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Chemistry of Renewables

An Introduction

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Foreword

What are we going to do now?

With an exponential increase in population, major concerns about global warming leading to climate change and with oil and gas becoming scarcer and more expensive to extract, we stand at a point in the world's history where everything we do needs to change - and quickly. We need to turn to renewable resources and to make sure that we have enough land to grow food as well as to provide all the essential and luxury items that are currently produced from fossil fuel based starting materials. Most of our static energy needs will be provided by wind, solar, wave and tidal power. Cars will be powered by electricity from renewable resources but how will we continue to fly? How will we provide all the essential and luxury items that are so familiar to us and we love to have without using fossil fuel-based resources whilst at the same time increasing the amount of food we produce.

The United Nations 17 *Sustainable Development Goals* provide a road map to a future of peace, justice, equality and prosperity in a pollution-free world espousing a circular economy. They hint at the end point but how will we actually get there? Many grandiose schemes are proposed but who will actually bring them into practice?

Much of the work will be done by chemists and chemical engineers working with a whole myriad of end users to provide solutions to all the problems. There has never been a better time to be starting out on a career in chemistry or chemical engineering. The challenges are huge, addressing them will require the most creative of minds and the rewards, intellectual, social and financial will be enormous. Are you up for this exciting journey? Where will it start and what is the final destination? Nobody knows the answer to the second question but, if you have been hooked into wanting to set out on this journey and do not know where to start, this book, *The Chemistry of Renewables*, which gives a snapshot of where we are at present and a hint at directions we might take, is the book for you.

There are some major differences between oil and naturally occurring feedstocks. Oil contains only carbon and hydrogen whilst feedstocks like natural oils, cellulose, lignin, etc also contain significant amounts of oxygen and sometimes other elements especially nitrogen, phosphorus and sulphur. Oil is mostly a mixture of various chain length hydrocarbons so is relatively simple. It has only C-H and C-C bonds and is mostly easy to handle as a liquid, which can be pumped from well-defined reservoirs. Natural resources are chemically much more complex and diverse often occurring naturally as solids, sometimes spread thinly over large areas making handling trickier but not impossible. Most of the many thousands of effect chemicals we use on everyday life contain oxygen or nitrogen as well as carbon and hydrogen so, to make them from oil, we must add these elements generally in oxidative-type chemistry whilst the chemistry of the future will require removal of oxygen or reductive chemistry.

One possible way to solve the problem would be to gasify biomass to give carbon monoxide and hydrogen then carry out Fischer-Tropsch chemistry to make a mixture of hydrocarbons rather like the oil that we use already and feed it into a standard oil refinery. However, taking all the oxygen out of biomass and putting some of it back in again is not only inelegant, it is massively energy intensive and expensive so we really have to look for the direct production of effect chemicals from biomass. A whole new chemical industry is begging to be invented and you could be in the forefront of that exciting development.

One of the great things about this book is that it is easy to read with its quirky titles, interesting anecdotes and liberal sprinkling of lovely colour pictures. You can dip in and out of it to find nuggets of information, what is been done already and what still needs to be done or you could read it as a bedtime story. Just to make sure you have not fallen asleep whilst reading there are “Quickie’s” at the end of each chapter; questions which check what you have learnt and that you have retained it. Do not worry, though, the answers are collected at the end of the book, but you should really try to get them without looking them up - just use them to check you were right!

The book starts like *Under Milk Wood* or the song *Do Ray Me* at the beginning with an excellent overview of the field and a critical appraisal of the advantages and disadvantages of the feedstocks that are available, before moving on to individual feedstocks starting with fats and oils because they are currently the most exploited. The discussion moves to glycerol, a coproduct when making many derivatives from natural oils and sugar before things get much more complicated with cellulose, the world’s most abundant organic polymer, starch and other carbohydrates. It then moves on to the toughest nut of all, lignin. Masses of lignin is available from trees but it is hardly exploited because its structure is complex; it is difficult to dissolve or break down and really hard to get single products form it. It can be done, for example, in a complex process for making vanillin, a flavouring compound that can also be used as a starting material for pharmaceutical production. However, this work is in its infancy. There is so much more to do. It is difficult but the rewards will be extremely high. Things get a bit easier with the naturally occurring hydrocarbons, terpenes and their polymers, where significant chemical advances have already been made. Then come amino acids and their condensation to form the elements of life, polypeptides and proteins followed by compounds which can be extracted from nature for use as dyes, flavours, vitamins, drugs or polymers, many of which are biodegradable.

Every chapter is peppered with some history, finds some interesting character, comprehensively explores some really exciting chemistry, shows applications and potential uses and explains how all of this can be done. In the end, the authors take a comprehensive look at the possibility of integrating many processes in a biorefinery. Here, agriculture, chemistry and chemical engineering are brought together to make everything else in the book a reality. One or more bio-feeds are transformed into a range of different useful chemicals and products just as in an oil refinery using oil as the feedstock. Biorefineries are usually more complex than oil refineries but they must become commonplace exploiting different feedstocks according to local availability. They must be run in a clean environmentally friendly way so it is a bit sad that the picture of the plant producing bio-ethanol as a platform chemical or fuel from sugar in Brazil appears to show dense grey smoke emanating from the chimneys. The pilot plant for biomass to liquid products in Karlsruhe looks much more environmentally friendly!

When you finish reading this book, you will be full of facts, ideas and enthusiasms - and you will be exhausted but I hope that you will be inspired to get involved, solve the major problems and really make a difference to our world by giving it a circular, sustainable and clean future.

As a bonus, you will also have read a prize winning text book because the original German version of *The Chemistry of Renewables* won the prize from the German Chemical Industry Association for the best German chemistry textbook of

2020. Well done to the authors for winning the richly deserved prize and to you for reading the book!

Quickies (You may have to read the book to answer some of these!)

1. What are the two most abundant renewable natural resources from which effect chemicals might be made?
2. What are the two most difficult natural resources from which to make effect chemicals?
3. Why can't we just grow plants in order to produce all the chemical feedstocks we need?
4. Where can you find renewable hydrocarbons in nature?
5. Name two resources where you can find aromatic rings in nature.
6. Cashew nut shell liquid is a non-food oil which is available at 800,000 tonnes per year. Can you find it in this book?
7. What problems would there be in making all the chemicals we need through hydrocarbons made by Fischer-Tropsch Chemistry using carbon dioxide and hydrogen produced by electrolysis of water using renewable electricity during periods of overproduction of electricity?

Scotland, UK,
June 2020

David Cole-Hamilton

Preface

This book is the English version of a textbook on renewable raw materials that was published in German by Springer Spektrum at the beginning of 2018. Due to the great success in the German-speaking world, the two authors have decided to publish an extended and updated version in English. The content of the book is based on a lecture that the authors have been giving at the TU Dortmund University (Germany) for many years. The book offers the reader an introduction to the different groups of renewable raw materials, especially fats and oils, carbohydrates and terpenoids. Also, more specific topics such as lignin and natural pharmaceuticals, as well as colorants and fragrances, are addressed. Individual chapters are dedicated to current topics such as biopolymers or biorefineries. All sections focus on the chemical conversion of raw materials into valuable products. Also, technical aspects such as the methods of recovery or the industrial processing of the reactions are discussed.

One of the authors, Prof. Behr, worked in the chemical industry for several years and acquired considerable experience in the process development of new processes with fats and oils, carbohydrates and terpenes. In addition, he has successfully carried out numerous research projects on these topics at the Technical University of Dortmund over the past 20 years. This unique knowledge from practice and research is passed on to the readers in this book.

This textbook is intended for students of natural and engineering sciences as well as for practitioners. The book is unique in such a way that students can follow up well on their lectures or acquire the curriculum chapter by chapter in self-study. Practitioners can quickly learn about important raw materials, products and processes, and can familiarize themselves more deeply with individual topics from the references.

What is the structure of the book?

- The book is divided into **20 chapters** of similar size. Each of these chapters starts with a chapter timetable, which roughly announces the content and closes with a compact summary. Detailed illustrations, photos, flow diagrams and chemical equations illustrate the text.
- At the end of each chapter, there are 10 test questions, so-called **Quickies**. In the appendix, the reader will find the answers to the 200 test questions.
- There is a short **literature** overview for each chapter. It consists mainly of references to textbooks and reviews but also includes some important current original references.
- In addition, the text contains numerous “**boxes**” that describe exciting aspects, such as historical backgrounds or current developments.

The authors would like to thank Springer Verlag, especially Dr. Charlotte Hollingworth and Dr. Rainer Münz, for their support in the realization of this book project and Miss Andréia Bracht for her help drawing the figures and formulas.

In recent decades, renewable raw materials have become increasingly important, and this trend continues. This book provides the basis for a better understanding of this future top topic. Have fun reading it!

Arno Behr
Thomas Seidensticker
Dortmund, Germany
August 2020

Prof. Dr. Arno Behr (right) and Dr. Thomas Seidensticker (left)

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The Overview - Introduction

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Chapter Timetable

- Here, you can find out which materials belong to the renewable raw materials.
- You will learn the most important renewable raw materials in terms of quantity (the primary ingredients), but also the structurally important secondary raw materials.
- The renewable raw materials are compared with the fossil raw materials coal, petroleum and natural gas. We are discussing whether the renewable raw materials will reduce fossil fuel consumption or can completely replace it.
- The advantages, but also the accompanying problems of the renewable raw materials, are explained.

