

Oleochemicals as a Feedstock for the Biorefinery: High Value Products from Fats and Oils

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Executive Summary

Oleochemistry (i. e., use of renewable fatty acids, fatty esters, and glycerol from oil crops as raw materials and platform chemicals) will play a significant role as one of the unit operations within the integrated biorefinery. However, R&D effort within DOE has traditionally focused only on a single product of this unit operation, biodiesel, because of its potential as a new renewable fuel. Accordingly, DOE commissioned this evaluation of the broader potential of these oleochemical building blocks and their derived products (including biodiesel) to identify: 1) barriers that prevent greater use of oleochemicals within the biorefinery; 2) general technology areas that, with DOE R&D support, would address these barriers, and 3) products that could be addressed by this R&D effort.

Important barriers within the biorefinery are immediately suggested by questions such as:

- Why are there so few methods for the conversion of oleochemicals into new products?
- Why isn't catalysis used effectively within the biorefinery?
- How does one identify the most appropriate market segments to target with oleochemicals?

The investigation detailed in this report addresses each of these areas, and has found, overall, that the primary oleochemical building blocks (fatty acids, fatty esters, and glycerol), will play two key roles. First, appropriate DOE supported R&D development will allow efficient use of these readily available materials as renewable platforms for the production of other chemicals and materials. This report will show that tailoring technologies such as *homogeneous catalysis*, *selective oxidation processes*, *new polymerization methodology* or *selective bioconversions* for these building blocks will lead to a wide variety of new and efficient market opportunities (including biodiesel) for the chemical industry. ***But much more importantly, a DOE supported R&D effort to develop the oleochemical unit operation offers the opportunity to address what is arguably the primary barrier facing the biorefinery: how can today's nonrenewables-based chemical industry be convinced to use unfamiliar starting materials for the production of either existing or new market products? As a result of the features inherent in their native structures, oleochemicals offer a unique and significant opportunity to help transition the chemical industry from nonrenewable to renewable feedstocks. Success with oleochemicals as building blocks will prepare the way for ready acceptance of less familiar renewable building blocks such as sugars (monomeric and polymeric), proteins, lignin, etc.***

The success of the biorefinery will ultimately depend on close integration with the existing chemical industry, and the building blocks offered by the oleochemical unit operation will neatly interface in the following ways:

1) *Glycerol*. Although the focus previously afforded to biodiesel within the unit operation must change, this report will show that from a volume standpoint, it could conceivably play an

important role given the volume of material that might be produced. If biodiesel becomes an important (albeit low value) fuel output of the oleochemical unit operation, glycerol will become a necessary high volume coproduct. As biodiesel production increases, the cost of glycerol will drop. Investigating glycerol and developing new uses for it are important parts of this study. This report will detail a range of R&D opportunities for the use of cheap glycerol as a starting material or platform chemical. More broadly, this report will also show how glycerol can serve an important transitional role in preparing the chemical industry for greater use of building blocks from the growing sugars platform. Since its structure closely resembles carbohydrates, technology development specifically tailored for glycerol will also be useful for carbohydrate conversion, and application within the sugar platform. Success with glycerol will mean success with sugars, and ready acceptance of their utility by the chemical industry.

2) *Fatty acids and esters.* After separation from the plant residue of oil crops, fatty acids and esters make up about 85 – 90% of the remaining material. Structurally, they closely resemble materials (hydrocarbons) already recognized and understood by the current nonrenewables based chemical industry. Raw material familiarity will be an important component in transitioning the industry from nonrenewables to renewables, and *general* technology and equipment present in the chemical industry today can be easily adapted to use these building blocks. For example, application of mature technologies well known to the chemical industry could lead to some of their traditional building blocks when applied to low value mixed fatty acids. This report will detail important R&D opportunities for development of new catalytic technologies for fatty acid conversion. This portion of the report will also describe how DOE's previous efforts in biodiesel can be much more clearly understood in the broader context of fatty acids and esters as raw materials. It is important to realize that biodiesel is simply one of many products that are derived from the oleochemical unit operation. Historically however, DOE efforts in oleochemicals have focused *only* on biodiesel as a program area. Such an approach makes an understanding of biodiesel within the larger context of renewables fragmented and difficult. Shifting the focus from a single product to the much broader oleochemical platform will greatly clarify biodiesel's position, and will allow R&D efforts to be directed at a range of products rather than a single material, that is, *fatty acids and esters must be a part of the integrated biorefinery, whether or not biodiesel itself becomes a biorefinery product.*

I. Introduction

Greater use of renewable feedstocks and all the advantages that would accrue from this use has led to the development of the *biorefinery* as a unifying concept.¹ In direct analogy to a petrochemical refinery, a biorefinery would take a variety of renewable raw material inputs, convert these inputs into an initial group of building blocks, and then, through various unit operations, convert these building blocks into chemicals, fuels, and power. The biorefinery model is extremely powerful, in that it eliminates an assessment of renewables on a highly fragmented product by product basis, and properly focuses on the concept of large, integrated unit operations, and a much smaller number of *platforms* from which a huge number of products can be derived. In this way, it is much easier to discern the impressive energy and petrochemical displacement benefits that the biorefinery offers. With this model in place, the various categories of raw materials, their conversion technologies, and their primary product outputs can be recognized more simply as different unit operations within the greater whole.

Evaluation of R&D opportunities within two potential biorefinery unit operations, the sugar platform and the syngas platform, is currently being carried out. This report will describe promising opportunities for a third, and equally valuable unit operation, the oleochemical platform. *The importance of the oils platform as an initial means to transition today's chemical industry from nonrenewables to renewables cannot be overemphasized. The use of oil platform building blocks currently makes up only a small proportion of the raw material feed of the chemical industry. However, their nature suggests that proper technology development support from DOE would provide a powerful impetus for significant use of oleochemicals by the industry.*

In its simplest form, the oleochemical unit operation begins by conversion of fats and oils into two initial materials: fatty acids (either as the free acid or as esters), and glycerol (**Figure 1**).

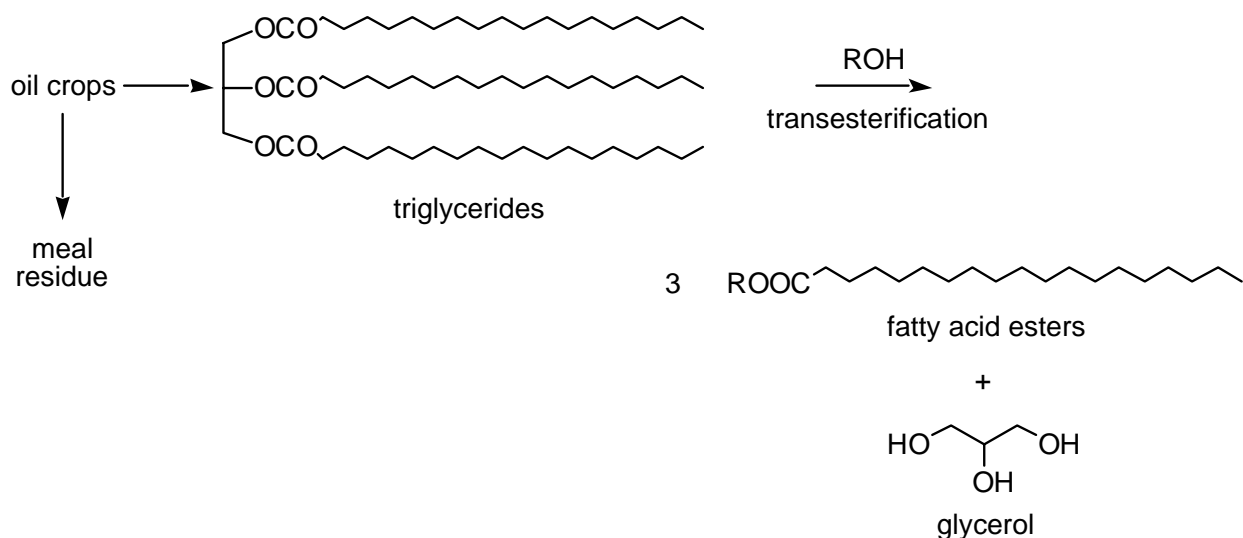


Figure 1 – Initial Processes For the Oleochemical Unit Operation of the Biorefinery

Oil crops are initially transformed into a meal fraction and an oil fraction. The more valuable oil fraction is composed primarily of triglycerides, which are fatty acid triesters of glycerol. In a process known as fat splitting, the triglycerides are further broken down into their constituent parts. Fatty acids and esters make up about 85 – 90% of the weight of the products, while glycerol makes up the remainder. The process shown in **Figure 1** is commonly used in the

production of biodiesel, which involves transesterification of the triglycerides by addition of an alcohol, normally MeOH. Initially, this evaluation was to focus primarily on byproducts from the production of biodiesel (generally glycerol derivatives). Within the DOE context, the attractiveness of biodiesel originally arose from the energy opportunity it targets. The U. S. annually consumes about 33×10^9 gal of petrochemically based diesel fuel for on road use, and almost twice as much, 60×10^9 gal, when all uses are considered. Secondly, it offers a secure and domestic source of sustainable fuel.

