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### Biomass-based green chemistry: sustainable solutions for modern economies

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## ORIGINAL ARTICLE

### Biomass-based green chemistry: sustainable solutions for modern economies

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Biomass and renewable raw materials are the basis and driver for an even greater alignment of industry to the principles of green chemistry and sustainability. Nature provides a remarkably wide range of renewable raw materials with varying properties and differing chemical compositions. Renewable raw materials are therefore especially interesting as alternatives to fossil resources for energy generation and as starting materials for industrial chemistry. Since various forms of biomass are also essential for human nutrition and animal feed, their use as feedstocks for other purposes must be balanced. Ideally, the biomass remaining after the nutritious components are removed can serve as a feedstock. Examples of applications that use biomass as starting materials include adhesives, textile and leather, cosmetics, cleaning agents, coatings, paints, printing inks, crop protection, lubricants and dietary supplements.

**Keywords:** biomass; green; chemistry; sustainability; renewable

#### Introduction

Green is a strong color often associated with life, fertility and health. Green is the color of chlorophyll, a vital component in natural systems. Green is also associated with the color of money in many countries. Being green has long been a battle cry of environmental activists and green political parties. Most recently, being green has become an important marketing tool for businesses. For chemists, it is becoming increasingly important to be green by applying the principles of green chemistry to all facets of the chemical sciences: basic and applied research, application technology, process development, manufacturing, and education.

Concern over the depletion of natural resources is not a new concept. The sustainable use of wood was considered important for economic reasons in earlier centuries. In fact, the term sustainability, *Nachhaltigkeit* (in German), originated in the eighteenth century when Hannß Carl von Carlowitz (Oberberghauptmann and Chief Executive of the Royal Saxon Mining Department) declared that forestry had to be “sustainable,” which meant that logging and reforestation had to be in balance (1). This was in order to conserve the wood supply for the important silver mines in the Erzgebirge, the economic backbone of the Kingdom of Saxony and its famous capital Dresden.

The year 2007 marks important anniversaries for a number of key events in the history of sustainability: it is 35 years since the Club of Rome published *Limits to Growth*; 20 years since the publication of the Brundtland Report *Our Common Future*; 15 years since the Earth Summit in Rio and 10 years since the Kyoto Protocol was signed. Each of these milestones has had a significant effect on global public opinion (2) and understanding of global environmental issues. Neither businesses nor individuals can afford to ignore environmental issues any longer. The sustainability trend is driven by society’s changing values, with consumers demanding that industry act more responsibly and governments around the world introducing increasingly strict legislation to ensure it does so. “Lifestyles of Health and Sustainability” (LOHAS) has become a “Mega trend” (Figure 1).

The year 2007 has also been a busy year for the advancement of sustainability in light of the mounting and irrefutable evidence of global climate change. At the very beginning of the year the *Stern Review on the Economics of Climate Change* was published by the HM Treasury of the UK Government (3). It was followed by the establishment of the Intergovernmental Panel on Climate Change (IPCC) by the World Meteorological Organization (WMO) and the United Nations Environment Program (UNEP)

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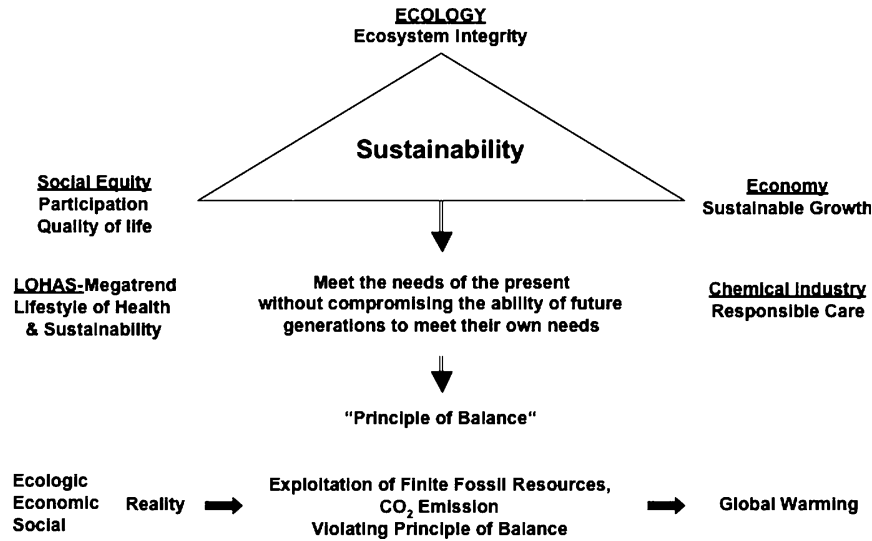


Figure 1. Triangle of sustainability.

in order to assess scientific, technical and socio-economic information relevant for the understanding of climate change, its potential impacts and options for adaptation and mitigation (4). After awarding Wangari Maathai the Nobel Peace Prize in 2004 for her contribution to sustainable development, democracy and peace and noting in her presentation speech “peace on earth depends on our ability to secure our living environment,” the Nobel Committee again distinguished sustainability efforts by awarding the 2007 Nobel Peace Prize to the IPCC and Albert Gore Jr (5). The recent award was for their efforts to build up and disseminate greater knowledge about man-made climate change, and for laying the foundations

for measures to counteract such change. In the Summary for Policymakers of the Synthesis Report of the IPCC Fourth Assessment Report (AR4) edited in Valencia/E, November 2007, a clear statement is made that “warming of the climate system is unequivocal, as is now evident from observations of increases in global average air and ocean temperatures, widespread melting of snow and ice, and rising global average sea level,” emphasizing that violation of the principles of sustainability is ongoing and one of the reasons that lead to global warming (Figure 1).

Two years stand out in any discussion of global climate change: 1816 and 2005. Due to a geological event, the eruption of the volcano Tambora in Indonesia in 1816, this year was the coldest year since weather records were established. In contrast, the year 2005 had the highest average temperatures and the mildest winter. The magnitude of the climate change between 1816 and 2005 can only be attributed to the action of men. Not coincidentally, the time span between the coldest and the warmest years on record also marks the beginning and maturity of the industrial age. Two hundred years of strong growth in world population and a phenomenal growth of industrial production have also lead to a resource consumption that by many accounts approaches or surpasses the limits of sustainability (Figure 2).

Almost exclusively, fossil resources fueled this fast-track development; particularly petroleum formed 10 millions of years ago. The petroleum reserves are not depleted yet, but easily accessible new reserves of significant quantities have not been discovered since the 1970s and the gap between demand and supply is becoming greater. A recent study by the German-based Energy Watch Group, (6)

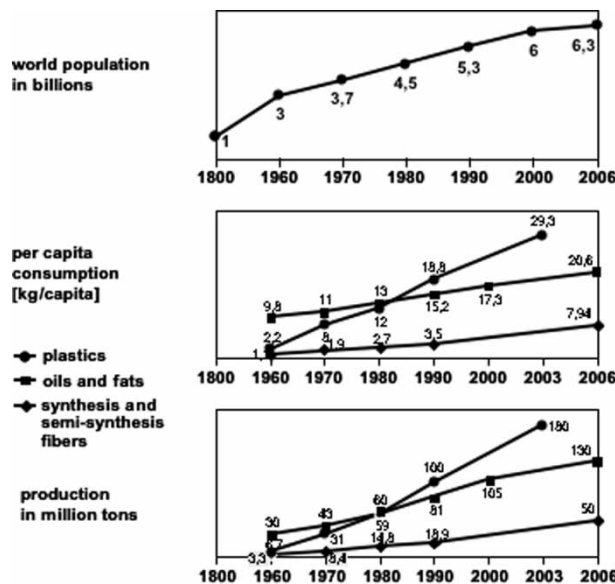


Figure 2. World population, per capita consumption and production of plastics, fibers, oils and fats.