1.1 Definitions

Actually, everyone knows what renewable raw materials are: These are substances that occur in nature and grow back every year. All plants, trees, plants, flowers, fruits, cereals, grasses and vegetables would be "renewable" according to this very general definition. In this book, however, mainly those substances are considered which can also serve as raw materials for the organic chemist, the pharmaceutical manufacturer or the energy producer. The food sector, e.g. the calorie content, the taste or the health advantages or disadvantages of different olive oils, is not covered in this book. But we must be aware that many of the natural substances considered are suitable both as food and as chemical raw materials and that, of course, the use for the nutrition of the continually growing human race has the higher priority.

In addition to the term renewables, there is also the term **biomass**, which is usually used in a very similar way. In order to exclude its use as a foodstuff, there is also the term industrial biomass. In this book, we want to use the term renewable raw materials throughout and determine the following definition:

Renewable raw materials are any organic materials that grow and are available again and again. They are used in agriculture or forestry and are mainly used for in the non-food sector. They can be used both materially and energetically.

Old trees that must be preserved are expressly excluded from this definition. The definition includes any organic residues from agriculture and forestry, e.g. sawdust from wood processing or straw from the grain harvest. Also, vegetable raw materials of marine origin, e.g. seaweed, are also considered, although they are not produced in traditional agriculture and forestry but have to be collected or cultivated specially.

The definition of renewable raw materials includes all living organisms and thus not only vegetable but also animal sources. In slaughterhouses, for example, large quantities of beef tallow are produced which are less suitable for our nutrition but can be used well for further processing into soaps.

The source of all renewable raw materials is ultimately the sun, because the growth of plants, and thus the production of food for animals and humans, is only made possible by the energy of sunlight. The decisive chemical reaction is the **photosynthesis** of carbohydrates from carbon dioxide and water with release of oxygen (Eq. 1.1.).

$$nCO_2 + nH_2O \overset{h\cdot\nu}{\rightarrow} (CH_2O)_n + nO_2 \qquad (1.1)$$

1.2 The Different Types of Renewable Raw Materials

Biology distinguishes between primary and secondary plant substances. The **primary ingredients** are substances that are essential for the structure and reproduction of plants. They ensure that the plant is stable but also elastic and, for example, that a tree is not blown down even by extreme winds. Many plants also build up energy reserves for their propagation, e.g.

◘ **Table 1.1** Primary substances of plants and animals and their sources (examples)

Renewable resource	Ingredients	Plant or animal origin
Fats and oils	Triglycerides	Soy, rape, sunflower, coconut palm, linens
Sugar	Glucose, fructose, sucrose	Sugar beet, sugar cane
Wood	Cellulose, hemicelluloses, lignin	Oak, beech, poplar, birch
Natural fibers	Cellulose, hemicelluloses	Flax, hemp, jute, sisal, cotton
Starch	Amylose, amylopectin	Potato, corn, pea, wheat
Exoskeletons	Chitin	Crabs, lobsters, shrimps, fungi, insects
Algae	Heteropolysaccharides, e.g. Agar-Agar	Red algae, brown algae
Proteins	Amino acids	Soy

◘ **Table 1.2** Secondary substances of plants and their sources (examples)

Renewable resource	Ingredient	Plant origin
Terpenoids	Monoterpenes, diterpenes, polyterpenes	Pine tree, rubber tree
Natural dyes	Alizarin, Tyrian purple, indigo	safflower, madder, woad
Natural pharmaceuticals	Pyrethroids, alkaloids, steroids	St. John's wort, fennel, belladonna, thyme, camomile
Vitamins	Vitamin E, Vitamin C	Soy, Rape, Citrus fruits
Nutraceuticals	Flavonoides, polyphenols, carotinoids	Soy, rape, sage, tomato, paprika
Natural fragrances	Essential oils, damascon, jonon	Rose, jasmine, violet, iris
Waxes	Monoesters	Jojoba
Cork	Suberin	Cork oak

the sugar beet hoards sugar reserves in its roots or the potato plant hoards starch reserves in its tubers. ◘ Table 1.1 provides an overview of these primary substances.

The first column in this table contains the different groups of renewable raw materials, Column 2 some typical representatives of these groups and Column 3 some crops containing these ingredients. You probably would not know all the terms in ◘ Table 1.1; however, you will learn all the terms in detail in the following chapters.

As ◘ Table 1.1 shows, many ingredients are found in a wide variety of plants, e.g. cellulose in wood, hemp and sisal. In these cases, it is, therefore, possible to decide which plant is to be used to obtain this renewable raw material. On the other hand, plants always consist of several ingredients: Soybeans contain not only fats and oils, but also proteins, for example. This results in the major task of separating these substances from each other and isolating them in sufficient quality.

The primary ingredients are found in particularly large quantities in nature. In addition to the primary ingredients, there are also the **secondary ingredients**, which occur in the plant in much smaller amounts, often only in traces. They were gradually trained in the course of a plant's development in order to pursue specific strategies, e.g. fending off predators or attracting pollinating insects. These include certain fragrances and dyes as well as substances that we now use as pharmaceuticals. ◘ Table 1.2 gives an overview and presents some typical examples.

◘ Table 1.2 shows that very complex molecules, e.g. steroids, vitamins or alkaloids, can be obtained from some plants. Some of these substances, e.g. the red dye of the purple snail, have been known for many centuries. But even today,

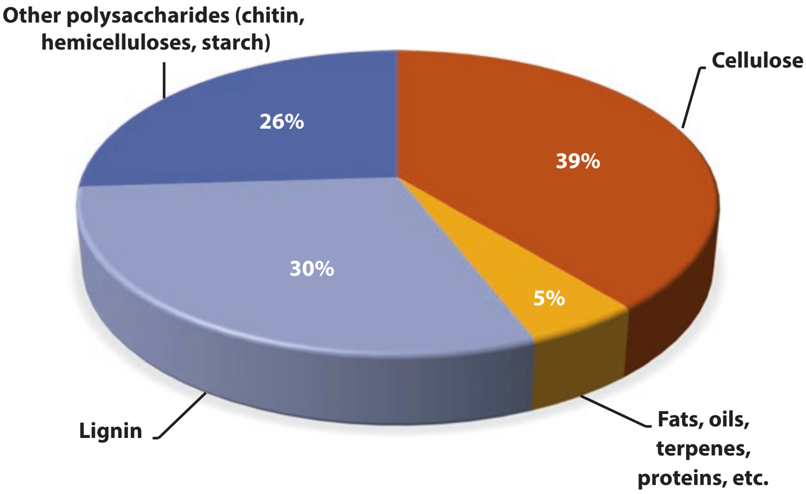


Fig. 1.1 Main ingredients of renewable substances (in weight-%)

plants with new active substances are still being sought in tropical forests that can either be used directly or serve as models for new synthetic pharmaceuticals.

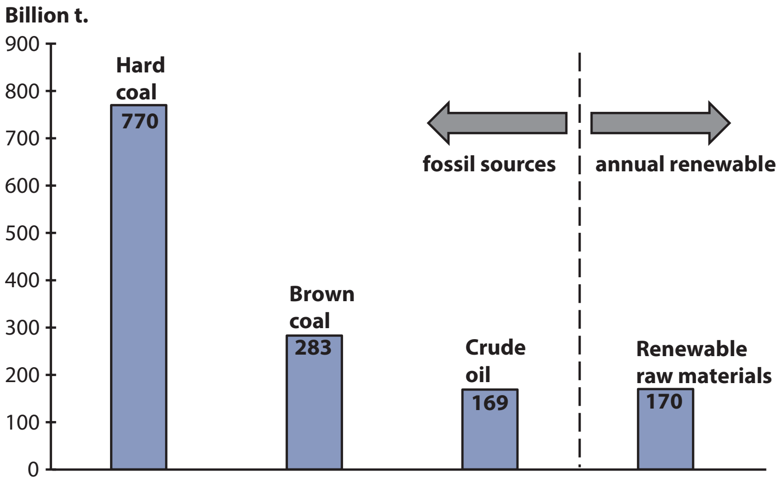
It is estimated that approximately 170 billion tons of renewable raw materials are produced annually worldwide of which only a small fraction (approx. 6 billion tons, i.e. approx. 3.5%) is used by mankind. However, these and other figures in this book should be handled with caution, as they are estimates only. In some literature sources, quantities of renewable raw materials of between 140 and 180 billion tons per year can also be found. Nevertheless, such figures are useful to get a feeling for the order of magnitude.

What are the **most important renewable raw materials in terms of quantity**? Here, too, there are only estimates shown in Fig. 1.1. The most important renewable raw material in terms of volume is cellulose, which accounts for over a third (39%) of the pie chart. Lignin accounts for almost another third (30%). These figures can be explained simply by the fact that a large part of the earth's landmass is covered by forests and that the main components of forest wood are cellulose and lignin. Cellulose belongs chemically to the polysaccharides. Other polysaccharides, such as chitin, starch and hemicelluloses, are also crucial in terms of quantity and represent a further quarter (26%). Chitin (Table 1.1) is a structural substance found in the crabs and cancers of our oceans and is the second most important polysaccharide after cellulose with an annual occurrence of about 100 million tons per year. All other natural substances (fats and oils, terpenes, proteins et al.) together make up only about 5% in terms of quantity, but due to their special structures and properties, they have to be classified very highly in terms of value.

1.3 Comparison with Fossil Raw Materials

Wood, a renewable resource, has been a companion of mankind for thousands of years, whether as a material for building houses and ships, as a fuel for generating heat or in the form of charcoal as a fuel for reducing ores for metal extraction. Other renewable raw materials have also long been used by humans, e.g. flax, wool and cotton for the production of clothing or certain plants for the production of natural remedies.