However, our more detailed investigation indicates that a primary focus on biodiesel is not sufficiently broad within the biorefinery context. Importantly, the general unit operation described by **Figure 1** is an equally valid platform for the production of chemicals. This evaluation becomes much more powerful and descriptive when biodiesel is simply considered one of many products that could be derived from an oleochemical unit operation within the biorefinery. In this way, the focus more properly moves from *products*, which is highly fragmented, to an oleochemical *platform* within a large *unit operation*, which is a much more integral approach. This approach is much more in line with the concept of an integrated biorefinery using renewable raw material inputs and converting them as appropriate into chemicals, fuels, and power. In the biorefinery context, oleochemicals are raw materials, analogous to crude oil in the petrochemical refinery, and fatty acid esters and glycerol become primary building blocks, analogous to ethylene or BTX in a petrochemical refinery.

This report will describe the opportunities that are available from an R&D based examination of the oleochemical platform. Both the glycerol and fatty acid components are examined.

II. Glycerol as an Oleochemical Building Block

A. Introduction

The oleochemical unit operation of **Figure 1** is necessarily a coproduct scheme, in that glycerol is always produced as a byproduct of triglyceride methanolysis. As a rough rule of thumb, about 1 lb of glycerol is produced for every 10 lb of fatty acid methyl ester.² Inclusion of biodiesel within the oleochemical product mix would exacerbate the situation. If biodiesel became a significant product of the oleochemical unit operation, capture of even a relatively small portion of the current nonrenewable diesel market would result in a large increase in the amount of glycerol available for the marketplace, e.g., capture of 5% of the total diesel market would result in the availability of an additional 1×10^6 tonnes of glycerol, between 2 and 2.5 times the current world production.³ With increasing supplies of glycerol will come a decrease in cost. Credibly projecting the amount of glycerol's cost decrease will be an important component of any discussion regarding new uses of glycerol. It should be noted that the European biodiesel experience in the period 1997-2000 led to an almost 40% drop in the price of glycerol. Diminished biodiesel production in 2001 led to a significant price recovery. While this is a relatively short time period on which to base a trend analysis, the impact of increased biodiesel production on glycerol prices is clearly demonstrated. However, Sonntag has pointed out that "...glycerol economic prediction is still among the most difficult among all of the world's chemicals."⁴ Further, it has been pointed out that prediction of glycerol demand has not been possible on an annual basis for over 80 years.⁵

Nonetheless, as the glycerol supplies increase and the cost decreases, the oleochemical unit operation will need to find ways to move this unavoidable coproduct to market. Interestingly, at the present time, the biodiesel market has been moving ahead in Europe without following the market demand for glycerol. This approach has left the European glycerol sector with excess

capacity of 10-20%.⁶ This situation cannot continue for the long term as biodiesel production increases. The Chemical Economics Handbook states:

“...plans by the European Commission to expand the European Union’s biofuels sector would shake the glycerin market...”,

as well as:

“...the rapid rise in biodiesel output will inevitably have a major impact on the oleochemicals sector”

and finally:

“Glycerin producers are seeking new product introductions based on glycerin in order to better balance supply/demand. New product introductions have been rare so far...”

It is obvious that the industry is looking for new ways to consume low cost glycerol. This industrial interest offers an important R&D opportunity for DOE.

B. Where Will New Sources of Glycerol be Used?

“The development of new use applications for glycerol would be welcomed enthusiastically by the entire glycerol industry.”⁴

The most broad based opportunity for the effective consumption of glycerol will arise from its use as a primary chemical building block. Because of price and availability, many current uses of glycerol do not employ further transformation of its structure.⁷ Once it is recognized that a ready source of low cost glycerol is available from the biodiesel unit operation, glycerol could be positioned within the biorefinery as a primary renewable building block analogous to those of the petrochemical industry (methane, ethylene, BTX, etc.). As the price of glycerol drops and its availability rises, glycerol ceases to become an “additive” for a fragmented list of small volume products, and assumes a position as the starting point for the production of fewer, but much larger volume materials. When the cost of a chemical drops, its range of industrial utility broadens, and the ability to absorb the cost of additional chemical transformations increases. Glycerol would transition from its current state as an advanced intermediate or chemical endproduct to utility as a starting material for a family of compounds.

Glycerol has not previously occupied this position within the chemical industry. Therefore, as is the case with any new product family, uncertainty exists as to exactly what might be done with large amounts of cheap glycerol. As a result, the members of a glycerol product family and the technologies for their production from glycerol can be described in a general sense, but unequivocal identification of a *specific* glycerol derivative on which all attention and effort should be spent is difficult, and premature at this stage. Conversely, it is entirely possible and proper, based on the known chemistry of glycerol, to define a few technologies that would be particularly appropriate for its conversion as well as several product *classes* where proposed glycerol derivatives might play a role. The primary barriers to be addressed in this type of product family development are 1) can the processes be made to occur in high yield, and 2) what are the product applications for the new products? These questions form the basis of the ideal DOE/industry partnership, with DOE R&D assuming the higher level of risk in addressing the first question, and developing close association with interested industrial groups to address

the second. Furthermore, a close government/industrial partnership will be necessary to avoid duplication of possible past industrial R&D efforts that have not been made public.

A number of different opportunities for glycerol consumption have been identified, and are summarized in **Figure 2**. The intent of this figure is not to imply that all areas should receive simultaneous R&D effort, but rather to provide a figure analogous to similar diagrams found for petrochemical industry unit operations. The petrochemical industry describes the families of products arising from their most basic building blocks as the “ethylene family” or the “BTX family”. Within the context of the biorefinery, **Figure 2** is suggested as a starting point of the definition of the “glycerol family”. Success in the development of an effective glycerol operation will have a synergistic effect on the production of biodiesel. Finding higher value, large volume uses for glycerol will help offset the low value of biodiesel, so that an integrated biodiesel/coproducts unit operation will end up being profitable.

Prioritization of needed R&D efforts will be most important, and will be carried out using well recognized process engineering evaluation techniques to provide “pointers” to the most promising lines of research. Of equal importance is the identification of general technical barriers impeding the development of the glycerol product family, i. e., while it is relatively straightforward to project a fragmented “laundry list” of specific product opportunities, true breakthroughs will occur only by identifying the more general barriers between glycerol conversion and product opportunities. In parallel, however, it is also important to remember that analysis will take the project only so far when one is trying to develop a product family that is currently only poorly defined. Although it is an obvious argument that R&D must be carried out to either validate or disprove the results of analysis, selling that argument is frequently much harder, for reasons that are not completely clear.

From a technical standpoint, glycerol’s multifunctional structure can be exploited by several different means, as shown by the potential glycerol product family in **Figure 2**.⁸ It is clear that a very large number of products and product classes could, in principle, be derived from glycerol. However, an attempt has been made in this section to avoid simple listing of each of the many separate structures. Instead, the very large number of product opportunities and types of technology that could be brought to bear on glycerol has been focused into three larger categories which leads to clearer definition of barriers. Again, interaction with industrial experts in the use and conversion of glycerol needs to be carried out in order to determine if these areas would be of eventual utility as the price of glycerol drops.

1. Selective oxidation of glycerol. Glycerol’s structure lends itself well to catalytic oxidative processes using inexpensive oxidizing agents such as air, oxygen, hydrogen peroxide or bleach. Combination of these inexpensive oxidizing agents with an inexpensive source of glycerol will allow the production of a number of new derivatives. A few research groups have investigated this technology, but focus has been limited to a small number of catalysts, leaving a number of questions of selectivity and yield unanswered.⁹ Further, the traditionally high price of glycerol as a starting material has brought the economic viability of such transformations into question limiting the potential use of these products to small niche markets such as cosmetic additives, tanning agent components, amino acid precursors, or selective metal chelants. Reconsidering these materials as products in the context of cheap glycerol helps to validate an industrial/government partnership to develop such processes and identify large scale uses of the available products. For example, NREL has specific expertise in the development of new catalytic oxidations based on novel polyoxometallate catalysts, and the use of simple radical based oxidations of polyols, which have been examined as new types of nylons.¹⁰ As their cost drops, these intermediates can be considered as components of new polyfunctional, glycerol

derived polymers, such as polyesters and nylons. Other selective oxidation products may find applicability as structural analogs of polylactic acid.