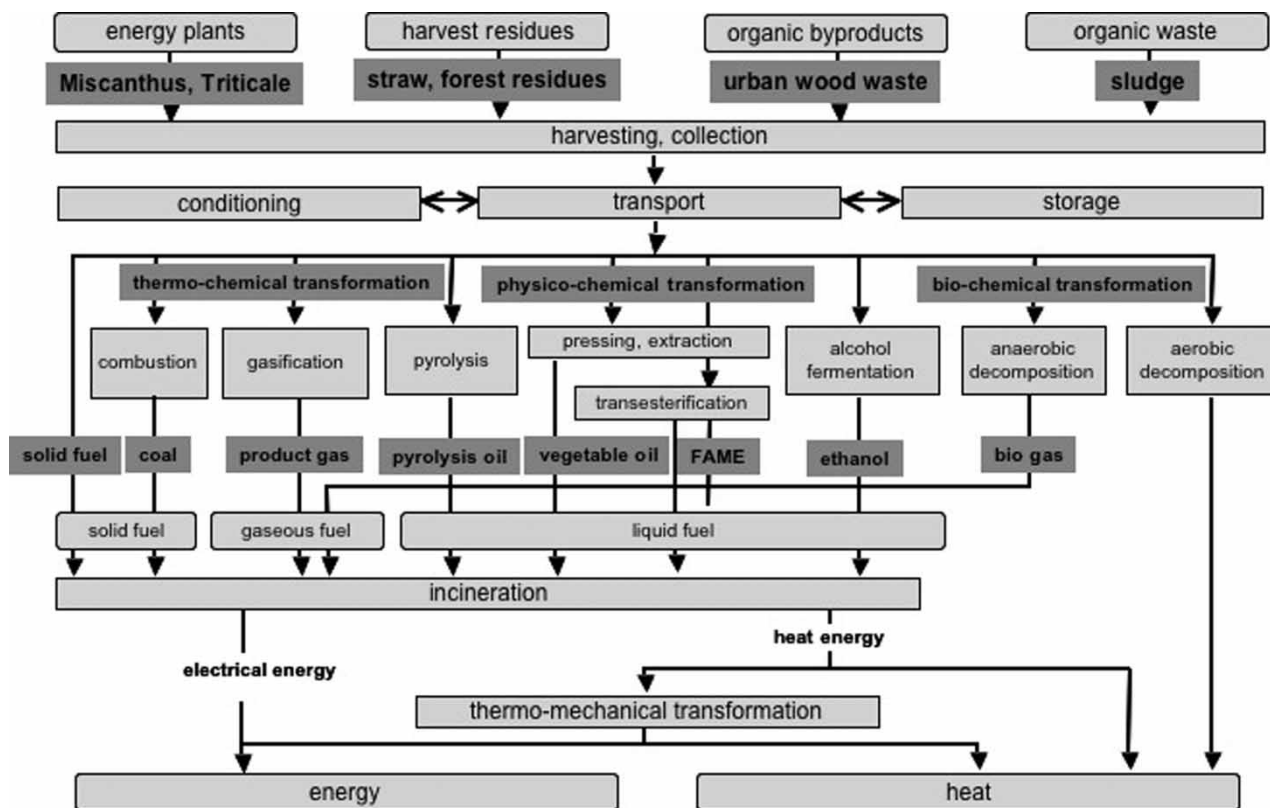


Figure 3. Transformation of biomass to energy.

in sharp contrast to the projections by the International Energy Agency (IEA), states that world oil production already peaked in 2006 and will decline by half as soon as 2030. The recent discovery of the eight billion barrels of light crude Tupi field off the coast of Rio de Janeiro does not fundamentally change the results of Energy Watch Group's analysis. The Tupi field lies below 2140 meters of water, more than 3000 meters of sand and rocks, and then another 2000 meter thick layer of salt. Getting the oil out of Tupi and eventually other yet unexplored ultra-deep fields will be a formidable challenge.

Although new discoveries of fossil fuels are declining, the combined energy demand of the industrialized world and emerging economies are continuing to grow. Some forecasts envisage an asymptotic relationship between current demands for petroleum products and their availability; the growth in demand is expected to be covered by alternative renewable energies. The use of renewable raw materials would safeguard the meager reserves of fossil resources, would be a major factor in preventing climate change and would be the solution to the energy issues of the future. Additionally, the decomposition of renewable resources or their use for thermal or mechanical energy generation only releases as much carbon dioxide as was previously

bound in the plant during growth. In this cyclic system there is no net increase of the CO<sub>2</sub> level in the atmosphere to contribute to the greenhouse effect.

Unlike their petroleum counterparts, products from renewable raw materials can be recycled, composted or thermally utilized. This represents an easing of, or even the solution to, disposal problems. Ultimately, agricultural generation of renewable raw materials creates sources of income for farmers outside the traditional foodstuffs industry. In the future it will be even more important to harness biomass to the extent that it either replaces fossil resources and nuclear fuels in covering the world's energy demand or at least provides an effective alternative. Availability is basically not a problem; the biomass generated naturally every year is estimated at 170–200 billion tons; of this, currently three to four per cent at most is utilized by mankind (7). Possible uses for renewable raw materials also go way beyond those provided by other groups of raw materials and sources of energy.

The amounts of biomass available suggest that there does not need to be a conflict between the different applications of biomass resources. In practice however, state subsidies policies and economic considerations on the part of the agricultural industry may lead to competition for space between foodstuffs production, bioenergy and industrial utilization. An

example of this is the recent “Tortilla Crisis” in Mexico (8) where corn prices, spurred by the demand for grain-based ethanol, lead to expensive tortillas – a dietary staple among the poor. The question of the reliability of the supply of renewable raw materials in the face of competing demands has also arisen for the chemical industry (9). Farsighted scientists like Friedrich Asinger have previously addressed this issue (10).

### Biomass for energy supply

Different forms of biomass, such as plants like miscanthus, switch grass or triticale, harvest residues, organic by-products and waste can be used for the generation of heat and electrical power (Figure 3). Transformation technologies such as combustion, gasification, and hard pyrolysis in combustion plants of various size and dimensions have been designed (11).

The key challenge to the use of biomass as an energy source is energy density, which is at least 10-fold lower than that of petroleum fuel. Additionally, the storage, conditioning and transport of biomass on a volume basis create a significant energy demand of their own. These may be some of the reasons why consumption of primary energies in a country like Germany actually relies 82% (compared to 79% in the European Community) on fossil resources (Figure 4). Although the use of renewable energies in the primary energy supply has more than doubled between 1999 and 2005 it still does not represent more than 4.6% of the total primary energy supply with 70% of these renewable energies coming from biogenic energy resources (12).

### Biomass for fuel (13)

The use of biofuels to power automobiles is not new. When Rudolf Diesel presented his diesel engine at the World Trade Show in Paris 1901 the engine used peanut oil as fuel, and the Model T Ford was originally designed to run ethanol. Fuel shortages

during WWII prompted searches for alternative fuels in Germany, Switzerland and other countries. One of the most unusual solutions involved the modification of vehicles for use with wood, charcoal, or coal. Typical modifications included a gas generator, a gas reservoir and carburetor modifications and additional plumbing to convey, filter and meter the gas into the engine.

Brazil was the first nation to introduce biofuels as a large scale alternative to fossil fuels. In response to the oil crisis of the 1970s the Brazilian Government campaign, *Proálcool*, made it a national priority to build distilleries that use domestic sugar cane as the raw material basis for fermentation into ethanol, requiring that this fuel can be mixed into all gasoline. Since the 1970s, Brazil has saved almost 50 billion US dollars in imported oil, while creating as many as one million rural jobs.

Bioethanol can be produced from many different raw materials, which are grouped according to the type of carbohydrates they contain, like sugar, starch or lignocelluloses. Sugar for ethanol production may be derived from any of the three classes of raw materials. Industrial processes for the production of ethanol by fermentation of molasses, beet, cane or grain sugars are well established (Figure 5).

Bioethanol manufacturing from corn grain results in three products: bioethanol, the primary end product; residual non-fermentable corn kernel components, which are typically marketed as “dried distillers’ grains with solubles,” known as “DDGS”; and carbon dioxide (14). The by-products are an important factor with regard to the economics of bioethanol synthesis. DDGS, a fibrous, high protein residue after drying and pelletizing, is sold to livestock producers as food for animals that can digest high proportions of fiber, primarily cattle. Carbon dioxide results from the fermentation stage during starch consumption and metabolic conversion by yeast. This by-product stream can be sold to specific compressed gas markets.