In the middle of the nineteenth century, the fossil raw material **coal** became increasingly popular. Coal was used for heating, and later, steam engines, steamships and steam locomotives were powered by coal: Industrialization began. People also learned - by coking the coal - to produce coke, coal tar and coke oven gases which are used to produce steel, to isolate aromatic hydrocarbons and to generate light. By coal gasification, the synthesis gas - a mixture of carbon monoxide and hydrogen - and by coal hydrogenation, coal fuel was finally produced. Until the 1950s, coal was converted to acetylene (ethyne) via the inter-



◘ **Fig. 1.2** Reserves of carbonaceous raw materials (World 2012). *Source* German Federal Institute for Geosciences and Raw Materials (Bundesanstalt für Geowissenschaften und Rohstoffe, BGR)

mediate stage of carbide, which in turn is an excellent reactive building block for the synthesis of numerous chemical intermediates such as ethanol, acetaldehyde or acrylic acid.

In the 1940s started the era of two further fossil raw materials, **crude oil** and **natural gas**. In many regions of the world, first in North America and then especially in the Middle East, large deposits have been discovered, the mining of which began immediately. Large quantities of oil have been used to meet the enormous energy demands of modern society, whether in form of heavy fuel oils for industry and shipping, as kerosene for air traffic, as light heating oils for private households, as gasoline and diesel for automobiles or for generating electrical energy for industry and households.

However, it soon became clear that the **reserves of fossil raw materials** are limited in quantity despite all the successes in the exploration of crude oil and natural gas. ◘ Figure 1.2 shows clearly that we still have relatively large reserves of hard coal and lignite (with currently approx. 169 billion tons), but that our recoverable oil reserves are slowly coming to an end. If we continue to use oil in the same way as yet, we would still have enough oil reserves - statistically speaking - for 41 years, that is, until 2058, but in this year we will certainly not come to a sudden end, because humanity is already looking for new solutions to the open energy issues, so that there are high hopes that crude oil for the synthesis of important chemicals will continue to be preserved for even longer. Similar considerations apply to natural gas: The current estimated world reserves of approx. 181×10^{12} m^3 will last - also statistically speaking - for another 63 years.

◘ Figure 1.2 shows that renewable raw materials represent an important alternative in the medium and long term: At 170 billion tons per year, they are of a similar order of magnitude to the current oil reserves, but through photosynthesis, they grow back each year from the raw materials carbon dioxide and water in the earth's carbon cycle. For this, only the sun must shine (cf. Eq. 1.1.), and hopefully, it will continue to do so for a few million years.

The reserves are one side of the coin, the **annual consumption of raw materials** is the other. ◘ Table 1.3 shows the consumption of various renewable raw materials in the German chemical industry in 2016 compared to the current consumption of fossil raw materials for the production of petrochemicals. It is interesting to compare ◘ Table 1.3 with ◘ Fig. 1.1, i.e. the global occurrence of the various renewable raw materials: Although the earth has mainly cellulose and lignin available because of the large forest stands, the German chemical industry uses vegetable and animal fats and oils (total: 1.17 million tons per year), followed by cellulose and starch by far. The lignin listed in ◘ Fig. 1.1 as a globally important component does not appear at all in ◘ Table 1.3!

◘ Table 1.3 Consumption of renewable raw materials in the chemical industry (Germany 2016)

Renewable resource	Consumption (*t*)
Oils and fats	1,170,000
Starch	296,000
Cellulose (pulp)	380,000
Sugar	156,000
Proteins	119,000
Others (natural fibers, waxes, resins, etc.)	572,000
Sum: renewable resources	2,690,000
Cf. Petrochemicals	17,700,000
Share renewable resources	ca. 13%

The reasons for this will be explained in more detail in the following chapters: Fats and oils have very defined structures closely related to petrochemical basic chemicals, while starch, cellulose and lignin are composed of macromolecules with completely different structures. In wood, lignin and cellulose are additionally linked (lignocellulose), which makes their pure production and their subsequent chemistry even more difficult. So, the chemical industry took the simpler (and cheaper) path and first developed an extensive chemistry of fats and oils, the so-called oleochemistry. Only in recent decades, increased efforts have been made to exploit lignocellulose.

At the end of ◘ Table 1.3, another important comparison can be drawn, namely the ratio of petrochemicals to the chemistry of renewable raw materials in Germany. 17.7 million metric tons of petrochemicals were produced in Germany in 2016 compared to 2.7 million metric tons of products on a renewable basis. This means that the **proportion of renewable raw materials** is around 13%, which is slightly lower worldwide. This relatively high percentage is partly due to the fact that more than 100 years ago already pioneers such as Fritz Henkel set up an extensive oleochemistry business in Germany.

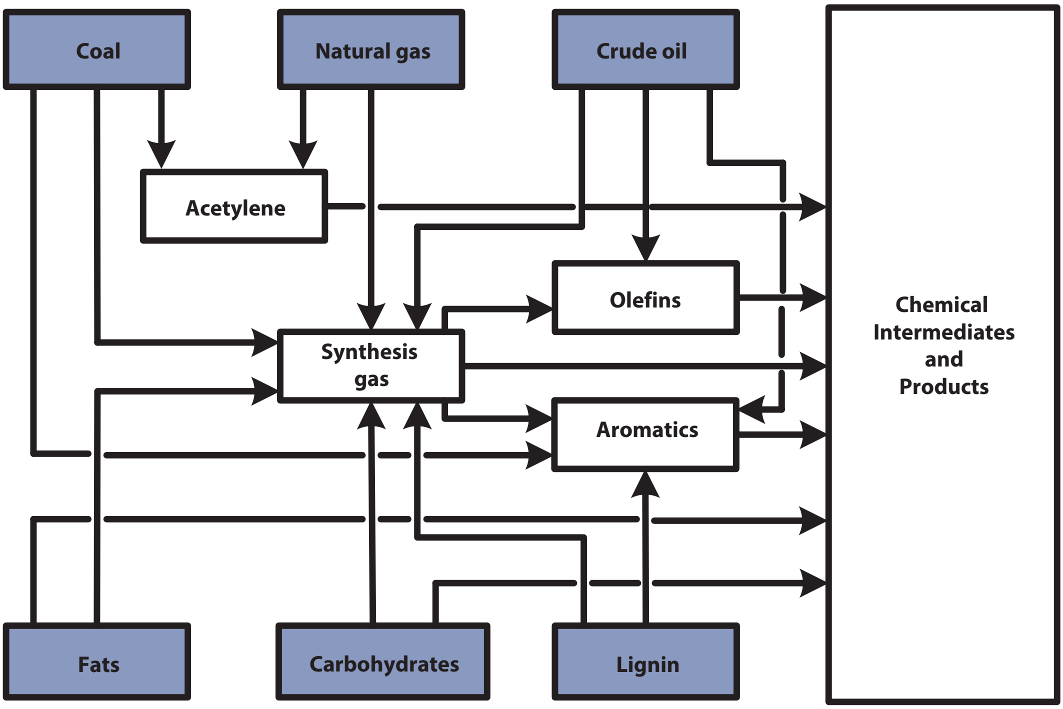
The declared political goal of both the EU and the USA at the beginning of the 2000s was to increase the share of renewable raw materials in chemical production to 20–25% by 2020, but since the introduction of completely new chemical processes requires careful process development of several years, this goal was clearly too optimistic.

The question quickly arises: Could renewable raw materials one day completely replace fossil raw materials? Radio Yerevan replies: "In principle, yes!" However, this would still be far too expensive at present, because despite the increase in oil and natural gas prices in recent decades, the use of renewable raw materials is still comparatively uneconomical in many cases.

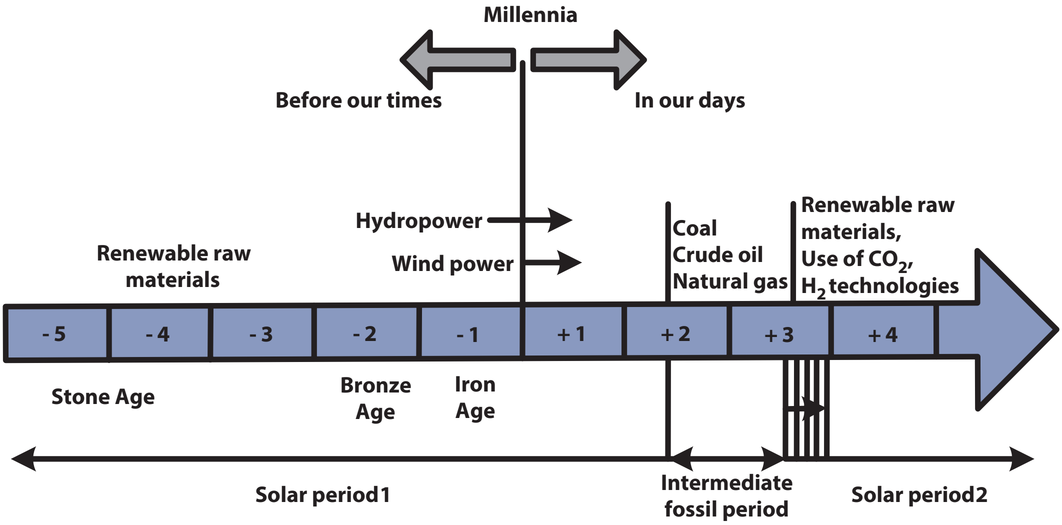
In a very simplified scheme, ◘ Fig. 1.3 attempts to compare the paths of the fossil raw materials coal, natural gas and crude oil (above) with the paths based on the renewable raw materials fats, carbohydrates and lignin (below) to the intermediate and end products of the chemical industry (right).