2. Glycerol carbonate as a new solvent and product. Glycerol carbonate is a relatively new material in the chemical industry, but one that could offer some interesting opportunities, as it can be prepared directly and in high yield from glycerol. Glycerol carbonate has been investigated as a novel component of gas separation membranes, polyurethane foams¹¹ as a surfactant component¹² as a new solvent for several types of materials, and as a component in coatings, as a potential component of the paint industry, acting as a nonvolatile reactive solvent, and as a component of detergents. As glycerol becomes less expensive, the use of glycerol carbonate in applications occupied by currently cheaper carbonates should be investigated. Dimethyl carbonate is being positioned as a green replacement for phosgene in the production of polycarbonates and polyurethanes. Inexpensive glycerol carbonate could serve as a source of new polymeric materials for this industry. Glycerol carbonate can be prepared by very simple processes, such as the direct reaction of glycerol with urea,¹³ or the treatment of glycerol with ethylene or propylene carbonate.¹⁴ Direct production of glycerol carbonate from glycerol and carbon dioxide under supercritical conditions has also been reported.¹⁵ Interestingly, glycerol carbonate has also been prepared as from nonglycerol starting materials, such as epichlorohydrin¹⁶ or tricaprilyn.¹⁷

3. Glycerol as a component of new polymers. Glycerol has traditionally played a role in the production of several types of polymers, some of which are available commercially. Selective etherification reactions can convert glycerol into polyglycerol esters, which have been suggested for use as biodegradable surfactants and lubricants¹⁸ and as replacements for conventional poly(oxoethylene) nonionic surfactants. Polyglycerol and polyglycerol methacrylates are used as treatments for wood to improve its stability.¹⁹ This application would compete with the more widely used polyethyleneglycols. However, glycerol based polymers offer additional benefits including lower amounts of leachability into the environment.²⁰ As the cost of glycerol decreases, processes to manufacture polyglycerols through modification of its structure become more affordable, and would lead to new optimized wood treatments.

More recently, significant attention is being given to preparation and properties of new, more highly branched polymers. Glycerol's multifunctional structure is well suited for the production of these new types of polymers, and preliminary work at NREL has demonstrated the production of new glycerol based polymers, and the ability to control the properties that they exhibit. In addition, glycerol has been used with lactic acid to prepare branched polylactide polymers.²¹

More generally, branched polymers exhibit a wide range of new properties that could be exploited in useful marketplace products. **Table 1** lists a number of physical properties that have been observed in highly branched systems, and suggests how these properties could be translated into properties of interest in production and commercialization.

A number of more specific product application areas have been suggested for branched polymers. Many of these could be very high value applications, such as use in sensors, personal care products, or organic conductors. However, the volume of such materials will be fairly low, thus, while they might help the profitability of a glycerol unit operation, they would not be able to offer a significant consumption of large amounts of glycerol. Other applications in larger volume markets have been suggested, and branched polymers could find utility as polyester polyols, surfactants, coatings and alkyd resins, new solvents, and polyurethanes. Each of these market areas is very large (**Table 2**).

Physical property	Potential product interest
Lower solution viscosity	Easier processability
Higher amorphous content	Higher reactivity
More end groups	Greater property control
Higher organic solubility	More versatility in processing
Novel 3-D architecture	New material properties
Large number of functional groups	Easier functionalization

Table 1 – Translation of Branched Polymer Physical Properties into Potential Marketplace Utility

Market segment	Market size (10⁶ lb)	Year
Polyether polyols	7643	2001
Polyester polyols	463	2001
Surfactants	1742 (detergents only)	2000
Alkyd resins and coatings	1691	2000
Polyurethane foam	3410	2001
Polyurethane elastomers	433	1997

Table 2 – Sizes of Various Market Segments Related to the Use of Branched Polymers

These possibilities again highlight the need for an effective industry/government partnership in this area. As is the case with any new product opportunity, a brief summary of an R&D effort (including the pertinent work carried out at NREL) to make new branched polymers is that a material can be made, and that it exhibits a certain set of properties. In some cases, these properties may equal or exceed those of existing polymer lines because of the unique features that the starting renewable feedstock exhibits. In other cases, the properties may be new or untested. Further investigation may suggest product opportunities or market segments that could be addressed (Table 2) by these new products. However, the key questions to be answered are 1) do these properties offer any advantage over the suite of properties currently available within a given market segment, and 2) do these advantages justify further investigation of a given material? Validation of these ideas and suggestions can only occur through an industrial partnership with groups that have the years of expertise in taking new materials and moving them to market as appropriate.

New highly branched polymers have been made using glycidol as a starting monomer. The resulting structure is a branched polyether polyol, but is frequently referred to as a polyglycerol.²² Glycidol is a high value component in the production of a number of polymers, including epoxy resins and polyurethanes. Glycidol has been conventionally synthesized from epichlorohydrin, which in turn is derived from the chlorination of allyl alcohol. More recently the high yield preparation of glycidol from glycerol carbonate, and thus, from glycerol, has been reported, making it likely that low cost glycerol could be used for the production of low cost glycidol and its family of products.²³ Small scale production of these highly branched glycidol polymers has been commercialized in Europe by Hyperpolymers (Germany).

Use of glycerol as a starting material for the production of other small molecules also offers a new opportunity. Glycidol has the advantage of being a current commercial, albeit specialty

product. Lowering of its cost through production from low cost glycerol presents new opportunities for further expansion of the glycerol product family. For example, extensive work has been carried out on catalytic transformations of epoxides. Should the cost of glycerol, and thus, the cost of glycidol drop, it will become important to investigate the ability of these processes to convert glycidol into a source of alcohols and other epoxide derivatives.²⁴

4. Selective reduction processes. Recent work carried out at NREL offers the opportunity to tailor catalytic reduction processes to selectively convert glycerol into 1,3-propanediol. While this work is currently in the developmental stage, the more general ability to selective transform a single structural unit within glycerol using catalysis would be highly valuable. More generally, this type of selective transformation would also be of great value in learning how to more efficiently transform the products of the sugar platform into new marketplace products.

5. Biochemical transformations. Glycerol can also serve as a feedstock in biochemical transformations. Glycerol has been investigated for the fermentative production of 1,3 propanediol, one of the primary components of DuPont's Sonora (1,3 PDO and terephthalic acid), a polymer being investigated for use in textiles and carpeting. Interestingly, the first reports of commercial PDO production were from Shell and their process for making Corterra, also based on PDO and terephthalic acid.²⁵ This is by no means a new process. Fermentation of glycerol to PDO was described as early as 1881.²⁶ Simple economic evaluation indicates that biochemical PDO production would be more economical than chemical.²⁷

A primary question for this application area is the proper choice of biochemical feedstock. Current prices of glycerol imply that an alternate fermentative route from glucose would give cheaper 1,3-PDO. Moreover, the ability to produce glycerol fermentatively suggests that glycerol and PDO production might be carried out from glucose by a single organism, which may be the basis of the DuPont commercialization effort.²⁸ These attempts are based on the assumption that glucose will always be cheaper than glycerol. However, we have no good projections, as yet, as to the cost of glycerol as a result of a large scale oleochemistry industry producing biodiesel in large amounts and coproducing glycerol. Nonetheless, considerable effort has been carried out to improve biochemical PDO production. Cameron has reported that minimizing the amount of methyl glyoxal and glycerol-3-phosphate produced during fermentation using engineered *E. coli* improves the conversion of glycerol to PDO by removing these two enzyme inhibitors.²⁹

Cameron has also described engineering *E. coli* for the production of 1,2-propanediol, a material with an annual market of over 1 billion lb.³⁰ This process proceeds through dihydroxyacetone as a metabolic intermediate, implying that proper choice of organism could lead to either 1,2- or 1,3-PDO from glycerol, since one of the first intermediates in 1,3-PDO production is also dihydroxyacetone.³¹

One of the drawbacks to production of 1,3-PDO from glycerol is that most organisms require a purified glycerol source. The so-called "industrial" glycerol, available directly from biodiesel production or oleochemical facilities, is frequently contaminated with salts from transesterification, which inhibits the biochemical process. Various research groups are attempting to solve this limitation with new fermentative organisms.³²

C. Other Areas for Consumption of New Glycerol Sources

There are two other primary areas where higher amounts of new, inexpensive glycerol might be consumed.

1) *Recovery of former glycerol markets and development of new glycerol markets.* Some opportunities for glycerol consumption exist in market segments that glycerol has lost to cheaper alternatives. For example, glycerol is a component in the production of alkyd resins, but lost that position to pentaerythritol and propylene glycol. Glycerol also sees competition from sorbitol in the oral care, food, and tobacco markets. As the price of glycerol drops, it becomes reasonable to investigate its reintroduction into those areas. The overall alkyd market is quite large ($1,691 \times 10^6$ lb in 2000)³³, and could offer an opportunity for consumption of some of the newly available glycerol.

An interesting opportunity appears when the relative costs of various industrial polyols are compared (**Table 3**).