Since sugars are already available in a degradable form and yeast cells can metabolize sugars directly, sugar-containing biomass as substrate requires the least costly preparation. The other carbohydrates, namely starch and lignocelluloses containing biomass, must be hydrolyzed to sugars before they can be metabolized, adding an extra step, called saccharification, to the process.

Lignocellulosic biomass is comprised of cellulose, hemicelluloses and lignin. Bioconversion of lignocellulosic material to bioethanol requires four major unit operations: pre-treatment, hydrolysis, fermentation and product separation and distillation (Figure 5). Pre-treatment is considered to be one of the most expensive processing steps for the conversion of

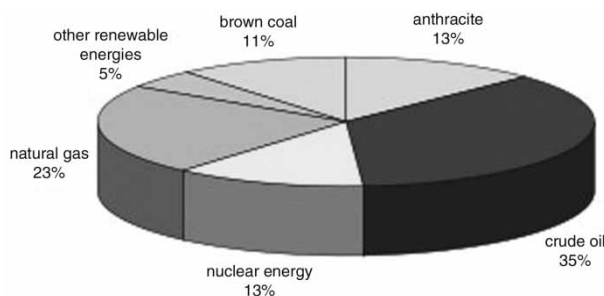


Figure 4. Primary energy consumption in Germany (2005) (Total: 14,2 EJ = 14240 PJ) (Source: Wikipedia, *Primärenergieverbrauch* (April 15, 2007)).

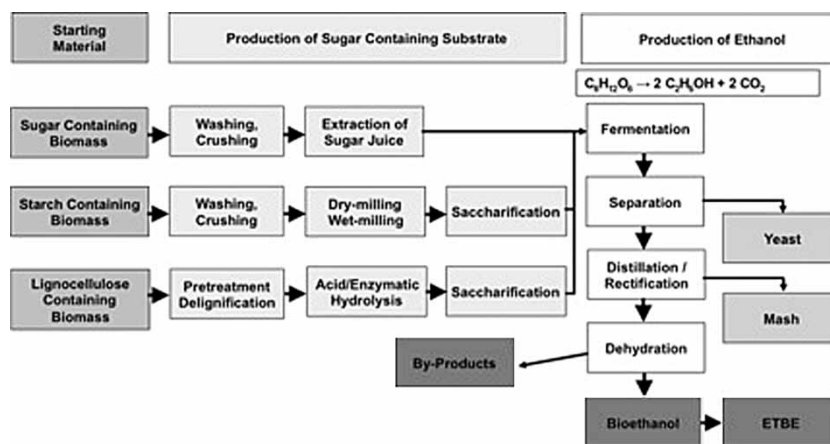


Figure 5. Production of bioethanol.

lignocelluloses raw material into fermentable sugar (15). Pre-treatment affects the structure of biomass by solubilizing hemicelluloses, reducing crystallinity and increasing the available surface area and pore volume of the substrate. Thermochemical pre-treatment methods appear more promising than biological options for the conversion of the lignin fraction of cellulosic biomass, which can have a detrimental effect on enzyme hydrolysis. The lignin fraction can also serve as a source of process energy and potential co-products that have important benefits in a life cycle context.

Bioethanol can be produced by batch, semi-continuous, and continuous processes. In particular the discovery of continuous fermentation, which permits the recycling of the yeast, was a revolutionary step, substantially increasing the speed of the process and reducing the cost of heating and cooling required in single-batch processing.

Unlike ethanol produced for beverages, fuel ethanol must be distilled to have only a very small amount of water content.

The extracted bioethanol is used in vehicles both in the pure form E100 and in specific mixtures with traditional petrol, such as E85 (85% ethanol). Flexible-fuel vehicles, already widely used throughout Brazil and to some extent in the USA, enable the use of different petrol-ethanol mixtures. Alternatively, bioethanol can react with isobutylene yielding ethyl tert-butyl ether (ETBE), which is used as an alternative to MTBE as an oxygenate gasoline additive and octane enhancer (16).

While bioethanol is used alone or in combination with traditional petrol in spark ignition engines, biodiesel is specifically used in compression ignition diesel engines. Generally, biodiesel requires much less engine modification than bioethanol; almost all modern diesel engines run biodiesel quite readily. The

principles of biodiesel synthesis are relatively simple and have been known and applied for many decades (Figure 6) (17). The basic process consists of a catalyst induced transesterification of a vegetable oil to create a fatty acid methyl ester (FAME). It is this methyl ester molecule that yields biodiesel. The catalyst used is a strong base, such as sodium or potassium hydroxide. Once the ester chains are broken off, the left over glycerine molecule is a by-product of the reaction. Like for bioethanol, different feedstocks can be used, such as more or less any vegetable oil, including recycled oils and soapstock (18).

Composition of the oil feedstock, more particularly the fraction of saturated fatty acids, has a decisive influence on biodiesel specifications and properties; more particularly on viscosity consistency and wax crystal settling, i.e. plugging at low temperature (Table 1).

Bioethanol and biodiesel are regarded to be the first generation of biofuels. The automobile industry is seeking alternatives to these biofuels and is particularly interested in the direct conversion of coal or gas (CtL, GtL, SynFuel) or biomass (BtL, Sun Fuel) into synthesis gas, which could be followed by Fischer-Tropsch synthesis in order to yield hydrocarbon mixtures very similar to regular fossil petroleum (19).

### Biomass for chemistry

Coal tar dyes were the starting materials of the chemical industry in the Rhine Valley for companies like Ciba, BASF, Hoechst and Bayer. Later, crude oil and natural gas became the key raw material sources for the modern chemical industry, yielding all base chemicals like olefins, acetylene and aromatics. A reliable and economically reasonable supply of carbon and hydrogen as the raw material source for

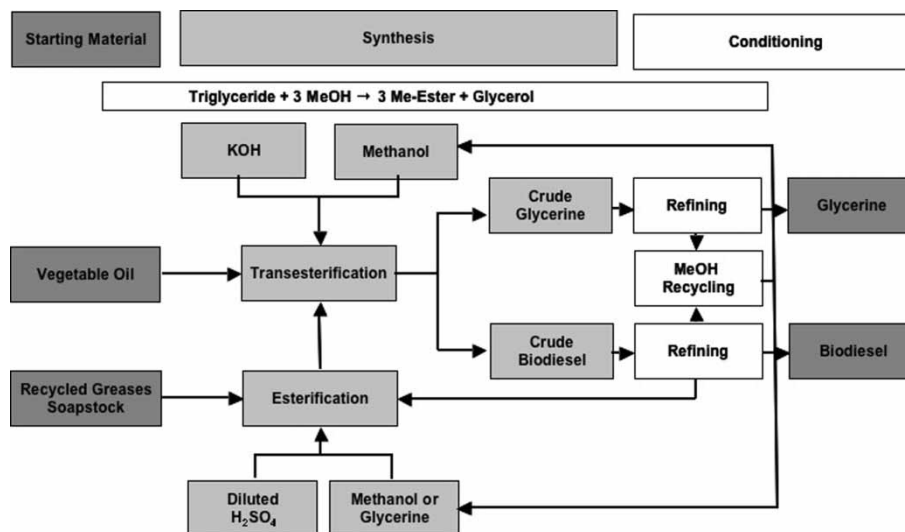


Figure 6. Production of biodiesel.

basic chemicals and their derivatives is the basic requirement for the chemical industry (Figure 7) (20).

Nature provides a remarkably wide range of renewable raw materials of varying material properties and differing chemical compositions.

While petrochemical feedstocks in a modern national economy like Germany account for 17 million tons of the chemical industry's raw materials, the use of renewable resources represents approximately 2.7 million tons or 14% of the total (Table 2).

Nonetheless, as mineral oil and ethylene prices increase, low molecular weight building blocks, particularly glycerine, (21) will become competitive as raw materials not only for specialty chemicals, but also for organic base chemicals like epichlorohydrine (projects Solvay, DOW; world production 1,2 Mio tons, 2005) or propylene glycol (projects Cargill/Ashland, Huntsman, Cognis; world production 1,6 Mio tons, 2005) (Figure 8).

Lower molecular weight alkanes also have potential to be manufactured from the conversion of glycerol into synthesis gas followed by Fischer-Tropsch synthesis (22) or from sorbit (23) by an aqueous-phase reforming process.