Follow the individual reaction arrows together with us:

- Currently, distillation cuts of crude oil in the steamcracker are used to produce the important olefins ethene, propene and butenes, and in the reformer the important aromatics benzene, toluene and xylenes (BTX). In addition, both crude oil, natural gas and coal can be converted into the synthesis gas of carbon monoxide and hydrogen. From these relatively small molecules (C1 to C8), the majority of chemical intermediates (alcohols, aldehydes, carboxylic acids, amines …) is produced, which in turn are starting compounds for significant classes of chemical end products, e.g. polymers, surfactants, pharmaceuticals or agrochemical chemicals. As already mentioned at the beginning, coal can also be converted via the intermediate stage of acetylene into intermediates.
- Fats, carbohydrates and lignin can also be gasified to synthesis gas. Since synthesis gas can be converted into olefins and aromatics via the intermediate stage of methanol (not shown in ◘ Fig. 1.3), the same basic chemicals and thus the same intermediate and end products are available from the renewable raw materials as on the basis of fossil raw materials.
- However, it is particularly advantageous if the chemist succeeds in using the renewable raw materials as directly as possible - i.e. without "breaking down" the starting materials into the synthesis gas - and producing end products such as biosurfactants or biopolymers from fats and/or carbohydrates, for example. In this case, the synthesis performance of nature is fully exploited and the renewable raw materials are converted into valuable products with energy benefits.

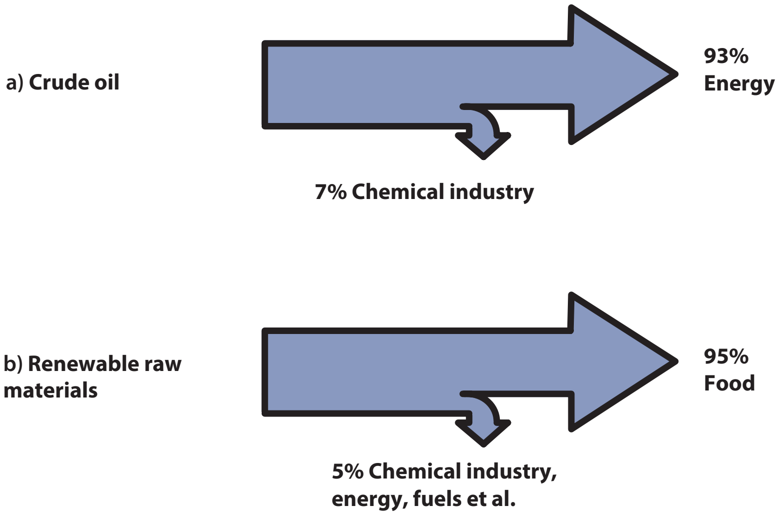


◘ **Fig. 1.3** Comparison of the paths from the raw materials to the intermediates and end products



◘ **Fig. 1.4** Substance and energy sources of mankind over the millennia

In the long term, renewable raw materials can replace fossil raw materials for the synthesis of organic materials without us having to significantly change the technologies already known. The readers of this book should realize that they live in a very extraordinary "interim". As ◘ Fig. 1.4 shows, since the beginning of its existence mankind has only been able to use energies and materials of solar origin ("first solar period"). We are currently in a very small "fossil interim period" from a historical point of view, in which the carbon deposited in the ground in



◘ **Fig. 1.5** Current fields of application of crude oil and renewable raw materials

millions of years as coal, natural gas or crude oil is removed from the soil and is mainly used for energy purposes. In these combustion processes, carbon is ultimately converted into carbon dioxide, which poses the problem of increasing CO_2 concentrations in our atmosphere.

In a few decades, the oil and gas reserves will slowly run out, in a few centuries also the coal reserves. By then at the latest, the "second solar period" of mankind will begin with the almost exclusive use of renewable raw materials and probably with increased use of carbon dioxide and hydrogen electrolytically produced from water.

But there is still a long way to go. The primary task at present is to reduce the enormous consumption of crude oil for energy purposes (◘ Fig. 1.5a), i.e. to build more economical cars or power plants or to better insulate our houses: 93% of crude oil is currently used in energy applications and only 7% in chemicals.

A similar balancing act currently exists for renewable raw materials (◘ Fig. 1.5b): The quantities of renewable raw materials currently used by humans (approx. 6 billion tons of the approx. 170 billion tons newly formed annually) are primarily used as food (95%) and only 5% are used industrially, e.g. in chemical synthesis. Another complicating factor is that in the last ten years, renewable raw materials such as biodiesel or bioethanol have also been increasingly used for energy purposes. Here, markets must be decoupled so that industrial and energy applications do not lead to a shortage of basic foodstuffs and thus to an increase in food prices. In the long term, the use of renewable raw materials for energy purposes makes little sense, but here hydrogen technology using solar energy is the much better way (◘ Fig. 1.4).

1.4 Advantages and Disadvantages of Renewable Raw Materials

Let us start with the **benefits**:

- Since renewable raw materials are constantly being created, unlike fossil raw materials (see ► Sect. 1.3), they are available to us almost infinitely. This means that we can first of all **conserve fossil raw materials** and also replace them in the long term. Renewable raw materials thus fit well into the concept of "sustainability" and can be assigned to "green chemistry".
- The renewable raw materials are **almost CO_2-neutral**, because the carbon released during their decomposition can be converted back into a natural substance through photosynthesis. This means that no additional greenhouse effect occurs when they are used. However, this calculation is somewhat simplified: The maintenance, fertilization, harvesting and processing of renewable raw materials always require energy, which is currently still predominantly generated by burning fossil raw materials.
- Products based on renewable raw materials often have ecological **advantages**. For example,

lubricating oils based on natural oils and fats are ecologically degradable and can therefore also be used safely in nature, e.g. for the lubrication of chainsaws in forestry operations. However, one must also consider this statement with caution: Products made from renewable raw materials are not automatically easily degradable, as even small molecular changes can cause a change in the degradation behavior. A "bioproduct" must therefore also be carefully tested for degradability or toxicity.

- In the last decade, one problem has played an important role in Germany's agricultural policy: the use of fallow arable land. Due to overproduction in Europe, not all agricultural land is used, and thus, the possibility arises to use these industrially for materially used plants, so-called **industrial plants**, or for energetically used plants, so-called **energy plants**. These measures can help to strengthen the agricultural economy and maintain or create new jobs in rural areas.
- Another major advantage of renewable raw materials has already been briefly mentioned during the discussion of ◘ Fig. 1.3: Renewable raw materials have relative complex structures that the chemist can use directly for specific purposes, without the complex synthesis steps required in the petrochemical industry. A well-known example of this is the synthesis of soaps, the alkali salts of long-chained carboxylic acids: While they are derived from alkenes or alkanes only in numerous steps, they can be produced in oleochemical industry in a single step by saponifying the fats and oils with caustic soda or potassium hydroxide solution. The **synthesis power of nature** is fully utilized for the desired end product and costly synthesis steps are omitted.

A major **disadvantage** of renewable raw materials is often their procurement and *logistics*. While it is relatively easy to extract crude oil or natural gas at the drilling site and transport it in pipelines, cellulose-containing tree trunks or starchy potatoes first have to be laboriously collected on a large area of forest or arable land and then transported to a central processing site. The same applies if you want to get any residual material, such as sawdust from numerous sawmills or straw from many individual fields. The procurement of renewable raw materials is therefore usually connected with complex (expensive) transport measures.

An important question in chemical industry is always the **economic efficiency** of a chemical process. The most beautiful chemistry is not carried out industrially if the customer is not willing to pay the price of the product. ◘ Table 1.3 has shown us that products based on renewable raw materials in the order of 2.7 million tons per year are already manufactured and sold in Germany. The economic efficiency of these products must therefore be guaranteed. But does this generally apply to all renewable raw materials? Let us look at ◘ Table 1.4, which lists the purchase prices for some important basic chemicals based on fossil or renewable raw materials. These prices are often subject to significant fluctuations. The values in this table are not based on current daily prices, but we are only interested in the order of magnitude and the rough value comparison of the products with each other.

◘ Table 1.4 shows us that the large basic chemicals based on crude oil, the olefins ethene and propene as well as the aromatics benzene and toluene, both in terms of production volumes and prices, are of a similar order of magnitude as the large products from the range of renewable raw materials, e.g. cellulose or sucrose. However, some renewable raw materials, e.g. the sugars D-xylose and L-sorbose, are currently only produced in small quantities and also have significantly higher prices. In the case of renewable raw materials, it therefore depends very much on the purposes for which they are to be used. An expansive starting compound can only be used if the product justifies this price.

BOX: The SWOT analysis

The SWOT analysis is a generally applicable method to systematically examine and evaluate a difficult situation, e.g. a new idea. The acronym SWOT is derived from the initial letters of the following four terms:

- **Strength**: What are the advantages and strengths of the new idea?
- **Weaknesses**: What are the disadvantages of the new idea?
- **Opportunities**: What opportunities will arise if I realize the new idea?
- **Threats**: What risks, i.e. dangers, arise when implementing the new idea?

In order to obtain a conclusive analysis, all relevant aspects must be considered when answering these four questions, i.e. all economic, social and environmental aspects. Today, SWOT analysis is the first step in strategic planning for many corporate decisions.