<i>Polyol</i>	<i>USD / ton</i>
<i>Glycerol</i>	1200 - 1600
<i>Trimethylol propane</i>	1,278
<i>Pentaerythritol</i>	1,278
<i>Propylene glycol</i>	1,000
<i>Ethylene glycol</i>	667
<i>Sorbitol (70 %)</i>	400

Table 3 – Comparative Prices of Various Polyols (source: Claude, S. *Fett/Lipid* **1999**, 101, 101)

Table 3 indicates that at current prices, glycerol is one of the more expensive of the polyols compared. However, if biodiesel is included as a large volume product of the biorefinery, production, glycerol will become a low cost platform chemical, and a key player in the overall oleochemical unit operation. Its price could drop to levels where a broad range of new applications in existing markets could be considered. Market sizes tend to be inversely proportional to cost, thus, the ability for glycerol to compete in markets currently dominated by other glycols would be an important opportunity to investigate.

2) *Consumption by existing glycerol markets.* Glycerol is currently a well recognized item of commerce with an annual world production of $600 - 750 \times 10^3$ tonnes. Although about 75% of this amount is produced from hydrolysis of triglycerides, very little is the result of biodiesel production. Instead, the current glycerol production is largely part of the existing oleochemical industry. One might conclude that existing markets, faced with a larger supply of cheaper glycerol, will simply absorb this new supply and increase their market size. For small amounts of glycerol, this may occur. The relatively small amount of additional glycerol produced in Europe from biodiesel was initially consumed by existing markets.³⁴ However, in the long term, this is unreasonable because of glycerol's position in the marketplace. In 1945, the work of Leffingwell described over 1500 different uses for glycerol.³⁵ Other sources have rolled up these uses into fewer categories (**Tables 4 and 5**). It should be noted that southeast Asia is a major source of glycerol, with over 200×10^3 tonnes of capacity. The world's largest supplier of glycerol is believed to be Malaysia, however, capacity and production data are not available. Much of the feedstock in this portion of the world is from palm and palm kernel oil.

In addition, glycerol and various simple derivatives of glycerol (such as glycerol triacetate, glycerol stearate, and glycerol oleate) are currently produced by the chemical industry at

companies such as Uniqema, Proctor and Gamble, and Stepan.³⁶ These materials find application in many of the categories shown in **Tables 4 and 5**.

The feature that unifies these reports is that, for the most part, glycerol consumption statistics are the result of a large number of small volume applications. That is, there are few, if any, uses of glycerol in large quantities for a single product. This is not unusual for a chemical whose market price hovers between \$0.70 – 0.90/lb. This cost allows very little opportunity for a glycerol based process to afford an additional process step for glycerol structural modification. Thus, many of these current outlets will quickly become saturated by even a relatively small increase in the amount of available glycerol from biodiesel. The diversity of the glycerol market is better understood with a more detailed examination of the current market segments addressed. These include:

- a. *Personal care products.* In 2001, 97x10⁶ lb of glycerol were consumed for the production of 58x10⁶ lb of skin care products (60% of the total; suntan lotions, cleansing wipes and cloths, creams, other cosmetics and toiletries), 29x10⁶ lb for hair care (30% of the total; moisturizers and conditioners), and 10x10⁶ lb for soaps (10% of the total; Neutrogena, designer soaps). This market is increasing at 3.1%/yr.
- b. *Oral care products.* In 2001, 69x10⁶ lb of glycerol were consumed, 52x10⁶ lb for toothpastes (75%) and 17x10⁶ for mouthwashes (25%), with the market increasing at 2%/yr. The primary competition is the more inexpensive sorbitol, however, sorbitol does not possess optimum taste and solubility properties. Low cost glycerol could capture more of the sorbitol market.
- c. *Drugs.* Glycerol is used to increase smoothness, lubrication, and in production of gel caps. It is also used in suppositories, cough syrups, expectorants, etc.

Application	Consumption (tons)
Cosmet./Soap/Pharmacy	202,200
Alkyd resins	43,800
Food and drinks	57,700
Polyglycerols	89,000
Tobacco	25,500
Cellulose films	35,000
Esters	93,400
Paper	7,300
Nitrates	2,900
Resale	103,700
Others	69,500
TOTAL	730,000

Table 4 – Uses of Glycerol, 1995 (source: Claude, S. *Fett/Lipid* 1999, 101, 101)

- d. *Foods and beverages.* In 2001, 92x10⁶ lb of glycerol were consumed, with 5x10⁶ lb used for meat casings and the remainder finding application in many different areas, such as emulsifiers, humectants, heat transfer media, flavors and colors, sweeteners, edible plasticizers (i. e., raisins saturated with glycerol remain soft when mixed with cereals,

Lowen R. Morrison, Procter & Gamble, *Kirk-Othmer Encyclopedia of Chemical Technology* (1994)). Certain glycerol esters, such as glycerol mono and distearate, are used for reduced fat foods. Polyglycerols find use as emulsifiers. Primary competition in this market segment is again sorbitol. However, sorbitol comes as a water solution, which is a problem for food manufacturers who want to minimize added water in their products. Again, a source of cheap glycerol could offer opportunities for recapture of some of this market. These market applications are increasing at 3 – 3.5%/yr

- e. *Tobacco*. In 2001, the tobacco industry consumed 49×10^6 lb of glycerol. 7.4×10^6 lb were used for production of triacetin (glycerol triacetate) as a plasticizer (15% of the total consumption). Glycerol is also an important humectant. Competition again comes from other polyols, such as sorbitol and propylene glycol.

	<i>U. S.</i>	<i>Europe</i>	<i>Japan</i>	<i>Total</i>
Annual capacity	169	315	59	543
Production	159	247	53	459
Consumption				
<i>Personal/oral care products</i>	75	46	15.5	136.5
<i>Drugs/Pharmaceuticals</i>	14	24	23	61
<i>Foods/beverages</i>	42	27		69
<i>Polyether polyols</i>	17	33	6	56
<i>Tobacco</i>	22	15	5	42
<i>Alkyd resins</i>	6	17	7.5	30.5
<i>Other</i>	13	79	29	121

Table 5 – Production, Consumption, and Uses of Glycerol, 2001 (in thousands of tonnes; source: Chemical Economics Handbook)

- f. *Other*. Glycerol has also found use in the production of other materials. The explosives industry used 2×10^6 lb of glycerol in 2001. Other uses include production of polyether polyols (foams for furniture, car seating, carpet underlay, packaging) and alkyd resins (coatings), both of which are large volume markets that could offer an opportunity for expansion of glycerol's utility. Glycerol also is used as a plasticizer, humectant, lubricant, and in textiles, photography, gas drying, and production of electrolytic capacitors. These other uses account for consumption of $25\text{-}30 \times 10^6$ lb in 2001.

D..Identification of Barriers to be Addressed by R&D

Each of the potential R&D areas described above offers a unique set of barriers to be addressed through a potential DOE/industry partnership directed at the development of an integrated oleochemical unit operation for the biorefinery.

Suggested initial barriers:

1) *Market development for glycerol*. Little information about what the market will do with large new supplies of glycerol from the manufacture of biodiesel is available. A key feature of any program will be a clear projection of what the level of biodiesel production will be, and a reasonable estimate of what the glycerol cost will be. All areas of new development will hinge on these kinds of numbers.

2) *Impact of glycerol purity on effectiveness in chemical production.* It is important to note that that over 95% of all glycerol applications use refined glycerol (Chemical Economics Handbook), and that current glycerol manufacturers will include a glycerol purification stage as part of their overall production scheme. Moreover, current glycerol consumers, will assume that a new glycerol producer, for example, a biodiesel operation, would also provide refined glycerol. Since glycerol consumers will presumably be important partners in helping to develop large scale glycerol consumption processes, it will be important to determine the effect of glycerol purity on the various conversion processes undertaken.

3) *Catalytic transformations of glycerol.* The chemical industry has embraced catalysis as a primary conversion technology for its basic building blocks to the point that over 80% of all chemical processes now include at least one catalytic step (Holderich ref). In a similar fashion, the biorefinery must endeavor to use catalysis in the same way. A barrier exists in that catalysis within the petrochemical industry has been optimized for nonoxygenated hydrocarbon feedstocks. Development of catalysts optimized for conversion of oxygenated, renewable feedstocks will be important for increasing the efficiency of the biorefinery. This effort will have a synergistic effect with the sugar portion of the biorefinery. In a sense, glycerol is a very simply sugar, and catalytic technology that works on glycerol could also work for sugar conversions.

III. Fatty acids and esters as feedstocks for the biorefinery

A. Introduction

The other components of the overall oleochemical process shown in **Figure 2** are the fatty acids and esters. By weight, these materials make up the bulk of the fat splitting process, and also serve as raw materials for an existing oleochemical industry. An enormous amount of plant based fats and oils is produced annually by the oleochemical industry, 101×10^6 tonnes in 1998 alone. From 1998 to today, production has increased roughly 3%/yr.³⁷ Most of this production is used by the food industry, however, a 1988 report indicated that oils and fats also constituted the largest segment of renewable raw materials consumed by the chemical industry (**Table 6**). Today, about 14% of the total oil and fat production is used for production of nonfood chemicals.