Table 1. Influence of saturated fatty acids fraction on the low temperature behavior of biodiesel.

Oil	CFPP* (°C)	Fraction of saturated fatty acids (%)
Rape seed oil	-12	7-8
Soy bean oil	-4	12-15
Palm oil	8	approx. 45

(\*CFPP=cold filter plugging point, DIN EN 14 214, the temperature at which a fuel will cause a fuel filter to plug due to fuel components, which have begun to crystallize or gel.)

Vegetable and animal oils and fats represent the main source of glycerol at around 45% of all renewable raw materials. Also consumption of sugar as a chemical feedstock has greatly increased. Sugar is primarily used in biotechnological production, which is gaining significance as an alternative to the classical chemical processes (24).

Renewable raw materials are especially interesting in industrial chemistry wherever nature's properties and performance is visible in the final product. This is particularly visible looking at the value adding chain of renewable raw materials (25) like starch, oils and fats, and proteins leading to highly sophisticated specialty chemicals employed in markets like cosmetics, nutraceuticals or engineering plastics (Figure 9).

### Natural oils and fats

Edible oils and fats are an important part of metabolism and in human and animal nutrition (26). They are indeed the most concentrated foods

Table 2. The use of renewable raw materials in the German Chemical Industry (2005).

Raw material	Quantity (t)
Vegetable oils	800,000
Animal fats	350,000
Starch	640,000
Cellulose/pulp	320,000
Sugar	240,000
Natural fibers	204,000
Other vegetable raw materials	117,000
Total	2,671,000

For comparison: Petrochemical raw materials: 17 Mio. t.

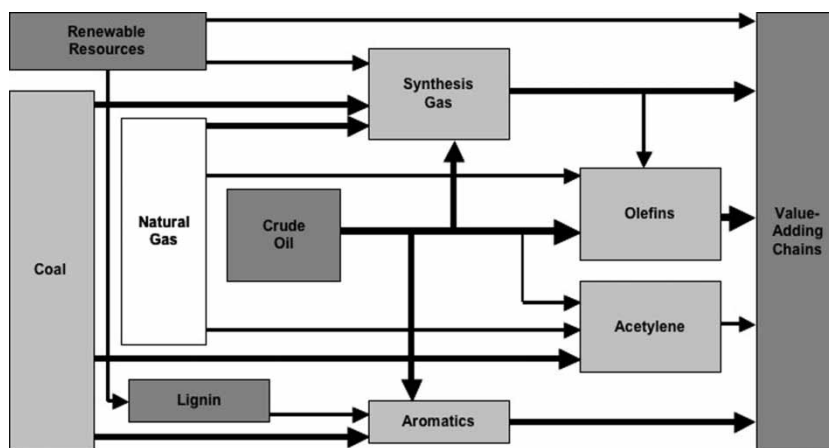


Figure 7. Alternative raw materials for the chemical industry.

we have. Securing their availability in sufficient quantity and equitable geographic distribution is the basic requisite to fight hunger and undernourishment on Earth. Natural fats and oils contain a wide variety of chemical compounds, which are essential for human nutrition. They remain in the oil if gentle processing methods for extraction, more particularly cold pressing, are applied. This is the reason why the Mediterranean diet based on cold pressed olive oil is generally regarded as particularly healthy.

Careful extraction of by-products like tocopherols or sterols and the addition to foodstuff as industrially produced dietary supplements is the basis of modern nutraceutical or functional food manufacturing. Such by-products are extracted from soybean oil steamer distillate, (27) from lecithin after degumming (28) or from crude tall oil, CTO (Figure 10) (29).

Chemically, natural oils and fats are triglycerides, which are fatty acid triesters of glycerine with different even-numbered, linear fatty acids. The fatty acids may be saturated or unsaturated. If they are solid or semisolid at 20°C they are designated as fats (edible fats in food technology); if they are liquid at 20°C they are described as oils (correspondingly edible oils in food technology). There are very few exceptions to this. The most well known exceptions are castor oil, a glycerol triester of 12-hydroxyoleic (ricinoleic) acid, vernonia oil, an epoxy oleic acid triglyceride, and tall oil, a by-product of the alkaline Kraft sulfate pulping process which consists of a mixture of unsaturated fatty acids (TOFA), rosin acids and unsaponifiables. Natural oils with a high degree of unsaturation like tung oil or China wood oil; dehydrated castor oil or linseed oil are called drying oils. The capability of highly unsaturated oils

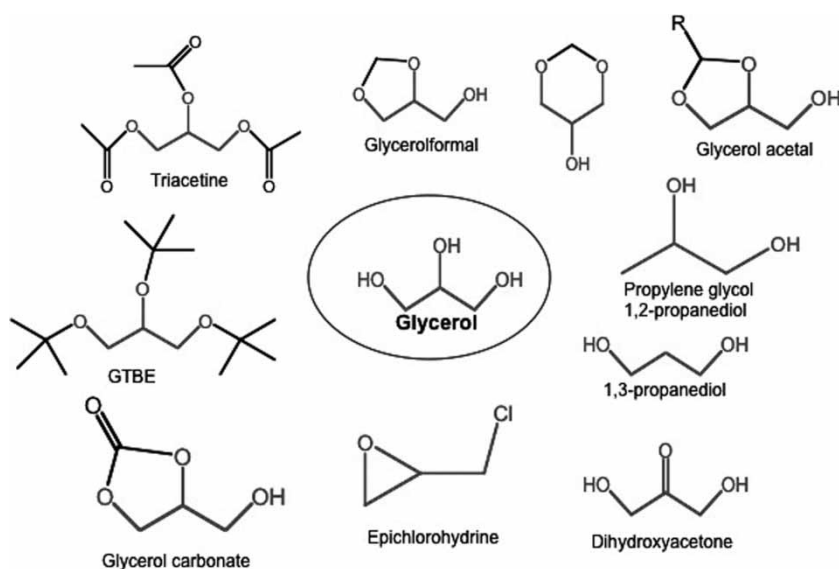


Figure 8. Glycerol, a C-3 building block.



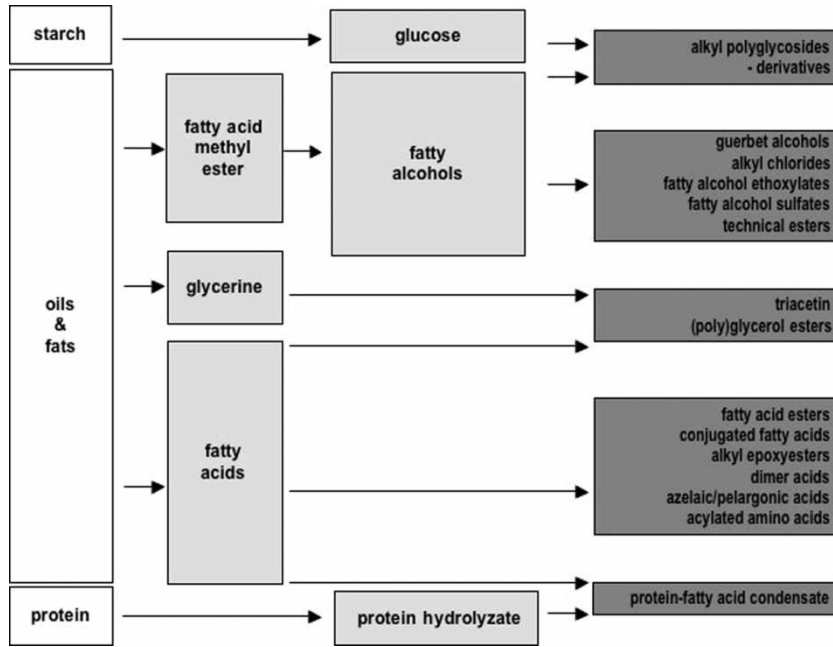


Figure 9. Renewable resources value chain.

to dry and form a film by simple action of atmospheric oxygen explains the historic importance and traditional usage of drying oils in lacquers and varnishes.