The SWOT analysis considering the use of renewable raw materials for energy and material purposes provides the following overall picture:

- **Strength:**
  - The limited, fossil raw materials coal, oil and natural gas are conserved.
  - This reduces greenhouse gas emissions.
  - Ideally, this will result in almost closed and thus sustainable cycles, e.g. of carbon dioxide.
  - The income of workers in forestry and agriculture will be expanded: Jobs will be created and regional benefit increased.
  - Products will be available locally and people are no longer dependent on foreign raw materials: The security of supply is increased.
  - The spectrum of useful plants is extended and crop rotation can be varied more widely: The cultural landscape is enriched.

- **Weaknesses:**
  - The available agricultural land must be divided between crops and food production.
  - For some uses of products (e.g. rape cultivation for the production of biodiesel), this competitive situation leads to acceptance problems among consumers.
  - In some markets, renewable raw materials are not (yet) competitive. This leads to undesirable long-term political regulations (introduction of biodiesel) and/or subsidies (use of biogas).
  - In order to convert renewable raw materials into innovative and competitive products, extensive and thus time-consuming and expensive research and development is required.

- **Opportunities:**
  - As a result of increased research and development, innovative products based on renewable raw materials are being developed that significantly improve competitiveness compared to fossil raw materials.
  - The supply of raw materials can thus be placed on a sustainable basis: Respective countries are no longer dependent on expensive imports.
  - Rising prices for fossil raw materials can lead to products based on renewable raw materials becoming economically attractive. However, it must be considered that rising prices for fossil raw materials can also lead to higher agricultural costs.
  - Breeding improvements in crops and technological improvements in their production can significantly strengthen the competitive position of sustainable raw materials.
  - In general, a trend toward greater sustainability and more natural approaches is recognized in industrialized countries. If, in addition, mandatory certification of sustainable products is introduced in these countries, this can significantly increase the social acceptance of products based on renewable raw materials.

- **Threats:**
  - The above-mentioned competition between commercial crop production on the one hand and food production on the other may lead to a situation in which the cultivation of commercial crops is not accepted by society in the long term.
  - With the world population continuing to grow and the increased demand for food, this effect may become even greater.
  - For many products based on renewable raw materials, it is highly questionable whether they can be produced economically in the long term compared to products based on fossil raw materials.

The opportunities offered by renewable raw materials seem to exceed their threats by far. However, only future will show how the opportunities of renewable raw materials will develop. Since different countries have different agricultural preconditions, different solutions will be found globally.

Table 1.4 Price comparison of basic chemicals on a petrochemical and renewable basis (World 2005, without guarantee)

Resource	Basic chemical	Amount (10^6 t a^{-1})	Price (€ t^{-1})
Crude oil	Ethene	100	1000
	Propene	64	1000
	Methanol	25	150
	Benzene	23	900
	Toluene	7	250
Renewable resources	Cellulose	320	500
	Sucrose	169	200
	Starch	55	250
	Bioethanol	32	650
	D-Glucose	30	300
	Isomaltulose	0.07	2000
	D-Xylose	0.03	4500
	L-Sorbose	0.06	7500

A **general problem** of renewable raw materials is related to their molecular structure and element composition. Petrochemical basic chemicals usually consist only of carbon and hydrogen. In the large groups of renewable raw materials, only the basic substances of terpenes belong to the hydrocarbons; all other renewable raw materials additionally contain oxygen, nitrogen or further elements. Table 1.5 gives the first comparison between fossil and renewable raw materials with regard to their **molar element composition**.

Oxygen is often present in large quantities in renewable raw materials. This oxygen is present in the form of carboxylic acid, aldehyde, ketone and/or alcohol groups and makes the molecules relatively hydrophilic, i.e. water soluble. For example, comparing the formulas of the industrially important C_6 hydrocarbons *n*-hexene[C_6H_{12}], cyclohexane[C_6H_{12}] and benzene[C_6H_6] with the C_6 carbohydrate glucose[$C_6H_{12}O_6$] reveals that the carbohydrate must have completely different properties: The hydrocarbons are almost insoluble in water, whereas glucose is very soluble in water due to its hydroxyl groups. If you want to use glucose for a similar chemistry as with hydrocarbons, you have to dehydrate or hydrogenate the carbohydrate in

Table 1.5 Comparison of fossil and renewable raw materials with respect to their elemental composition (the molar C/H/O/N ratio is given in relation to carbon)

	Resource	Molecular formula	C	H	O	N
Fossil resource	Coal	C	1	0	0	0
	Crude oil	$-CH_2-$	1	2	0	0
	Dry natural gas	CH_4	1	4	0	0
Renewable resource	Oleochemicals, e.g. glyceroltrioleate	$C_{57}H_{104}O_6$	1	1.8	0.1	0
	Carbohydrates, e.g. glucose	$C_6H_{12}O_6$	1	2	1	0
	Terpenes, e.g. myrcene	$C_{10}H_{16}$	1	1.6	0	0
	Amino acids, e.g. alanine	$C_3H_7O_2N$	1	2.3	0.7	0.3

◘ **Table 1.6** Elementary composition of the raw materials (in % by weight)

Resource	C	H	O
Crude oil	85–90	10–14	0–1.5
Fats and oils	76	13	6
Lignocellulose	50	6	43

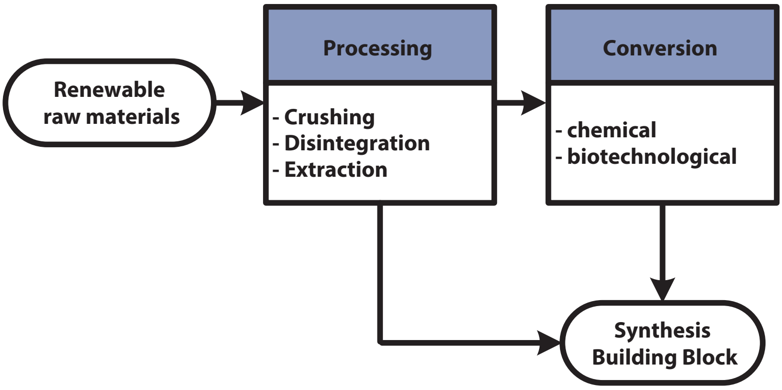
order to remove the “excess” oxygen. In the eyes of a petrochemist, the carbohydrates are therefore **overfunctionalized** and first have to be defunctionalized for some applications.

The particular characteristics of renewable raw materials in terms of their elemental composition become even more obvious when one looks at the **weight ratios** rather than at the molar ratios as shown in ◘ Table 1.5. ◘ Table 1.6 shows the approximate compositions of carbon, hydrogen and oxygen in percent by weight for crude oil, fats and oils and for lignocellulose. While fats and oils are still relatively similar to crude oil, lignocellulose, with only 50% C but 43% O, is a completely different raw material for which new processing and recovery methods have to be developed.

The details of **processing** depend strongly on the renewable raw material and are discussed in the special chapters of this book. In general, however, the basic scheme described in ◘ Fig. 1.6 applies to natural raw materials (cf. ► Chap. 20): After transport, the raw materials are usually first crushed mechanically in mills and/or isolated in sufficient purity by disintegration processes or extractions. Either they can then be used directly as synthesis components (e.g. sucrose from sugar beet) or they are first chemically and/or biotechnologically converted into a more manageable synthetic building block (conversion), e.g. starch, which is often first hydrolyzed biotechnologically into smaller carbohydrate fragments (see ► Chap. 8).

Summary (*Take-Home Messages*)

- **Renewable raw materials** are organic materials from nature, which can be used as substances or energetically in the non-food sector.
- Important **primary ingredients** are triglycerides in fats and oils and the carbohydrates, which can be subdivided in sugar, cellulose, hemicelluloses, chitin and starch.
- Important **secondary ingredients** are terpenoids and natural coloring agents, fragrances, pharmaceuticals and vitamins.
- The renewable raw materials are formed worldwide annually by photosynthesis in a **quantity of approx. 170 billion tons.** The fossil raw materials coal, natural gas and crude oil are still available to us for many years, but its reserves are finite.
- The **share of renewable raw materials** in the production of chemicals amounts currently in Germany approx. 13%. Fats and oils are most commonly used, followed by cellulose, starch, proteins and sugars.
- Renewable raw materials have completely **different structures and compositions** than petrochemicals.



◘ **Fig. 1.6** Pretreatment and conversion of renewable feedstocks

Nevertheless, it is theoretically possible to replace the current petrochemical industry in the long term with the chemistry of renewable raw materials.

- However, some renewable raw materials, especially carbohydrates, are “overfunctionalized” and methods for **defunctionalization** must be developed.
- Great **advantages** of renewable raw materials are their “infinite availability”, their CO_2 neutrality and their good degradability. In addition, they can help with the use of uncultivated farmland. They are particularly advantageous when they can be used directly for chemical purposes without complex multistage syntheses due to their usually complex structures.
- A **disadvantage** is the complex cultivation and/or collection of renewable raw materials. As a result, their prices are often still too high compared to petrochemicals. But there are also a number of renewable raw materials that are already available in sufficient quantities and at a reasonable price which can be used in a wide range of applications.
- In the chemical use of renewable raw materials, a **physical treatment** must usually first be carried out before a chemical or biotechnological **conversion** can be applied.

Ten Quickies

1. Formulate the general equation of photosynthesis!
2. Name some important sugars! If necessary, see ◘ Table 1.1 or ◘ Table 1.4.
3. Compare the molecular formula of the terpene myrcene (◘ Table 1.5) with that of the petrochemical decatriene!
4. Are there also renewable resources in the oceans?
5. Does cellulose only occur in tree wood?
6. Do soybeans contain exclusively oils and fats?
7. What can be derived from the jojoba plant?
8. Name the two most important renewable raw materials in terms of quantity!
9. Which group of renewable raw materials is used in Germany at the most often processed into chemicals? Who was one of the pioneers of these developments?
10. Differentiate between industrial and energy crops! Do you know any examples?