Raw material	European consumption (10^3 tonnes)	World consumption (10^3 tonnes)
Sugar	65	800
Starch	390	1750
Cellulose	600	5014
Oils and fats	2700	9500

Table 6 – Estimated Consumption of Renewable Raw Materials by the Chemical Industry in 1985 (source: Baumann, H.; Buhler, M.; Fochem, H.; Hirsinger, F.; Zoebelein, H.; Falbe, J.; *Angew. Chem. Int. Ed. Eng.* **1988**, 27, 41)

The fatty acid structure undoubtedly contributes to the greater relative amounts of oleochemicals consumed by the chemical industry. In contrast to the highly oxygenated structure of carbohydrates, oleochemicals are hydrocarbons (**Figure 3**), closely related to petrochemicals, and well suited for many transformations understood by the chemical industry.

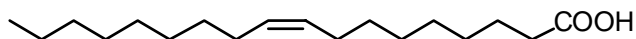


Figure 3 – Oleic Acid, a Typical Oleochemical

As a renewable feedstock, oleochemicals are positioned for immediate integration as a unit operation into the biorefinery. They offer all the benefits normally associated with increasing uses of renewables, and interestingly, offer the added benefit of long term price stability. In the period between 1962 – 1992, the average rate of increase of oil prices has been lower than that of inflation, and much lower than for petrochemicals.³⁸ Projections from Henkel/Cognis have indicated that natural oils and fats are a cheap and largely available source of raw materials.³⁹

A starting point for discussion of the opportunities requires realization of three key issues:

1) A key barrier to the oleochemical unit operation is acceptance of a new form of raw material by the chemical industry. It is our belief that fatty acids and esters, with appropriate development of new technology (as described below), can serve as an important transitional raw material as the chemical industry evolves from nonrenewable to renewable raw materials. It is interesting to observe that the hydrocarbon nature of fatty acids offers the industry more potential for shorter term payoff than glycerol, or more generally, carbohydrates. However, use of crude oil still dominates the industry, while oleochemistry remains a specialty sidelight. Thus, as a sidelight, the oleochemical industry might be considered “mature”, in the sense that it has not undertaken serious modernization of its separation and conversion technology. This situation, as is the case with any commodity technology, could change radically upon introduction of new conversion technology for the raw materials and a realization of their potential by the chemical industry. Demonstration of that potential is an exciting opportunity for DOE supported R&D that will directly address this important barrier. The presence of an existing industry based on plant fats and oils offers a nice advantage for partnership in development of this renewable as a chemical raw material.

2) As noted earlier, the genesis of this evaluation was an interest from DOE in the impact of increased amounts of fatty acid esters and glycerol from biodiesel production. Large scale biodiesel production will result in a significant increase in the available amounts of both fatty acid esters and glycerol. The fatty acid esters produced in this operation can be diverted to either biodiesel or chemical production as necessary. In this way, the petrochemical industry is modeled. Market and supply issues will determine the day to day process swings, and if chemical demand is down, fatty acid esters are dumped to the fuel stream, which, presumably being much larger than the chemical stream, will serve as an important process sink and eliminate any possible buildup of excess fatty acid ester inventory. However, glycerol is currently *only* useful for chemical production, thus, the availability of much larger amounts of glycerol results in the necessity of developing new markets for this material, as current markets might be overwhelmed. The fatty acid esters have much more flexibility in this regard.

3) In contrast to glycerol, fatty acid esters are not a single product. The wide variety of oil sources lead to a wide variety of fatty acid structures that could be available from the oleochemical unit operation, and therefore, a potentially larger slate of products as unit operation outputs. **Table 7** shows the broad range of oil sources that could conceivably be used to supply the biorefinery. The major oil sources in the U. S. are soybean and tallow. Other major oil sources are canola (rapeseed), sunflower, palm, palm kernel and coconut from southeast Asia, and castor. **Table 8** summarizes the yield of oil from several of these sources along with a typical market price. Interestingly, soybeans offer the lowest yield of oil, but also

one of the lowest prices. The immense size of the annual U. S. soybean crop undoubtedly contributes to this observation.

As is the case with glycerol, fatty acids and their derivatives find utility in a large number of applications (**Table 9**). However, there is no one single application that consumes the majority of FA produced. FA production and chemistry relies on relatively simple and well known technology, lagging behind processes commonly employed in today's chemical industry.

<i>Edible vegetable oils</i>	<i>Palm oils</i>	<i>Industrial oils</i>	<i>Animal fats</i>	<i>Marine oils</i>
Canola Corn Cottonseed	Babassu Coconut Palm	Castor Linseed Oiticica	Butter Edible tallow Inedible tallow and grease Lard	Fish Menhaden Sperm
Olive Peanut Rice bran Safflower Sesame Soybean Sunflower	Palm kernel	Rapeseed Tall Tung		

Table 7 – USDA Classification of Fat and Oil Types (U.S. Department of Agriculture, Foreign Agricultural Service, Chemical Economics Handbook)

<i>Oil source</i>	<i>Price (\$/kg – 2000)</i>	<i>Oil Yield (%)</i>
Cottonseed	0.463	18
Corn	0.300	45
Peanut	0.785	35
Soybean	0.324	18
Rapeseed	1.984	
Safflower	1.764	28
Sunflower	0.324	25
Coconut	0.432	63
Palm kernel	0.632 (1999)	45
Palm	0.373	20
Castor	1.036	45
Linseed	0.794	34
Tung	1.301	35
Tall	0.172 (1980)	
Inedible tallow	0.198	60-90

Table 8 – Prices for Various Oil Crops (Chemical Economics Handbook, “Fats and Oils Industry Overview”)

Use	Consumption (10⁶ lb – 2000)
Personal care products	631
Industrial lubricants, corrosion, oilfield	292
Plastics	266
Cleaners	251
Coatings and adhesives	184
Fabric softeners	184
Emulsion polymers	102
Foods	92
Rubber	86
Paper	81
Crayons, candles, waxes	59
Mining	56
Animal feed	40
Textiles	34
Asphalt	34
Buffing compounds	25
Agricultural	22
Exports	92
Other	84
Total	2615

Table 9 – North American Consumption of Fatty Acids by Market Segment (Chemical Economics Handbook, “Natural Fatty Acids”)

B. Research Opportunities in Fatty Acid Chemistry

Since a larger industry for the use of fatty acids already exists, comparison of the opportunities for fats and oils with those of glycerol is instructive. Three areas for glycerol use and consumption were defined: 1) existing glycerol markets, 2) recovery of old glycerol markets, and 3) new glycerol markets. For glycerol, the last opportunity was seen as offering the best possibility for consumption of new supplies of biodiesel derived glycerol, as it would be possible to saturate existing and former markets with the anticipated amounts of glycerol that might be available with capture of even a small portion of the current diesel fuel market.

In the case of oils and fats, the situation is different. A biorefinery unit operation based on oils and fats could, in principle, decide to swing all fatty acid esters toward biodiesel, depending on supply and demand. This offers a much greater level of flexibility for oil and fat use, in that the biorefinery operators would have control over the amounts of oil and fats available for production of higher value chemicals. By careful monitoring of market trends, the operators could tune the biodiesel/oleochemical ratio to maximize profitability of the overall unit operation. Excess glycerol *must* have new, alternate markets. Fatty acid esters *benefit* from new, alternate markets, but might not require them. It is important to realize, however, that only producing biodiesel from fatty acid esters will offer the lowest possibility for profit. The greatest value from this unit operation will come from balancing the oleochemical/fuel output for maximum profitability. As has been seen with other platforms, the profit derived from a chemical operation can be used to boost the low margins inherent in fuel production.

What does this mean with regard to research opportunities? Overall, it suggests that the biorefinery could focus more on existing oleochemical market segments. Developing of new technology would be carried out for the invention of next generation products in the most promising growth areas. Partnership with industry would help guide the technology development effort, and would provide the necessary market insight. There are advantages to this situation, in that the market infrastructure is already understood by the industry. As is the case with glycerol, it is almost impossible to define an exact target structure of a single fatty acid ester derivative and state with certainty that such a structure is the best to pursue. Moreover, such an approach may be inappropriate, in that our ability to call the research “precompetitive” becomes much less certain. Work on a single molecular structure would be much more closely linked to a single company. In contrast, one can appropriately discuss application areas in a general sense. For fatty acid esters, these might include growth segments such as surfactants, lubricants, and polymers. From a market standpoint, these segments are huge. From an infrastructure standpoint, they represent markets into which oleochemical derivatives already are sold. Improved products and technology will allow capture of a greater proportion of these markets by renewables. From a technical standpoint, the research offers opportunity to more selectively and cost effectively convert these raw materials into market products exhibiting properties deemed of value. Finally, work on compound classes would clearly be of benefit to an entire industry.

1) Chemical Conversion Technology

As is the case with the glycerol component of triglycerides, fatty acids find application in a number of different areas, but no one single use provides “blockbuster” consumption of the bulk of the oleochemicals produced. Use of FAMES as biodiesel could provide that blockbuster application, but only at the expense of producing a low value product that will require support from other areas of the biorefinery to realize an overall profitable operation. New uses of fatty acids based on new technology could offer higher value products to the biorefinery, the value of which could be used to offset the anticipated low margins that biodiesel production will afford.