The actual chemical reactions involved in the drying process (Figure 11) are still incompletely understood; they do, however, involve oxygen attack on the fatty acid chains at or near the double bonds, catalyzed by certain organic salts of multivalent

metals, called dryers or siccatis (30). Similar chemical reactions are involved with operations like manufacturing of stand oils, blown oils, and conjugated oils, (31) as well as with formation of linoleum (32) and other derivatives of linseed oil, (33) such as epoxidized linseed oil, ELO, by action of hydrogen peroxide on the double bonds; which means, to a certain degree, incorporation of reactive oxygen in the molecular structure of the oil. By this, the polarity

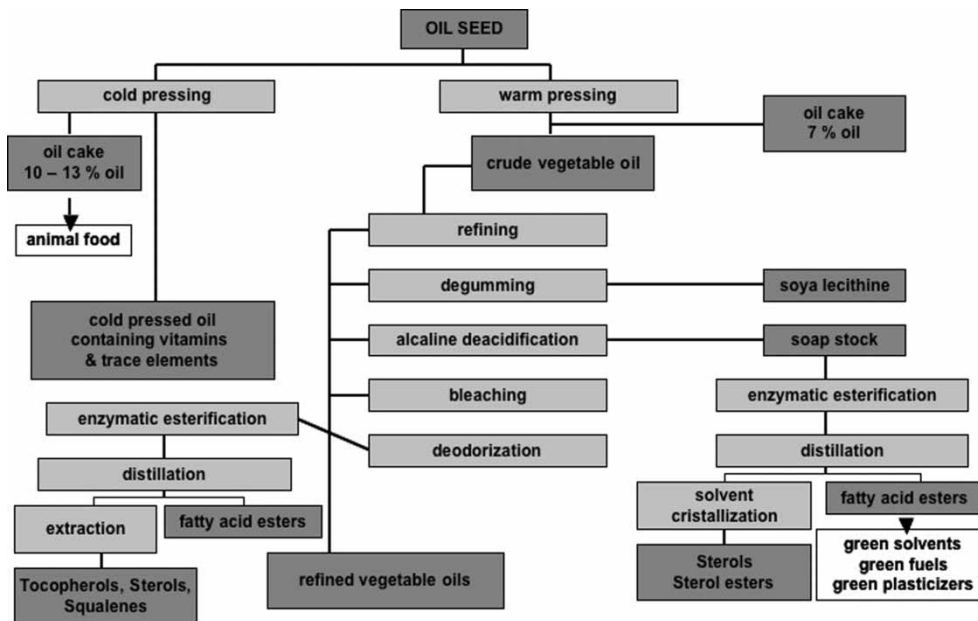


Figure 10. Processing of vegetable oil for food and chemistry.

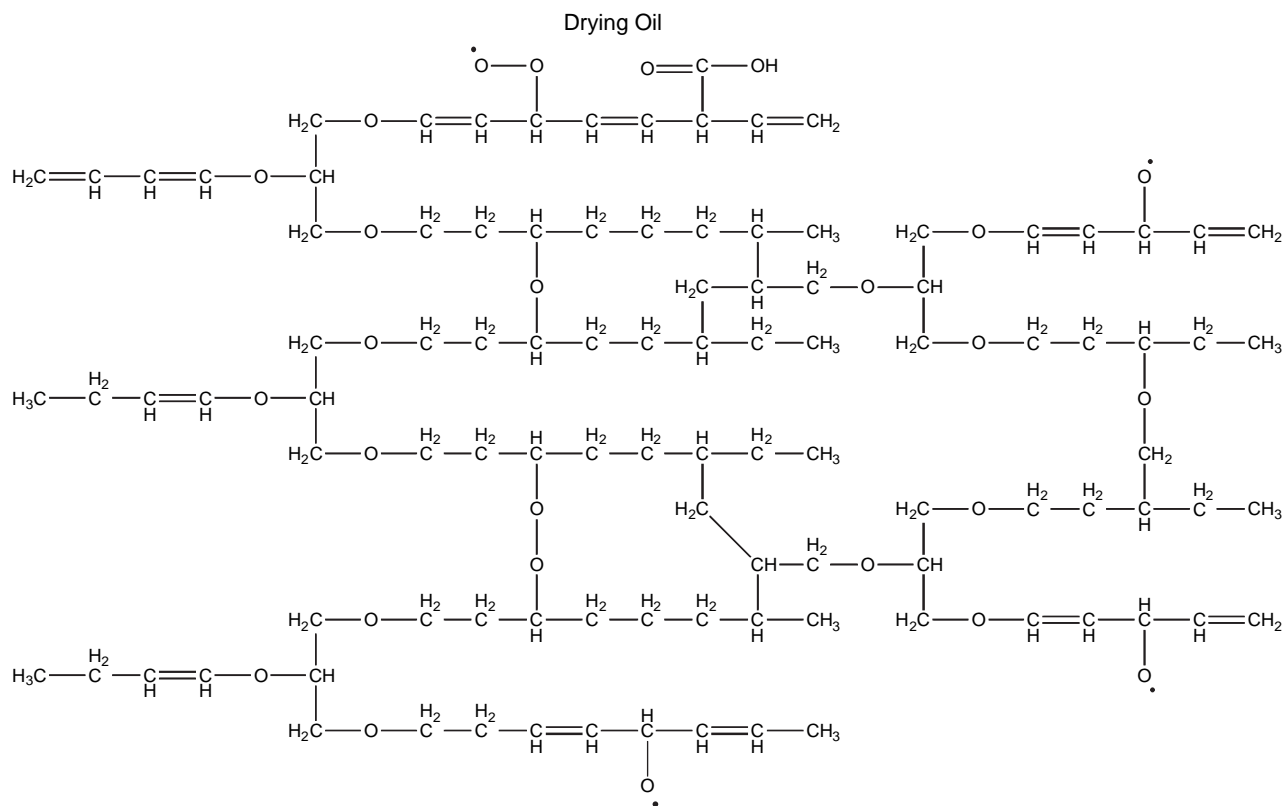


Figure 11. Polymer film formation with drying oils vs. polymer building block potential of epoxidized oils.

and the reactivity of the molecule increase significantly. Whereas the natural oils themselves have mainly solvent properties, epoxidized natural oils are well known as phthalate-free, non-volatile, extraction and migration resistant plasticizers.

Due to the reactivity of the oxirane group and due to the high degree of oxirane functionality, epoxidized oils, more particularly ELO, are used as polymer building blocks for plastic and coating applications (Figure 11).

The ring-opening reaction of ELO with rosin at 180°C followed by mixing with maleinized linseed oil at 100–120°C allows manufacturing of synthetic linoleum cement within hours, a tremendous step forward compared to the classical process, which needs weeks for linoleum to ripen (Figure 12)(34).

Ring opening of oxirane comes again into the game, when ELO is used to substitute triglycidyl isocyanurate (TGIC) as a crosslinking agent for hydroxyl or carboxyl terminated polyester, polyurethane or polyacrylate powder coating resins (35). And again, using the same advantages of ELO-high functionality and by that high crosslinking density – and the same reaction principles, carboxyl- or hydroxyl-functional polyesters can be crosslinked with ELO and, after neutralization, combined to aqueous polyacrylates and aqueous polyurethane dispersions, yielding physically drying aqueous industrial coatings (36).

Epoxidation of oils or oleic acid esters and (partial) ring opening of the oxirane group reacting with mono- and polyfunctional alcohols or acids yields a relatively new group of functional derivatives of natural oils, called *oleochemical polyols* (Figure 13) (37). Oleochemical polyols have been available commercially since the 1980s. More particularly, polyol derivatives of fatty acids instead of fatty acid triglycerides offer outstanding hydrolytic stability against both alkali and acids and very high chemical resistance against corrosive solvents like super fuel.

Oleochemical polyols are used for polyurethane foams, (38) PUR adhesives, (39) for solvent-free heavy duty multilayer coatings in concrete protection, and for high-performance anticorrosion coatings, for example for wind turbine blades in offshore eology power stations (40). Reaction of epoxidized oils with acrylic acid yields radiation curable oleochemical polyols, e.g. Photomer® 3005.