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Fats and Oils

2

The Raw Materials of Oleochemistry - Oil Plants

A. Behr and T. Seidensticker, *Chemistry of Renewables*,
https://doi.org/10.1007/978-3-662-61430-3_2

Chapter Timetable

- The nomenclature of oleochemistry is explained and the most important fatty acids are discussed.
- You will learn which fats and oils are of technical importance and why.
- The twelve most important vegetable fats and oils are presented, each with a description of the plant, the oil, its extraction, its composition and its most important applications.
- The animal fats and oils are briefly introduced to you.
- At the end, you will get an insight into the production figures of fats and oils.

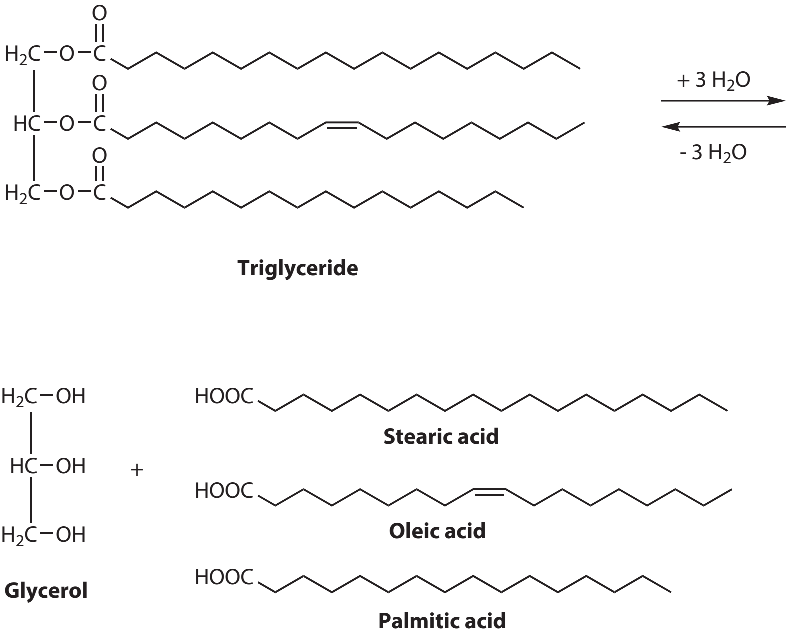
2.1 Introduction to Oleochemistry

Fats and oils have the same chemical structure; they differ only in their melting points. Oils have a melting point below room temperature, are therefore (viscous) liquid, fats have a melting point above room temperature and are therefore solid. In oleochemistry, however, the term "solid" usually refers to an aggregate state similar to margarine. Fats can thus be thermally converted into oils and vice versa. Anyone who has ever kept liquid olive oil in the refrigerator will certainly have observed a slight cloudiness after some time. In the following sections, we will simply refer to "fats", but we will always refer to "fats and oils".

Fats are chemically predominantly triglycerides, i.e. triesters of glycerol (1,2,3-propanetriol) with long-chain carboxylic acids, the so-called fatty acids. The three fatty acids in triglyceride can have the same but also different structures. A typical example of a fat molecule is shown at ◘ Fig. 2.1. By splitting with three moles of water, the triester can be converted into the triol glycerol and the three fatty acids, in this example into the fatty acids stearic acid, oleic acid and palmitic acid. This process is also called fat splitting or hydrolysis.

In ◘ Fig. 2.1, the fat chain is represented by dashes; this simplifies considerably the writing of the long chemical structures. The figure also shows that this reaction is reversible, i.e. triglycerides can also be synthesized chemically from glycerol and fatty acids. In the laboratory, an acid is usually used as a catalyst.

In ◘ Fig. 2.1, we see three different fatty acids (from top to bottom): the saturated octadecanoic acid with the trivial name stearic acid, the unsaturated cis-9-octadecenoic acid, the oleic acid, and the saturated hexadecanoic acid with



◘ **Fig. 2.1** Fat splitting of a triglyceride with water in glycerol and fatty acids the trivial name palmitic acid. It is obvious that these are only even-numbered carboxylic acids. In fact, odd-numbered carboxylic acids such as pentadecanoic acid are rarely found in nature. All carboxylic acids have an IUPAC designation; however, this is rarely used in oleochemistry. Trivial names were often introduced many decades ago.

BOX: The Lazy Oleochemist

The oleochemist often makes it a little easier and describes the fatty acids with an abbreviation. In this abbreviation stands first the symbol of carbon, followed by the number of carbon atoms. Then comes after a colon the number of C=C double bonds. Stearic acid is therefore C18:0 acid, palmitic acid C16:0 acid and oleic acid C18:1 acid (◘ Fig. 2.1). If the oleochemist still wants to indicate at which position the double bond is located, he writes this in brackets after a large Greek delta Δ. If he wants to indicate a *cis* double bond, this is done with the abbreviation "c.", a trans-double bond correspondingly with "t.". The complete abbreviation for oleic acid is therefore: C18:1 (Δ9/c.). If there are several double bonds in the fat chain, these are listed one after the other in parentheses. The eicosapentaenoic acid in fish oil, for example, consists of 20 C-atoms and has five cis double bonds in positions 5, 8, 11, 14 and 17; the abbreviation is C20:5 (Δ5, 8, 11, 14, 17/all c.).

Which long-chain carboxylic acids are found in natural fats? Here, somewhat different data are given in the literature, but usually the even-numbered saturated or unsaturated aliphatic carboxylic acids in the C number range between C8 and C22 are included; in exceptional cases, also carboxylic acids up to C30 are considered. In very rare cases, fatty acids with chains that contain an aliphatic cycle or are branched are also found. The most important saturated fatty acids are listed below in ◘ Table 2.1 and the most important unsaturated fatty acids in ◘ Table 2.2. This information is not intended for memorization, but for reference.

In addition to these fatty acids, which have exclusively an aliphatic hydrocarbon rest, there are also some fatty acids, which carry a further functional group, e.g. a hydroxy, keto or epoxy group, in addition to the carboxyl group. The best-known representatives of these fatty acids are listed in ◘ Fig. 2.2.

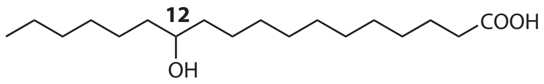
In the following, ► Sect. 2.2 the plants and animals are introduced, in which fats with the most different fatty acid patterns occur. ► Chapter 3 explains the technical processing of fats into fatty esters, fatty alcohols and fatty amines. In ► Chap. 4, you will find an overview of the further follow-up chemistry of fats, especially unsaturated oleochemicals. In ► Chap. 5, we then turn to glycerol, the inevitable by-product of oleochemistry (◘ Fig. 2.1).

◘ **Table 2.1** Important saturated fatty acids

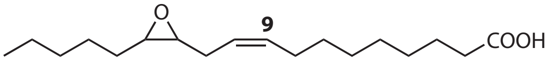
Abbreviation	IUPAC name	Trivial name	Occurrence
C8:0	Octanoic acid	Caprylic acid	Butter, coconut oil
C10:0	Decanoic acid	Capric acid	Butter, coconut oil
C12:0	Dodecanoic acid	Lauric acid	Animal fats, coconut oil
C14:0	Tetradecanoic acid	Myristic acid	Animal fats, coconut oil
C16:0	Hexadecanoic acid	Palmitic acid	Animal fats, palm oil
C18:0	Octadecanoic acid	Stearic acid	Animal fats, palm oil
C20:0	Eicosanoic acid	Arachidic acid	Peanut, beet and cocoa oil
C22:0	Docosanoic acid	Behenic acid	Canola oil, peanut oil

Table 2.2 Important unsaturated fatty acids

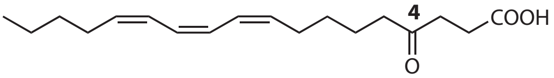
Abbreviation	IUPAC name	Trivial name	Occurrence
C16:1(Δ9/c.)	*cis*-hexadecenoic acid	Palmitoleic acid	Seed oils
C18:1(Δ6/c.)	*cis*-6-octadecenoic acid	Petroselinic acid	Parsley seeds
C18:1(Δ9/c.)	*cis*-9-octadecenoic acid	Oleic acid	Palm oil, animal fats
C18:1(Δ9/t.)	*trans*-9-octadecenoic acid	Elaidic acid	Ruminant fats
C18:2(Δ9,12/c.c.)	Octadecadienic acid	Linoleic acid	Sunflower oil
C18:3(Δ9,12,15/all c.)	9,12,15-octadecatrienoic acid	Linolenic acid	Hemp/linen oils
C18:3(Δ8,10,12/t.t.c.)	8,10,12-octadecatrienoic acid	Calendulic acid	Marigold
C20:1(Δ5/c.)	*cis*-5-eicosenoic acid	Eicosenoic acid	White marshbill
C20:4(Δ5,8,11,14/all c.)	all-*cis*-5,8,11,14-eicosatetraenoic acid	Arachidonic acid	Liver, fish oils
C22:1(Δ13/c.)	*cis*-13-docosenoic acid	Erucic acid	Old canola
C22:1(Δ13/t.)	*trans*-13-docosenoic acid	Brassidic acid	Isomerization of erucic acid



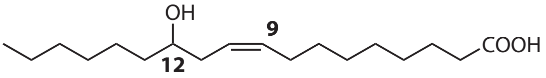
12-Hydroxystearic acid



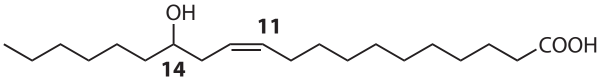
12,13-Epoxy-9-octadecenoic acid
(Vernolic acid)



4-Oxo-9,11,13-octadecatrienoic acid
(Licanic acid)



12-Hydroxy-9-octadecenoic acid
(Ricinoleic acid)



14-Hydroxy-11-eicosenoic acid
(Lesquerolic acid)

Fig. 2.2 Natural fatty acids with several functional groups

2.2 Overview of Important Vegetable Oils and Animal Fats

In advance, Table 2.3 gives you an overview of the most important fats in food and chemical industry. A very first glance at this table reveals that there are two very different classes of fats: One class contains in particular the short-chain C12 and C14 fatty acids, namely coconut oil and palm kernel oil. These short-chain fatty acids are simply called laurics in industry, a term that naturally comes from the C12:0 acid, lauric acid. As we will see in ► Chap. 3, the laurics are of great importance for the production of special surfactants. Coconut oil and palm kernel oil are therefore used exclusively for the production of these surfactants. The second major class of fats contains predominantly C18 and C16 fatty acids.