The state of the art in chemical modification of fatty acids focuses almost entirely on simple, incremental changes at the COOH group of the molecule. Indeed, a broadly cited statistic regarding industrial uses of fatty acids indicates that over 96% of commercial transformations are carried out at the COOH group. Only 4% are directed at modification of the side chain. Clearly, from a research viewpoint, a great opportunity exists to develop cost effective and efficient technology for the selective structural modification of fatty acid side chains, and it is likely that the greatest growth in new oleochemicals will come from side chain modifications. Partnership with industrial experts in fatty acid manufacture and use will result in clear definition of the types of structural modifications that will have the greatest impact. Similarly, it is unlikely that effort on new transformations of the COOH group will result in any strikingly new compounds. Effort in this area is best left to process optimization chemists within the oleochemical industry.

a. Opportunities by market segment

1. Surfactants. An area of potential opportunity is in the production of alkyl polyglycosides.⁴⁰ These are surfactants based entirely on renewables as starting materials, and are the result of the reaction between a carbohydrate and a fatty acid or alcohol to give an amphiphilic molecule possessing a polar sugar based headgroup and a long nonpolar oleochemical tail. The research challenge in producing these materials arises in developing technology suitable for the selective reaction of a fatty acid at a single site of the carbohydrate molecule without the requirement of a

complex series of protection/deprotection sequences. While there are currently commercial products based on this technology, the materials are mixtures of mono, di, and triesters, which limits their utility to particular applications. Recent work by Cognis has resulted in the development of new materials, and has capacity for the production of 50×10^3 tonnes/yr. Given that the performance of these materials will be based on their structure, development of selective functionalization technology for both the sugar and fatty acid components would be an ideal research barrier for DOE investigation. Sugar functionalization would include methods for selective esterification and etherification.⁴¹

Although at present, industrial decisions to move from a nonrenewable to a renewable feedstock base will still be determined almost exclusively on economics, the use of fatty acids for the production of surfactants has also been studied from an environmental standpoint. LCA investigations by the oleochemical industry have indicated that a direct comparison of fatty alcohols and linear alkybenzene sulfonates as surfactants leads to energy savings and CO_2 reduction when the former is used.⁴² Further analysis has verified and expanded these findings.⁴³ Life cycle analyses indicate that, as is the case for other renewable based raw materials, oleochemical based materials exhibit better environmental compatibility than their petrochemically derived counterparts.⁴⁴

2. Polymers. Another very large potential market for consumption of fatty acid derivatives is the polymer market. Use of oleochemicals as polymer components is known but its share of the total polymer market is very small. The current world market for polymers in 1997 was 330×10^9 lb.⁴⁵ A specific example is in the use of diacids. This portion of the polymer market is dominated (87%) by materials such as adipic or terephthalic acid, while use of oleochemically derived diacids (azelaic, sebacic, and dimer acids of oleic acid) accounts for only 0.5% of the total. Displacing the commodity acids will be difficult, however, the use of oleochemical diacids offers access to an interesting suite of properties including elasticity, flexibility, impact strength, hydrolytic stability, hydrophobicity, lower T_g , and flexibility (Hill, K.; *Pure Appl. Chem.* **2000**, *72*, 1255). These materials might be ideal candidates for biochemical conversions as new organisms have been developed that convert fatty acids into diacids. For example, oleic acid can be converted into the corresponding α,ω -diacid upon reaction with the yeast *Candida tropicalis*.⁴⁶

Long chain fatty acids are used as plasticizers in the polymer industry, with the most important fatty acid being erucic acid, an unsaturated 22 carbon material ($22:1^{\Delta 13}$). Erucic acid is derived from canola, and is the source of components used in the engineering plastic, nylon 13,13. At one time, the demand for specialty materials such as nylon 13,13 was expected to be around 10^6 tonnes.⁴⁷ However, plant sources of erucic acid generally contain only 56% of this material, a number limited by the biosynthetic process. Development of new high erucic cultivars could contribute to greater availability of materials such as nylon 13, 13.

3. Lubricants. A final market opportunity may exist in the production of biolubricants from oleochemicals. Petrochemically derived lubricants possess an environmental problem in that they are often released during their use, for example, in various engines, metal working, chain saws, etc. It has been estimated that in Europe, the market for more biodegradable, oleochemical based lubricants could be 1.35×10^6 tonnes.⁴⁸ The U. S. production of lubricants in 1991 was 8.9×10^6 m³, indicating that a large market opportunity for new materials also exists domestically.

b. Opportunities by chemical transformation

For the technical expert, these types of transformations are the most easily recognized, and represent an incredibly diverse range of opportunities within the technical development necessary for the biorefinery. Since fatty acids are hydrocarbons, these transformations have the additional advantage of being able to draw on the broad knowledge possessed by the petrochemical industry. However, as these opportunities are transferred to decision makers, they frequently blur into a confusing array of technical jargon. It is best to remember that the transformations described in this section in a technical fashion are directly linked to 1) invention of cost effective processes for the industry and 2) the development of products and performance parameters deemed valuable by the market.

Depending on the oil source used, the fat splitting process can lead to a broad range of different fatty acid esters, each possessing different types of structural units. These structural units can be used to introduce new functionality that can be translated into marketplace properties. Partnerships with industry will be key in determining how these structural modifications are manifested in the product performance, and whether these properties will be valuable to the market.

1. Catalytic transformations. As a general technology, metal catalyzed transformations of fatty acids are less well studied than more conventional transformations. Many of the more specific research opportunities listed below could be carried out catalytically. However, because fatty acids are hydrocarbons, they are well suited to many of the kinds of catalytic transformations understood by the petrochemical industry, and a number of investigators have described new methods of modifying fatty acid structures in the presence of catalysts. Moreover, development of catalytic transformations would directly model the trend in the chemical industry toward catalysis, because of the well recognized benefits in economics, environmental impact, and process efficiency. The most well studied catalytic transformations of fatty acids include selective hydrogenation, for example, the conversion of linoleic acid to oleic acid, isomerization, oxidation, oxo-type carbonylation, olefin metathesis, C-C bond formation, and olefin addition reactions.⁴⁹ The breadth of catalytic processes available suggest that many more opportunities exist in this area.

2. Transesterifications/selective esterifications. Selective ester forming processes offer an important R&D opportunity for both the initial raw material producing step in the oleochemical unit operation (**Figure 1**) as well as for the manufacture of the oleochemical product suite. Fat splitting processes rely on transesterification, usually with MeOH. However, existing processes typically leave the glycerol portion as an aqueous solution that must be separated later. In contrast, new biochemical fat splitting processes that can operate in the presence of MeOH or other alcohols would offer an important advantage in developing oleochemicals as feedstocks for the chemical industry. Moreover, the current oleochemical industry makes a large number of different kinds of esters from their fatty acids. Frequently, the glycerol and specific fatty acids produced during fat splitting are recombined to make a variety of products (e. g., glycerol stearate). However, these products are normally mixtures of different types of esters. Selective processes that could control the structural purity of the products would lead to much greater control over the properties inherent in the product, and the ability to tailor various products to address specific market segments.

3. Reactions at the double bond of unsaturated fatty acids. A common structural unit found in fatty acids is the isolated double bond, which offers the most accessible site for further structural transformation. A wide range of fatty acids contain this functionality, and it is the site

of a fairly broad range of conversion processes.⁵⁰ A deeper investigation of unsaturated oils and their transformation might offer synergy between the interests of the oleochemical industry, which is looking for monounsaturated oils, and the interests of the food industry, also looking for monounsaturates (Claude, S.; *Oleag. Corp. Gras Lipid.* **1999**, 6, 418). Henkel/Cognis has described a market potential for high oleic sunflower and canola oil in Europe of 100×10^3 tonnes (Claude, S.; *Oleag. Corp. Gras Lipid.* **1999**, 6, 418). The goal is to replace tallow oleic acid, and to offer competition to palm oil derived oleic acid being produced in southeast Asia.

