the use of tin chloride and cobalt chloride as catalysts in the esterification of castor oil and oleic acid. The goal is an alkyd resin with limited volatile organic carbon (VOC) emission. Very long chain fatty acid methyl esters have been synthesized using omega-iodo esters and complexes formed from methyl copper (I) and Gignard reagents (Kling, et al., 1993).

Glycol diesters and mixed mono- and diesters have been made using calcium acetate/barium acetate catalyst with methyl esters of partially hydrogenated soybean oil. The results suggest that the products may have use in lubricating oil (Basu, et al, 1994). Nakamo, et al. (1985) have patented a lubricating oil based upon esters of boric acid, glycerol and fatty acids. Fatty acid esters are also epoxidized in a similar manner (e.g. Maerker, et al., 1966; Rusling, et al., 1968).

Summary

Triglycerides and fatty acids offer an array of unusual chemistries and properties for the production of new functional fluids and polymeric materials. The chemical basis for many of the reactions is the making or rearranging of the ester bond. Advances are being made rapidly in the development of new materials and new uses for these materials. At the same time, there is increasing attention being paid to the reaction engineering and reactor design issues unique to the application of these materials.

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