Table 2.3 also shows two examples that fats can be modified and further developed by breeding or by using genetic engineering. The original rapeseed oil ("old") contains a lot of erucic acid (C22:1) and is therefore unsuitable for human consumption. The "new" rapeseed oil was developed by breeding, which contains a lot of oleic acid (C18:1) and linoleic acid (C18:2) instead of erucic acid. The development was similar for sunflowers: the old variety contains a lot of linoleic acid; the new sunflower quality is also called high oleic because it contains up to 91% oleic acid. In order to be able to draw a comparison with animal fats, grease is also listed at the end of Table 2.3.

It should be noted that the information in Table 2.3 on the fatty acid composition of the various fats are mean values. There are not only the one coconut palm, but very different breeds with different fatty acid contents. For fats where the fat composition varies greatly (e.g. peanut oil and linseed oil), sub and upper values were given in the table. In addition, the quantities harvested and the composition of the fats are also strongly dependent on the course of growth and thus on the weather.

2.2.1 Coconut Oil

Palms are important plants that supply fats, starch and protein. With approximately 2000 different species, the "Palmae" form one of the largest botanical families in the tropical region. An important representative is the coconut palm (*Cocos nucifera*), whose distribution is limited to the equatorial zone. The coconut palm can grow up to 30 m high and bears 10–15 coconuts that ripen throughout the year (Fig. 2.3). A coconut weighs 1–2.5 kg.

Each coconut contains the flesh (the copra) inside, which contains about 60% fat. In young, unripe fruits, there is still some coconut water, in a cavity of the fruit flesh (Fig. 2.4). The copra

Table 2.3 Overview of industrially important oil plants and their fatty acid composition (typical mean values in % by weight)

Fat/oil	12:0	14:0	16:0	18:0	18:1	18:2	18:3	20:1	22:1
Coconut oil	48	17	9	2	7	1	0	0	0
Palm kernel oil	50	15	7	2	15	1	0	0	0
Palm oil	0	2	42	5	41	10	0	0	0
Rapeseed oil (old)	0	1	2	1	15	15	7	5	50
Rapeseed oil (new)	0	1	4	1	60	20	9	2	2
Sunflower (old)	0	0	6	4	28	61	0	0	0
Sunflower (new)	0	0	4	2	91	3	0	0	0
Soybean oil	0	0	8	4	28	53	6	1	0
Peanut oil	0	1	10	4	36–72	13–45	1	1	0
Linseed oil	0	0	6	3	15–25	10–30	50–60	0	0
Grease	0	1	31	13	46	6	0	0	0

Fig. 2.3 Coconut palm (© tobrother/Fotolia)

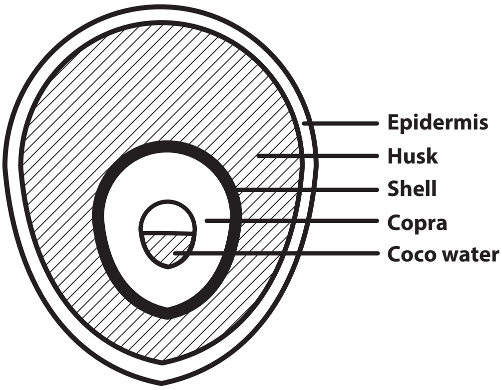


Fig. 2.4 Cross-section through a coconut

is surrounded by a wooden stone shell, which in turn is surrounded by the husk, a layer of coconut fibers several centimeters thick, the bast layer. The outermost layer of the coconut is a leathery epidermis. Newer varieties of the coconut palm aim to develop coconut palms with shorter stems. They are thus better able to withstand tropical storms, have increased resistance to disease and are easier to harvest, e.g. with harvesting machines. Meanwhile, there are dwarf mutants of the Cocos nucifera, which grow only about 2 m high.

BOX: The Trained Monkeys

The classic harvesting of coconuts is done in several ways: You can drop the ripe nuts on the ground and collect them there. However, this leads to harvest losses. In Africa and Asia, the harvest is still carried out by pickers who climb up the 30 m high stems to reach the fruit stands. In Malaysia, there are specially trained monkeys for the harvest, the macaques, which climb up the palms and throw down the fruits.

The epidermis and bast layer is removed from the coconuts and the stone shell is mechanically broken to preserve the copra. The typical further processing of oil fruits is presented below using the example of copra. This processing is carried out in the following steps (◘ Fig. 2.5):

- The copra is first **crushed** roughly and then finely by crushers and roller mills.
- The crushed plant material is finally **heated** in a heat pan to temperatures of e.g. 70 °C: This lowers the viscosity of the oil, which becomes more fluid. In addition, cell membranes are destroyed and proteins coagulated: Both lead to a better extractability of the oil.
- The next stage of processing is the pressing of the oil in a continuously operated press. For this purpose, screw presses are used in which a press shaft in the form of a screw is located, similar to a meat mincer. In order to increase the pressure in the course of the pressing process, the diameter of the worm gear tapers in the conveying direction. The pressing pressure produces temperatures of up to approx. 100 °C. The screw presses have a sieve on the outside through which the oil runs out. This turbid oil is filtered in a filter press and then flows into a storage tank. Both the crushing and pressing processes can be repeated to increase the oil yield.

The remaining plant residues usually still contain a residual oil content of 8% or more after this process. These residues can be used as very high-quality animal feed, but often the oil content is further reduced by subsequent **extraction**:

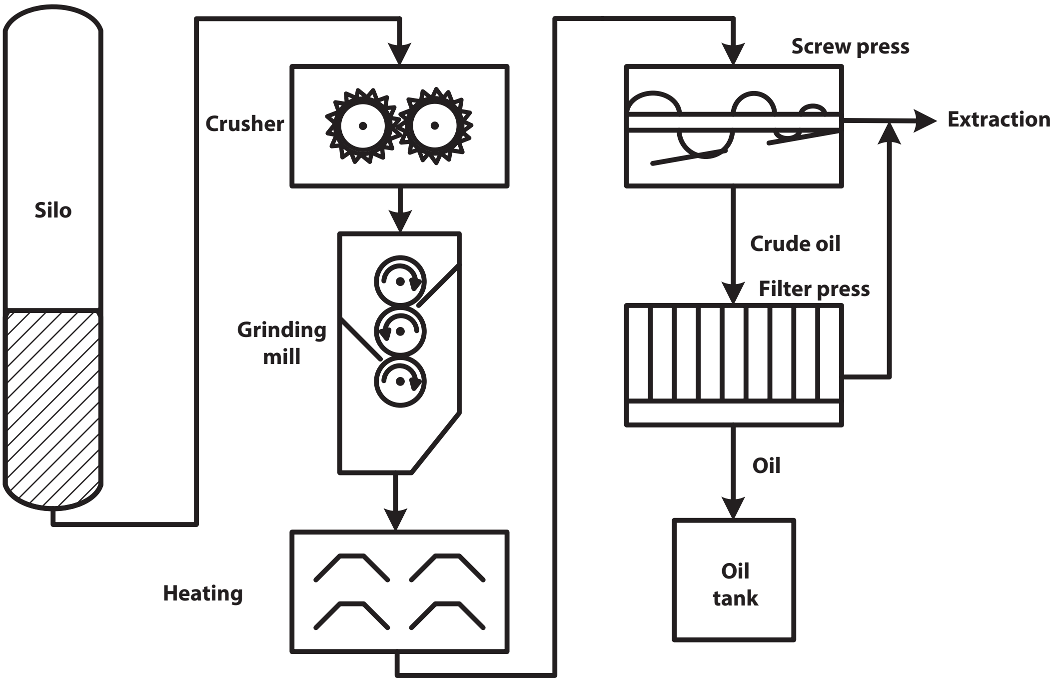


Fig. 2.5 Mechanical processes for oil extraction from oil fruits

- This extraction can be carried out, for example, with *n*-hexane or with gasoline, whereby the extraction material is fed in countercurrent to the solvent. The solvent is then separated off again by distillation.
- Modern processes use supercritical carbon dioxide ($scCO_2$) as extraction agent. However, these processes require high pressures and are therefore more expensive. The advantage is that the carbon dioxide evaporates completely when the solution is released and thus no residual solvents are contained in the oil.