Unsaturated and saturated short-chain dicarboxylic acids such as maleic, fumaric, oxalic, succinic and adipic acid are well-known industrial chemicals manufactured on a petrochemical basis (41). Natural oils supplement these to provide longer-chain diacids (Figure 14). For example sebacic acid is produced from ricinoleic acid or castor oil by oxidative cleavage in an alkaline medium. Oleic acid reacts with ozone forming azelaic acid and pelargonic acid. However, oleic acid can also be oligomerized catalytically under heat. This industrial process leads

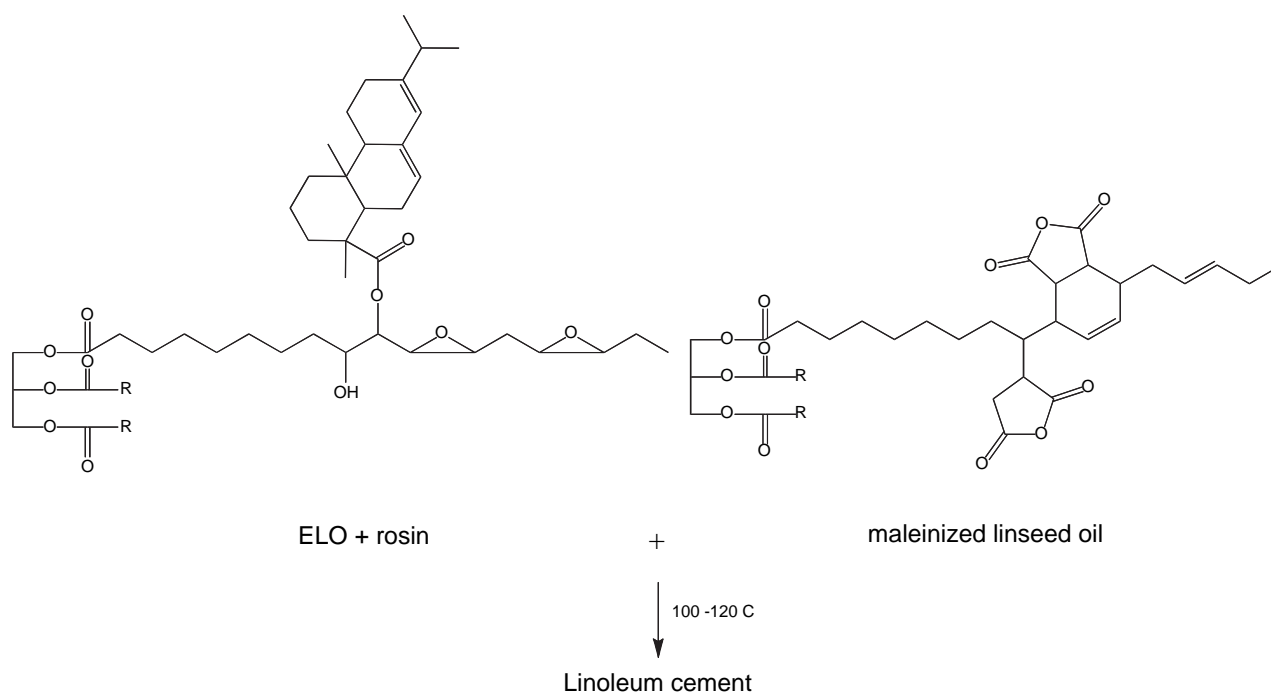


Figure 12. Manufacturing of ELO based linoleum cement.

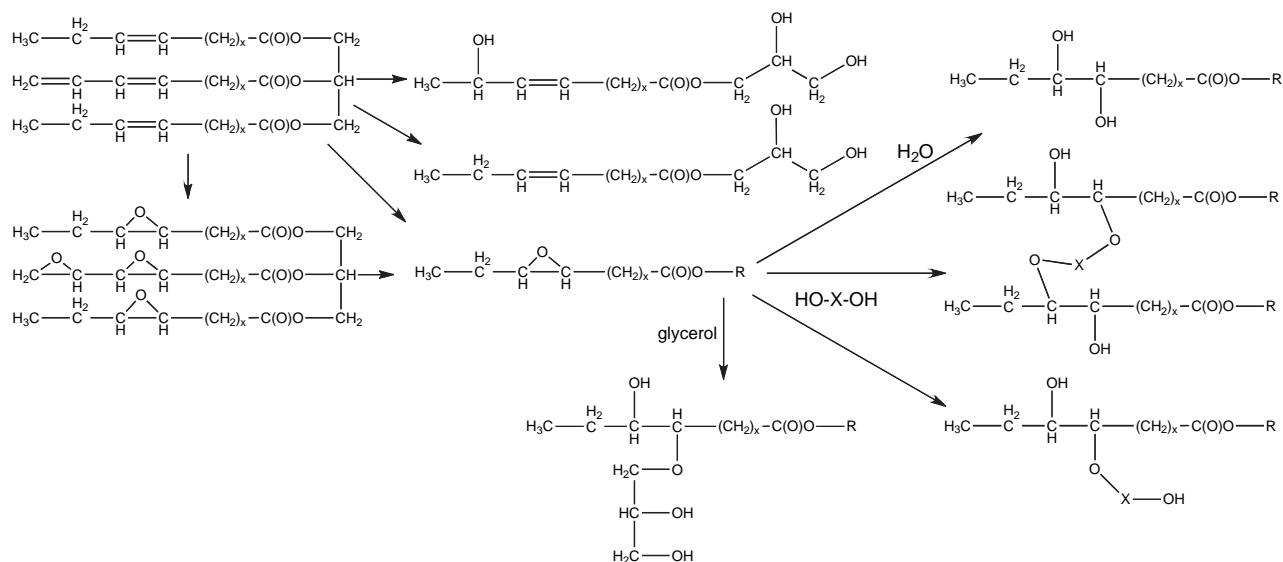


Figure 13. Oleochemical polyols.

to a mixture of branched C18 monomer fatty acids, C36 dicarboxylic acids, C54 trimer fatty acids and higher oligomers from which the dimer fatty acids can be separated off by distillation (42). Together with dodecanedioic acid manufactured by oxidative butadiene oligomerization and the 11-aminoundecanoic acid also synthesized starting with castor oil, azelaic acid, sebacic acid and dimer fatty acids serve as polymer building blocks for high-performance engineering plastics, hot melt adhesives, printing inks and coating resins made of polyamide, polyester or polyurethane. Biotechnological processes to manufacture higher molecular weight dicarboxylic acids as an alternative to these, in part, highly energy-intensive syntheses are under development. Octadecanedioic acid is to date only available via this

process (43). Starting from dimer acids derivatives like the difunctional dimer diol (Table 3), dimer diamine and dimer diisocyanate are produced. Other oleochemical diols like 12-hydroxy-stearyl alcohol and 1,10-decane diol (Table 3) are produced by hydrogenation of the corresponding esters.

Historically, industrial oleochemistry began when Ernst Twitchell at Emery (now Cognis) in Cincinnati successfully performed the first catalytic acid cleavage of fat (44). Thus, in contrast to alkaline saponification which only provided lard soaps of low chemical reactivity, the chemically reactive fatty acids were readily available (Figure 15). This laid the foundation for a variety of chemical reactions which was further expanded when the hydrogenation of fatty acids to

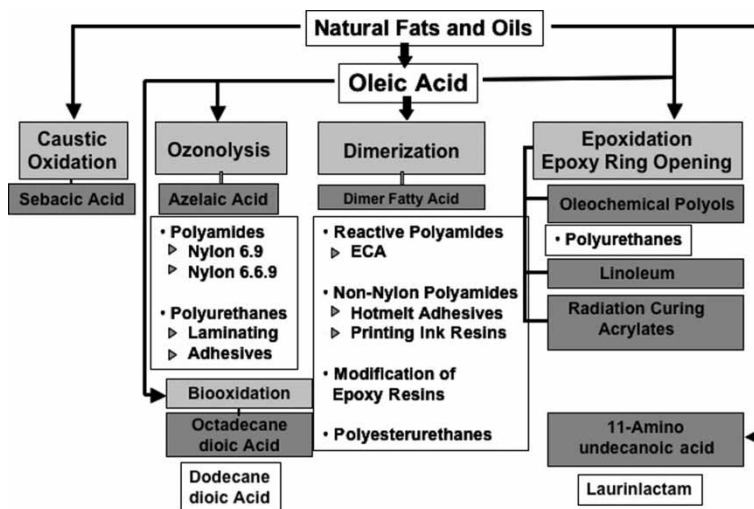


Figure 14. Polymer building blocks based on natural oils.