Epoxidation of the double bonds in fatty acids is an area of current interest, as oil epoxides have utility as PVC stabilizers. Methyl oleate has been epoxidized and further modified with acrylic acid to form a pressure sensitive adhesive (for example, Post-It notes).⁵¹ Polymerization of oleochemical epoxides has also been investigated for eventual application in the industrial polyether market.⁵² Different epoxidized oils have been used for this purpose including palm⁵³ and soybean.⁵⁴ Research barriers in this area would include development of effective and high yield epoxidation catalysts, and development of efficient polymerization technology for longer chain epoxides, so that the properties they exhibit can be more effectively studied.⁵⁵

The double bond in unsaturated fatty acids is also a point for oxidative cleavage. Commercially, this transformation is carried out by large scale ozonolysis, for example, in the conversion of oleic acid into azelaic and pelargonic acids. However, given the hazards associated with large scale use of ozone, it would be useful to examine new catalytic methods of double bond cleavage (**ref: see ACIE paper**). Catalytic processes based on O_2 or HO_2H as oxidants would have the benefit of being both inexpensive and environmentally friendly, but recent approaches to these processes proceed in only fair yield.⁵⁶

Cationic olefin polymerization is a well known approach for the production of commodity level polymers. Soybean oil has been incorporated into alkene polymerization schemes to give new renewable containing copolymers.⁵⁷

4. Reactions at unactivated sites of the fatty acid chain. The most available and least explored functional group of fatty acids are the aliphatic C-H bonds. A significant barrier exists with the current inability of modern chemical or biochemical techniques to effectively select and functionalize a specific C-H bond from among many similar bonds. New metal catalyzed processes are beginning to develop the understanding necessary to effectively carry out these types of transformations. Most work on functionalization of C-H bonds has been carried out on simple hydrocarbons. The advantage possessed by fatty acids for implementation of this type of chemistry is the presence of additional functional groups that however, a more concerted effort to effectively use the functional groups present in fatty acids.

These types of transformations describe a very challenging, but perhaps ideal example of the type of research that could be supported by DOE programs. It is a high risk problem that has not yet been solved, but whose solution, if general, would have extremely broad application to the chemistry industry as a whole.

5. Biochemical transformations. A transformation of particular interest is the direct epoxidation of the double bonds in unhydrolyzed triglycerides. One of the problems in the production of biodiesel from lower value triglyceride sources, such as recovered oils and greases, is the presence of high levels of free fatty acids. However, it has been found that enzymatic epoxidation of the double bonds in certain triglycerides is enhanced by the presence of free fatty acids, thus converting an initial problem into a solution.⁵⁸ Given that vegetable oil epoxides (epoxidized soybean oil) are becoming useful industrial additives for plastics,

combination of fatty acid promoted epoxidation of waste oils with an enzymatic triglyceride hydrolysis would lead to a new source of components for the very large plastics industry.

c. Separation Technology

A key issue in the greater use of oleochemicals as chemical feedstocks is developing methodology for their separation into individual fatty acids. Most commodity sources of triglycerides supply a mixture of fatty acids of differing chain length and structure. This issue can be addressed in two ways:

a. development of more selective triglyceride sources, for example plant technology to develop high oleic soybean or sunflower, or high erucic acid rapeseed.

b. development of new, highly selective separation technology. This is a true research barrier that could result in good benefit to the oleochemical industry. The structure of the fatty acids are all quite similar. Distillation can be used to achieve some level of separation, but isolation of pure requires significantly more effort. The difference can be noted in the relative costs of materials. Aldrich sells tech grade oleic acid (90%) for roughly \$50/gal. However, pure oleic acid (99%) is \$8.00/g! The current makeup of the oleochemical industry accommodates acid mixtures, however, the versatility of the product streams could be enhanced with simple, cost effective separation technology. The ideal technology would need to selectively differentiate fatty acids based on chain length.

Interestingly, highly selective separation processes were developed by UOP for the petrochemical industry for the separation of paraffins and olefins. The Pacol-Olex process is used for this type of separation.⁵⁹ Adaptation of this technology to oleochemicals would result in lower cost sources of higher purity materials.

C. Market Overview

As is the case with glycerol, improvements and breakthroughs in existing conversion technology for fatty acids and esters would also have an important impact in existing market segments and applications. Accordingly, it is useful to understand how the current market consumes fatty acids and esters.

1) *Product breakdown by major category* (Chemical Economics Handbook, "Natural Fatty Acids")

1) Fatty amine derivatives – these compounds are derived from the reaction of fatty acids with ammonia to give fatty nitriles. They are subsequently hydrogenated to give primary, secondary, and tertiary amines, which are converted to other materials. These compounds consumed 204×10^6 lb of fatty acids in 2000.

Other materials in this class include the following:

Quaternary ammonium salts - This consumed 101×10^6 lb of FA in 2000. The largest product type is dimethyl dehydrogenated tallow ammonium chloride (DHT quat). It is primarily used as a fabric softener. Products such as Downy, Final Touch, Bounce, and Cling Free use DHT quat. DHT quat is also used as a lubricant and viscosifier in the oil, paint, and lubricant industries. Other uses are found in dyes, textiles, and as additives to a number of materials.

Amines, diamines, ethoxylate amines – This consumed 103×10^6 lb of FA in 2000. As primary amines, these materials are useful as lubricant additives, and find specific application in industrial gear boxes and oilfield chemicals. Reaction with acrylonitrile (Michael addition) leads to fatty alkyl diamines, used as emulsifiers and lubricants. Reaction of the amines with ethylene oxide leads to ethoxylated amines, useful for the agricultural industry. For example, Roundup is emulsified using an ethoxylated adduct of tallow derived FA.

2) Other fatty acid derivatives – this is a broad category of materials, and accounted for the consumption of 1317×10^6 lb of FA in 2000. The following groups of materials are included:

Esters – Production of esters consumed about 353×10^6 lb of FA in 2000, and the products were used in lubricants, plastics, food, personal care products, textiles, fabric softeners, and paper. Esters of both simple and complex alcohols are made. These include glycerol esters of defined structure, which are made by the selective reesterification of glycerol after fat splitting. Approximately 90×10^6 lb of FA were used to make mono- and diglycerides used as emulsifiers in foods. Another 25×10^6 lb were used to make personal care products. About 80×10^6 lb of shorter chain FA (caprylic, C8, and capric, C10) were converted to (for example) pentaerythritol esters for use in synthetic lubricants. About 50×10^6 of oleic acid is converted to glycerol monooleate, which is a fire retardant hydraulic fluid. The material is also used in foods.

Heavy metal salts – About 239×10^6 lb of FA were converted to (primarily) metal stearates in 2000. More specifically, these salts included 193×10^6 lb of dry products (various salts), 80×10^6 lb of Ca salts as a 50% aqueous dispersion, and 44×10^6 lb of Ca salts as a 44% wax dispersion.

Ca salts make up the bulk of these materials (160×10^6 lb of Ca stearates in all forms), with lesser amounts of Zn, Mg, Al, and other metal salts making up the remainder. These materials are used mostly in the plastics industry to provide lubrication during molding. 50% aqueous Ca stearate is used in the paper industry as a lubricant for coated products. Metal stearates use is summarized in **Table 10**.

Use	Consumption (10^6 lb – 2000)
Plastics	170
Paper	40
Rubber	15
Food, drugs, cosmetics	10
Lacquers	5
Cement	5
Grease	4
Petroleum	2
Textiles	1
Other	3
Total	255

Table 10 – Industrial Consumption of Metal Stearates (Chemical Economics Handbook, “Natural Fatty Acids”)

Monomer/dimer/trimer acids – Unsaturated fatty acids undergo oligomerization at elevated temperatures to give monomers, dimers, and higher oligomers. This application consumed

about 211×10^6 lb of FA in 2000. Interestingly, tall oil fatty acids have accounted for over 85% of this use. Dimer acids are used primarily in the production of non-nylon polyamide resins. The process also generates about 70×10^6 lb of monomer fatty acids, such as isostearic acid. Stearic acid is also generated in this process.

Ester quats – Fatty acids undergo reaction with di- or triethanolamines to give diesters with a tertiary nitrogen. The material is converted to a quat salt with an alkylating agent. This material is finding utility as a replacement for DHT quats. This reformulation has led to considerable growth in this area, consuming 144×10^6 lb of FA in 2000.

FA-polyamine condensates and quats – Heterocyclic adducts of FA with polyamines (e. g., diethylenetriamine) consumed about 114×10^6 lb of FA in 2000. These materials found uses in several applications, including corrosion inhibitors, emulsification, mining, and fabric softeners.

Anionic specialty surfactants – About 87×10^6 lb of coconut FA were consumed in this application in 2000. 77×10^6 lb were consumed in the production of acyl isethionates, used in soap products such as Dove, Caress, Lever 200, Oil of Olay, and baby soap.

Fatty acid amides – About 86×10^6 lb of FA were consumed in the production of fatty acid amides in 2000. Most amides were made from long chain FA, such as stearic, oleic, and erucic acids. Their primary application is as slip agents and lubricants in plastics. The largest volume material (52×10^6 lb/yr) is EBSA [N,N'-ethylenebis(stearamide)], that is used as a lubricant for injection molding. About 70% of its use is in this application. The remainder is used in textile and paper applications.

Amphoteric Surfactants – About 52×10^6 lb of FA were used in the production of specialty surfactants. These materials are used in shampoos, dishwashing liquids, liquid hand soaps and industrial cleaners.