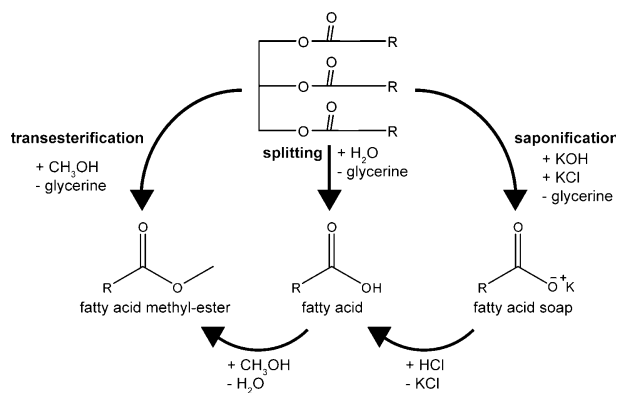


Figure 15. Processing of fats and oils.

form fatty alcohols succeeded at Dehydag (now also part of Cognis' company history) in Rodleben (45).

Fatty acid esters of mono and polyfunctional alcohols are the workhorses of oleochemistry due to their oily consistency. They are components in odorous substances like perfumes, and cosmetic and drug formulations such as ointments, creams or lotions and have many different properties (Figure 16).

The increasing prices of mineral oils, though, mean that the substitution of mineral oils by fatty acid esters in the past primarily for ecological reasons is now also economically viable. This applies especially to the lubricant sector where rising economic competitiveness on the one hand and ecological safety on the other hand, have helped biogenic lubricants

achieve the breakthrough; (46) for example as hydraulic fluids, cooling lubricants, chain-saw oils, switch point and wheel flange lubricants, but also as motor oils for combined heat and power units fuelled by vegetable oil (47). In these applications lubricants form thin films on metal surfaces and reduce or prevent friction and wear between machine parts.

Hydrogenation of liquid fats prevents them becoming rancid and they become spreadable. Hydrogenation of fats became one of the most important technologies in food chemistry and the basis for margarine production. But it is also an important technology in industrial chemistry. Esters of saturated, long-chain fatty acids with long chain fatty alcohols, such as stearyl stearate, have a waxy characteristic. These waxes develop lubricating effects in plastics processing; that means they prevent friction between plastic molecules and thus permit faster transport of the molten plastic mass through the processing machines (internal lubrication). At the same time they reduce the friction of the molten plastic with the surrounding machine parts (external lubrication). Partial glycerides of hydrogenated fatty acids, especially glycerine monostearate, do not only have a lubricant function but are also important antistatic agents for plastics. Hydrogenated castor oil also has a two-fold function as a plastics lubricant and, in particularly fine, micronized form, as a thixotropic agent in paints.

Fatty Acids			
Short/Medium Chain Primary Alcohols	Polyols (+ dicarboxylic acid)	Metal Oxides / Hydroxides	Fatty Alcohols
<i>Liquid fatty acid esters</i>  (Dehysol® BS) (Agnique® ME 610) (Edenol® EFC 100)	<i>Solid/liquid Polyol (partial or complex) Esters</i>  (Synative® ES TMP 05) (Synative® ES 3256)	<i>Metal Soaps</i>  (e.g. CaSt) (Perenol® 1097 A)	<i>Solid Waxes</i>  (Loxiol® G 32)

Figure 16. Vegetable esters by Cognis.

Table 3. Oleochemical diols.

Chemical designation outer appearance	Dimer diol yellow liquid	Dimer diol colorless liquid	12-hydroxy-stearyl alcohol white flakes	1.10-decane diole white flakes
Hydroxyl value	180–200	180–210	345–360	625–645
Acid value	<1	<1	<1	≤1
Viscosity at 25°C (mPa's)	3500–4300	1800–2800	Solid	solid
Melting point (°C)	–	–	61–65	68–73
Monomer (%)	13	2	–	–
Dimer (%)	68	>96	–	>98
Trimer (%)	19	2	–	–
Trademark designation	Sovermol® 650 NS	Sovermol® 908	Sovermol® 912	Experimental

In industrial applications liquid fatty acid esters are well known as plasticizers for pyroxyline varnishes and as secondary plasticizers for PVC (48). They are used as thinners and carrier oils and have become established as green solvents (49) for printing inks, and in industrial surface cleaning due to their low volatility, environmental compatibility and contribution to work hygiene and industrial safety (Table 4).

As green solvents, together with green surfactants, fatty acid esters also play a key role as “inerts,” non-active formulation aids in modern crop protection (49). Also, certain liquid fatty acid amides, particularly capryl dimethylamide, are increasingly creating interest as green solvents (Table 4) (50,51).

Proylene glycol monooleate has recently become commercially available as an emission-free film formation aid and leveling agent for aqueous paints and adhesives. The latter application demonstrates the multiple facets of fatty acid esters acting as plasticizers and co-solvents coalescent; as they improve film formation of resinous or polymeric material when water evaporates from an emulsion or latex system permitting contact and fusion of adjacent latex particles (52).

## Surfactants

Bathing in animal milk and oils in Roman times was the precursor to modern skin care bath oils. Today's modern trend cosmetics include natural oils such as olive, evening primrose and almond oil as well as natural waxes such as beeswax and carnauba wax. Emulsifiers in bath oil concentrates distribute fatty

substances or oils in water and prevent them from being deposited on the bathtub. Bath oils are enriched with essential oils and aromatic substances for aromatherapy. These preparations are used specifically for the body and circulation. Depending on the type of essential oil or corresponding mixtures, relaxing, invigorating or anti-spasmodic effects can be achieved. Skin care oils have a carrier function in this case. Essential oils must be well distributed in water by the surfactant components since they can irritate the skin in concentrated form. Natural surfactants based on renewable raw materials (53) combine a high emulsifying power with good electrolyte stability and extremely good skin compatibility. Special tenside combinations are aimed at producing a feeling of relaxation, care, health and the modern term, *wellness*, in skin care concepts (54). For example protein fatty acid condensation products, (55) special surfactants solely based on renewable raw materials (vegetable oils for the hydrophobic fatty acid residue, plant proteins for the hydrophilic protein group), favorably interact with the collagen in the skin, feel especially mild even in the smallest amounts and reduce any irritant effects of other constituents of the formulation.

Acylglutamates work in a similar way. Therefore, surface-active derivatives of proteins and amino acids have gained importance for cleansing applications that need to be particularly gentle on the skin and eyes like infant and child washes, hair care products and cold perm preparations. The development of new surfactants and new formulations that conform to these demands require application technology testing but also toxicological and sensory testing to ensure

Table 4. Specifications of oleo-based solvents.

	Titer (pour point) (°C)	Flash point (°C)	Boiling point (°C)	Visc. at 25°C (Mpas)	Kauri butanol value	Anilin point	Iodine value (Wijs)
Short chain fatty acid methylester	-28	75	204-244	2,7	107	<-20	<1
Rapeseed fatty acid methylester	-3	155	335-365	6	66	-1,7	90-100
Soybean fatty acid methylester	-6	170	335-365	10	67	3,69	115-135
n-Butylstearate	22	190	344-385	8,7	42	10	<1
Isobutylstearate	19	>170	341-381	8,4	41	10	2
Soybean fatty acid-2-ethylhexylester	-13	180	369-389	9,9	46	-7	85-95
Epoxy stearic acid methylester	-	-	348-386	13,5	>150	-19	-
Di-n-octylether	7	139	298	3,5	41	27	<1
Capryldimethylamine	-	-	294	6,6	>150	<-20	-
Propyleneglycol monooleate	-	210	284	30	-	-	76

skin compatibility and to rule out skin and mucous membrane irritation. Testing methods on alternative membranes including those of red blood cells and chicken egg yolk membranes or skin models are being developed to partly or completely replace the conventional animal tests of the past (56).

The presence of surfactants in water is accompanied by foaming, (57) which is often desired and expected in products like shampoos. In the case of detergents and cleaning agents, a large amount of foam is subconsciously associated with great washing power. This foaming power is also imperative in fire extinguishing foams.

The different uses of foam and foaming demonstrates the many properties that surfactants provide in the different applications they are used for, such as detergency, (58) foam formation and control, (57,59) manufacturing of oil and water emulsions, emulsion polymerization, (60) pigment wetting and dispersions (61).

Foams and surfactants become a problem when they are discharged into the environment if they are not readily biodegradable. There are practically no applications for surfactants in which they are recovered and recycled. The manufacturers of detergents and cleaning agents were especially aware at a very early stage of the potential environmental burden due to their products. As early as the late 1950s, when the detergent industry made a dramatic changeover from soap to synthetic surfactants in cleansing and laundry formulations, the German detergent manufacturer Henkel began to measure the tenside load in the Rhine using the level at Düsseldorf as an indicator (62). The surfactant concentrations in the Illinois River and other rivers were also observed in the USA

(63). At that time, regular foam mountains and carpets formed on sweet water lakes and rivers and fish kills occurred more frequently. The dramatic situation in German rivers, especially during very dry summers, prompted legislators to act. Even though the surfactants were not the only cause of the increasing environmental pollution, they were recognized as being primarily responsible. Correspondingly, Germany was the first country, in 1962, to issue the "Detergent Ordinance" which initiated the trend toward biodegradable surfactants, initially in detergents and cosmetics, and later in technical surfactant applications.

The biodegradability of chemical substances depends on their chemical structure. Branched hydrocarbon chains such as tetrapropylene alkylbenzene sulfonates, alkylphenol polyglycol ethers, and quaternary ammonium compounds show poor biodegradability, more particularly under anaerobic conditions (Table 5) (64).

The nature of renewable raw materials especially fulfils the requirement for biodegradability under aerobic and anaerobic conditions. The linear hydrocarbon chains facilitate biodegradability, for example, of fatty alcohol sulphates, fatty acid polyglycol esters and fatty alcohol polyglycol ethers without the formation of ecotoxic metabolites as is the case with alkylphenol polyglycol ethers. The nature of renewable raw materials is shown to particular advantage when the hydrophilic constituent of the tenside molecule also comes from a renewable source, e.g. starch, as in the alkyl polyglucosides, (65) a finding supported by current Life Cycle Assessments, LCA (66).

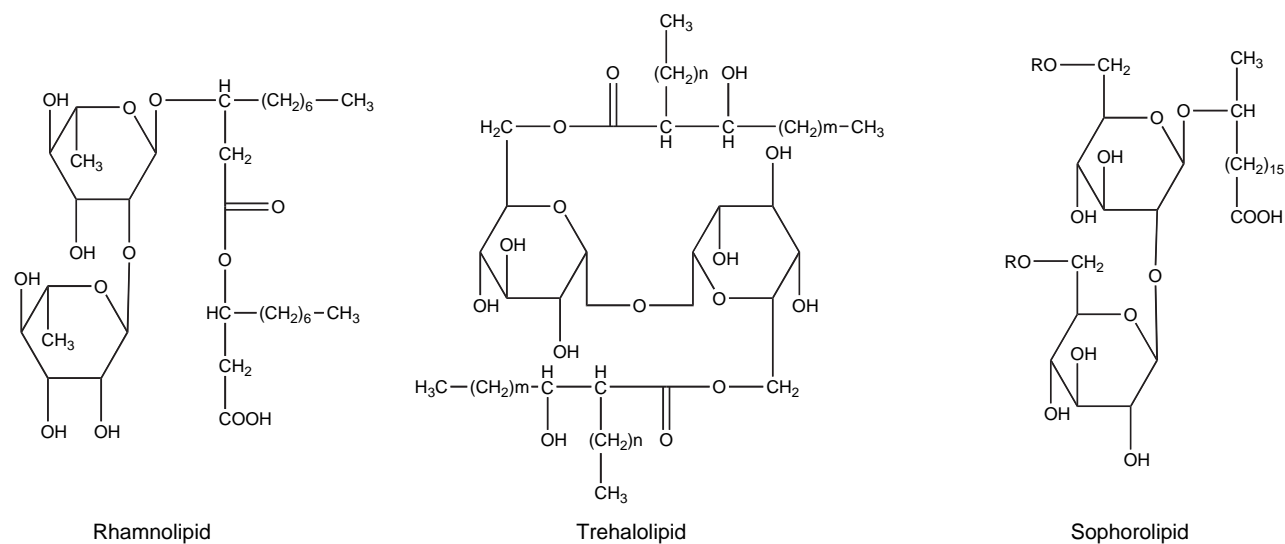


Figure 17. Biosurfactants.

Table 5. Biodegradability of various surfactants.

Surfactant type	Biodegradability
Sulfonated anionic surfactants (LAS, SAS, MES)	Poor
Sulfated anionic surfactants (fatty alcohol sulfates, alcohol ethoxysulfates)	Good
Fatty acids and soaps	Good
Fatty alcohol ethoxylates	Good
Sugar-based surfactants (alkyl polyglucosides, glucamides)	Good
Alkylphenol ethoxylates	Partial, leaving alkylphenol residues
Mono- or di-alkyl quaternary compounds (TMAC, DTDMAC)	Poor
Esterified mono- or di-alkyl quaternary surfactants (esterquats)	Good

Modern biorefinery concepts also consider the use of agricultural waste and by-products made of wheat and wheat substrates for value added specialties like a new generation of natural, vegetal renewable sugar surfactants based on alkylpolypentosides (67).

Similar to esters, which are essential components that are a result of vegetation metabolisms, chemicals with surface-active properties (biosurfactants, Figure 17) are synthesized by an amazing variety of living bodies: from plants (e.g. saponins) to microorganisms (e.g. glycolipids) to higher complexity animal structures including the human body (e.g. bile acids). The purpose of the biosurfactants in the biological systems is for intracellular and extracellular activities ranging from emulsification of feedstock, to the transport of material across cell walls, to recognition of cells (68). All biosurfactants are of the non-ionic or anionic type and made up of a biochemical hydrophile such as a polysaccharide, an amino acid or a peptide and a fatty acid, hydroxy fatty acid or a fatty alcohol. They are produced mainly by aerobically growing microorganisms in aqueous media from a carbon source feedstock, e.g. carbohydrates, hydrocarbons, oils and fats or mixtures thereof.

Existing and potential industrial applications of biosurfactants are tank oil cleaning, oil spill dispersants, microbial enhancement of oil recovery (MEOR), heavy oil transportation, and heavy-oil combustion (69). Some biosurfactants, more particularly sophorolipids, have shown particularly good skin compatibility and are sold commercially for anti aging applications in skin care cosmetics (70).

### Summary and outlook

Renewable raw materials are already making an extensive contribution to positioning the concept of sustainability even more firmly in the public mind worldwide. For example, the impact on the megatrend LOHAS is obvious; this megatrend would possibly not exist without renewable raw materials. They may in the future also be the only solution when

gradually, and based on 200 years of the industrial age, fossil fuels are exhausted.

However, the current figures speak for themselves: 4.6% of primary energy consumption is based on renewable energies, 45 million tons of worldwide biodiesel capacity (forecast for 2010 based on published projects (71); a more conservative estimate envisages 32 million tons by 2012 (72)) compared to four billion tons of annual mineral oil consumption. 2.7 million tons of renewable raw materials compared to 17 million tons of petrochemical base materials for the chemical industry in a country like Germany. These figures demonstrate the rift that must be overcome before renewable resources can completely substitute fossil fuels and supplies of raw materials. The problem of space for the agricultural crops must also be solved. The "Tortilla crisis" in Mexico may have been only an initial indication of the worsening conflicts in this connection.

We are tackling this issue at an advanced level. The past 200 years of industrialization and 200 years of scientific research and development have created a knowledge base that was simply not there at the start of the industrial age before the discovery of applications for coal, petroleum and natural gas.

If both the emerging energy gap and the fuel crisis are to be solved while at the same time providing sufficient feedstock for the chemical industry and foodstuffs for humans and animals by massive cultivation of biomass, that is renewable raw materials; then a well-organized, anticipatory, cross-border cultivation policy including water management is required. This entails concrete measures to increase yields per area unit; that means concentrated advancement of green agricultural research and green crop protection, including white biotechnology and green genetic engineering.

A great deal could be gained by giving worldwide priority to sparing fossil resources to permit development of constructive and long-term successful solutions based on renewable raw materials.



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