Shorter chain fatty acids – Shorter chain length products are made via ozonolysis of the double bond in oleic acid. Approximately 48×10^6 lb of oleic acid were converted into azelaic and pelargonic acid. The challenge for this process is balancing the market demand for the two products because they are used in different applications. Azelaic acid esters are a component of plasticizers and synthetic lubricants, while pelargonic acid is the principal component of sodium nonanoyloxybenzene sulfonic acid, used as a bleach activator in detergents.

Alkyl ketene dimers – These materials are used as sizing agents in the paper industry and their manufacture consumes about 33×10^6 lb of FA.

Other – CEH also cites the use of about 10×10^6 lb of FA for other uses.

3) Fatty acids and their salts – This category is very large, and consumed 1094×10^6 lb of FA in 2000. There are several end uses for these materials.

Cosmetics, soaps, polishes, household and industrial cleaners – Over 680×10^6 lb of FA were used in these applications in 2000. CEH notes an interesting market reporting quirk. If a manufacturer is making soaps by continuous saponification of fats and oils, no FA is isolated, and therefore, its production level is not counted as FA production in the oleochemical industry. However, in batch-type noncontinuous processes, the FA is isolated and then neutralized, and is therefore counted in production statistics. Fatty acids are added to soaps such as Dove,

Caress, and Lever 2000 in a process called superfatting. Some household detergents, such as Liquid Tide, also contain fatty acids.

Alkyd resins – Alkyd resin coatings require drying oils, and about 85×10^6 lb of FA were used in this application in 2000. Most FA in these applications come from tall oils, with some additional material being provided from soy oil.

Emulsion polymerization – This process uses FA as emulsifiers, and consumed about 100×10^6 lb of FA in 2000, particularly in the production of styrene-butadiene rubbers and ABS resins.

Rubber compounding – Production of rubber uses FA in the vulcanization process, and as a lubricant for the rubber. About 72×10^6 lb of FA were used in this application.

Animal feed – About 40×10^6 lb were used as animal feed.

Mining – The mining industry used about 40×10^6 lb of FA, mostly from tall oil, in 2000.

Buffing compounds – Stearic acid is used as a buffing compound, and in 2000, 25×10^6 lb were used for this purpose.

Crayons, waxes and candles – This is a rapid growth segment, particularly with the gradual displacement of wax in candles with fatty acids. About 47×10^6 lb were consumed in this application in 2000.

4) *Fatty alcohols* – A large amount of fatty acids are reduced to fatty alcohols for use in the detergent market. Industrially, reduction is carried out continuously on the methyl ester at up to 3000 psi, normally using a copper chromite catalyst. In 1998, a total of 2265×10^6 lb of detergent alcohols were produced in North America, Japan, and Western Europe. Again, there is considerable additional capacity (974×10^6 lb) in southeast Asia. Over 94% of the detergent alcohols in North America were compounds with chain lengths between C12 and C18. **Table 11** shows how these alcohols were distributed in the three major global market areas.

Production of detergent alcohols can be “natural”, starting from the alcohol exchange reaction on triglycerides, or synthetic, relying on the use of hydrocarbons to build up mixtures of long chain alcohols. In North America, a significant proportion of detergent alcohols (78%) are made synthetically. The trend reverses somewhat in Europe, with 59% of detergent alcohols being made from natural sources. Production in Europe also exceeds that in North America, with 1170×10^6 and 1466×10^6 lb being produced, respectively. In recent years, all new capacity is based on natural oils, reflecting the interest in SE Asia for greater commercialization of palm, palm kernel, and coconut oils. A limitation to production of synthetic oils is that unsaturated fatty alcohols cannot be made by this method. High pressure hydrogenation of natural fatty acids over the appropriate catalyst will selectively reduce the ester group and leave the olefin untouched.⁶⁰

The comparison in costs between natural and synthetic detergent alcohols is interesting (**Table 12**). In all cases, natural sources of detergent alcohols are less expensive than their synthetic counterparts. In addition, many of the synthetic materials are mixtures of a relatively large number of different chain lengths, reflecting the nonselective nature of their manufacture,

<i>Derivative</i>	<i>North America</i>	<i>Western Europe</i>	<i>Japan</i>
<i>Alcohol ethoxylates</i>	805	608	144
<i>Alcohol sulfates</i>	60	181	46
<i>Polymethacrylate esters</i>	25	64	
<i>Fatty nitrogen derivatives</i>	20	35	
<i>Alcohol glyceryl ether sulfonates</i>	16		
<i>Alkylpolyglucosides</i>	16		
<i>Hindered phenols</i>	8.5		
<i>Thiodpropionate esters</i>	6	11	
<i>Other</i>	15.5	159	40
<i>Free alcohols, C₁₂ – C₁₈</i>	41		24
<i>C₂₀₊ alcohols</i>	20		
<i>Consumer inventory</i>	3		
Total	1036	1058	254

Table 11 – Distribution of Fatty Alcohol Products in North America, Western Europe, and Japan (10⁶ lb) – 1998 (Source: CEH, Detergent Alcohols)

<i>Chain length</i>	<i>Trade name source</i>	<i>Synthetic oil price (\$/lb)</i>	<i>Natural oil price (\$/lb)</i>
<i>C₁₂</i>	Alfol 12	1.15	
<i>C₁₂</i>	Alfol 14	1.15	
<i>C₁₂ – C₁₄</i>	Epal 1214	0.91	
<i>C₁₂ – C₁₄</i>	Alfol 1214	0.95	
<i>C₁₂ – C₁₄</i>	Alfol 1412	1.19	
<i>C₁₂ – C₁₄</i>	Alfol 1216	0.95	
<i>C₁₂ – C₁₄</i>	CO 1214		0.70
<i>C₁₂ – C₁₅</i>	Neodol 25	0.82	
<i>C₁₂ – C₁₃</i>	Neodol 23	0.82	
<i>C₁₄ – C₁₅</i>	Neodol 45	0.82	
<i>C₁₄ – C₁₆</i>	Epal 1416	0.82	
<i>C₁₄ – C₁₈</i>	Epal 1418	0.91	
<i>C₁₆</i>	CO 1695		0.75
<i>C₁₆ – C₁₈</i>	Alfol 1618	1.03	
<i>C₁₆ – C₁₈</i>	TA 1618	0.70	
<i>C₁₆ – C₂₀</i>	Alfol 1620	0.93	
<i>C₁₆ – C₁₈</i>	Epal 1618	0.84	
<i>C₁₈</i>			0.75
<i>C₂₀₊</i>	Epal 20+	0.66	
<i>C₂₀₊</i>	Alfol 20+	0.70	

Table 12 – Comparative Prices of Natural and Synthetic Detergent Alcohols – 1999 (Source: CEH, Detergent Alcohols)

normally through catalytic oligomerization of lower olefins. The greater proportion of synthetic oils in the North American detergent market most likely reflects the entrenched position of the

petrochemical industry, and the desire to use existing capital and technology, rather than an economic benefit. The situation in Europe is reversed, with the prices for natural oils being higher than those of synthetic.

A potentially large opportunity could exist for these materials, as the general surfactant market is huge. In 2000, almost 11×10^9 lb of detergents were consumed in the U. S. alone, and all of it requires the addition of some form of surfactant. Worldwide, the total surfactant market is almost 21×10^9 lb (Hill, K.; *Pure Appl. Chem.* **2000**, 72, 1255). As stated in the Chemical Economics Handbook (CEH, Surfactants, Household Detergents and Their Raw Materials):

“The choice of surfactant used in a detergent involves a detailed cost/performance evaluation of the entire formulation. A complex matrix of formulations might ideally achieve acceptable performance and provide the manufacturer with considerable latitude in minimizing costs, depending upon the prevailing raw material prices at the time.”

The point becomes that with proper study and partnership with industrial experts, FA based surfactants stand to capture a larger proportion of a huge market, greatly increasing the impact of renewables on that segment of the industry.

5) *Fatty alkanolamides* – A smaller outlet for the consumption of fatty acids is the fatty alkanolamide market. Fatty alkanolamides are produced from the reaction of FA with dialkanolic amines. The market is generally decreasing, as the material has been superceded by other FA derivatives. In 2000, the U. S. consumed 24×10^3 tonnes of fatty alkanolamides.

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³ Calculated as follows:

$(60 \times 10^9 \text{ gal})(3.79 \text{ L/gal})(0.88 \text{ kg/L}) = 200 \times 10^9 \text{ kg diesel}$
5% of market = $10 \times 10^9 \text{ kg biodiesel}$, gives $1 \times 10^9 \text{ kg glycerol coproduct}$
 $(1 \times 10^9 \text{ kg glycerol})(1 \text{ tonne}/10^3 \text{ kg}) = 1 \times 10^6 \text{ tonnes glycerol}$

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⁷ New, larger scale uses of glycerol have not been widely addressed because the availability and cost of glycerol fairly well defined what market segments would be available. Although the cost of glycerol has recently been lower than normal (\$0.50 – 0.60/lb), tight supplies have raised the price to around \$0.80/lb, and as recently as 5 years ago, it was in the \$0.80 – 1.00/lb range.

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