The “crude oils” isolated in this way still have to be processed in a further refinery:

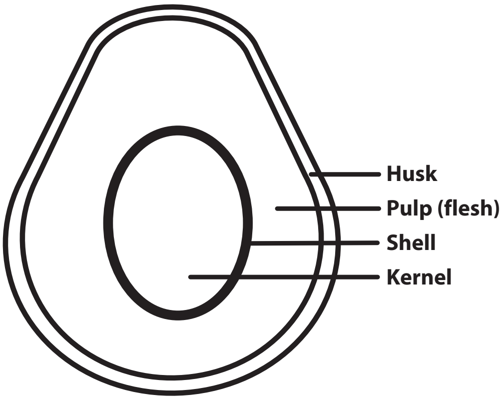
- During **degumming**, hydrolysis precipitates proteins and phospholipids, making the oil much more stable in storage.
- Enzymatically or microbially the triglycerides can split off free fatty acids which give the oil unfavorable properties. These fatty acids are neutralized in **deacidification** by adding alkali solutions, e.g. diluted NaOH.
- Oils may contain natural colorants, e.g. carotenoids or chlorophyll. Most of these substances are already removed in the first two steps. If necessary, **bleaching** with bleaching earth or adsorption on activated carbon can follow.
- The last step is **damping** the oil. Volatile products of the oil are removed according to the well-known principle of vacuum steam distillation. Since unpleasant odors are also removed during this damping process, this is referred to as deodorization of the oil.

If one examines the chemical composition of the coconut oil thus obtained, the fatty acid distribution already presented in ◘ Table 2.3 (line 1) results: The triglycerides of coconut oil contain in large proportions the “lauric”, i.e. the lauric acid and the myristic acid, and in only small proportions the palmitic, stearic and oleic acids. Coconut oil is therefore an excellent raw material for detergent alcohols (cf. ▶ Chap. 3).

2.2.2 Palm Oil and Palm Kernel Oil

Another important type of palm is the oil palm (*Elaeis guineensis*). It originates from the rainforests of Guinea and has therefore been given its botanical name. Already in 1466, the Portuguese

◘ Fig. 2.6 Fruit of an oil palm (© Thomas Leonhardy/ Fotolia)



◘ Fig. 2.7 Cross-section of a palm fruit

got to know the oil palm during their exploration trips through West Africa, but it was not until the middle of the nineteenth century that the Dutch brought the first specimens to Indonesia, where today - as in neighboring Malaysia - large plantations of the oil palm exist. While the coconut palms are very slender and the aging leaves shed completely, the Elaeis is relatively compact. The oil palms have a height of 6 to a maximum of 15 m; their stem remains intact for many years. The oil palm supplies oil fruits with an annual production of up to 6 tons per hectare for 50 years. Thousands of small fruits (◘ Fig. 2.6) grow closely pressed together in the 20 kg heavy fruit stands of the oil palm. These fruits contain a soft flesh rich in fat and three rock-hard seeds. If the nutshell of these seeds is broken, the "palm kernel", which also contains fat, is reached (◘ Fig. 2.7).

Both components of the oil fruit are processed separately and produce oils with different compositions: palm kernel oil, like coconut oil, contains many laurics. The palm oil obtained from the flesh consists mainly of the triglycerides of palmitic acid (which takes its name from the oil palm) and oleic acid. The pulp must be processed immediately after harvesting; otherwise, the damaged fruit will undergo enzymatic decomposition, which greatly increases the acid number of the oil (BOX: Quality Criteria for the Oleochemist). The hard-shelled cores, on the other hand, can be stored well.

BOX: Quality Criteria for Oleochemists

In order to be able to assess the quality of the raw materials quickly, the oleochemist has introduced several fast measures that can be determined relatively quickly by titration:

- The **iodine value (IV)** is a measure of the number of C=C double bonds and thus of the content of unsaturated fatty acids. It is determined either by titration with elemental bromine or by determining the uptake of hydrogen.
- The acid **value or number (AV or AN)** is a measure of the content of "free" (i.e. not glycerol-bonded) fatty acids that have split off from the triglycerides upon aging. The AV is the mass of KOH (in mg) used to neutralize one gram of oil. Oils with a high acid number are of lower quality and therefore also lower in price.
- The **saponification value or number (SV or SN)** indicates the mass of KOH (in mg) required to bind the free acids contained in a gram of oil and to saponify the esters.
- The **hydroxyl value (HV)** is a measure of the OH groups present in the oil. To determine the hydroxyl value, the oil is first esterified with acetic anhydride. The hydroxyl number then indicates the mass of KOH (in mg) required to neutralize the amount of acetic acid released during esterification.

2.2.3 Rapeseed Oil

Rapeseed oil is obtained from the seeds of rape (*Brassica napus oleifera*). Rapeseed has long been one of the most important oil plants in the temperate zone. Rapeseed grains were already found in excavations of Germanic settlements. In the late MiddleAges, rape oil was used in Germany for lighting purposes. With the introduction of petroleum at the end of the nineteenth century, however, it lost this use.

Rape belongs botanically to the cruciferous family. The plants grow up to 1.5 m high; the bright yellow flowers (◘ Fig. 2.8) later form the seed pods. The almost spherical seeds contained therein have a diameter of up to 3 mm. If the seeds are shiny black, the rape can be harvested and processed.

Former (“old”) rapeseed oils mainly contain erucic acid (C22:1), oleic acid (C18:1) and linoleic acid (C18:2) (◘ Table 2.3). However, erucic acid is worthless for human nutrition because it cannot be digested in the human body. Larger amounts of erucic acid can even lead to coronary artery disease. In 1974 succeeded the breeding of rape varieties low in erucic acid, the so-called 0 variants. In 1978, a further improvement was achieved, namely the introduction of the “00 variants”. With these 00 rape variants, it was also possible to prevent the formation of glucosinolates (mustard oils bound to glucose, bitter substances), which can lead to thyroid dysfunction. The “new” rapeseed mainly contains oleic and linoleic acid and, in smaller quantities, linolenic acid. The old rape is of some importance as an industrial and energy plant; the new rape can be used safely for high-quality food.

◘ Fig. 2.8 Rapeseed field (© artaxx/Fotolia)

2.2.4 Sunflower Oil

The original home of the sunflower is North America. In 1510, the Spaniards brought the sunflower to Europe, but it was not until the nineteenth century that its importance as an oil plant was recognized, when Peter the Great had it planted on a larger scale in southern Russia. The sunflower (*Helianthus annuus*) belongs to the daisy family and is an annual plant that can grow up to 5 m high. For commercial cultivation, however, 1–1.5 m high varieties are preferred, which can be harvested mechanically. The plant forms a disk-shaped inflorescence (see title picture of the book), which can contain several thousand small fruits. These sunflower seeds have an oil content of up to 57%, the rest are mainly proteins, carbohydrates and minerals. The (old) sunflower oil contains mainly linoleic acid (44–70%) and oleic acid (14–43%, ◘ Table 2.3) and is an excellent raw material for the production of edible oil and margarine due to the high proportion of essential linoleic acid (BOX: MUFA or PUFA?). In the industry, it is processed to soaps and varnishes and partly serves as a substitute for linseed oil. The press cake remaining after extraction contains up to 50% protein and is often used as animal feed.

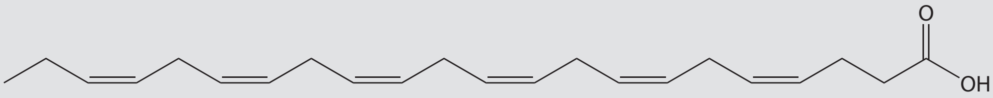
Important new sunflower varieties have been introduced, particularly in Russia. The “new” sunflower is also called “high oleic” because it contains up to 91% oleic acid but only a little linoleic acid (3%) (◘ Table 2.3). This raw material leads to an oleic acid with a high degree of purity and is therefore ideally suited for chemical use, e.g. for the production of lacquers, paints and technical esters as well as for cosmetic products.

BOX: MUFA or PUFA?

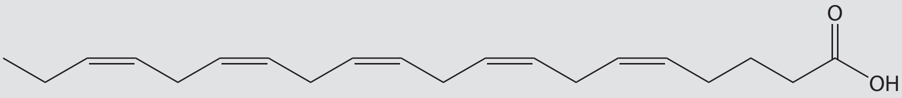
MUFA and PUFA are not sea monsters, but only common abbreviations used by oleochemists and nutritionists:

- MUFA are monounsaturated fatty acids, e.g. the frequently occurring oleic acid.
- PUFA are polyunsaturated fatty acids. These include linoleic acid (C18:2), linolenic acid (C18:3), eicosapentaenoic acid C20:5 (Δ5, 8, 11, 14, 17/all c., EPA) and docosahexaenoic acid C22:6 (Δ4, 7, 10, 13, 16, 19/all c., DHA). EPA is a precursor of prostaglandins and thus has important pharmacological properties.

The polyunsaturated fatty acids belong to the essential fatty acids, which must be supplied to the human body with food, since it cannot produce them itself (◘ Fig. 2.9).



Docosahexaenoic acid (DHA)



Eicosapentaenoic acid (EPA)

◘ **Fig. 2.9** Chemical structures of EPA and DHA

2.2.5 Soybean Oil

The soy plant (*glycine max*) belongs to the legume family and was planted in China as early as 1000 BC. It was not until the nineteenth century that it reached Europe and America. The soy plant produces soybeans, which contain both the oil (20%) and larger amounts of protein (40%). On the outside, the plant resembles the bush bean: It is heavily hairy and grows in the form of shrubs up to 80 cm high (◘ Fig. 2.10).

The soy oil is obtained by extraction and contains approx. 50% linoleic acid, 30% oleic acid and between 3 and 11% linolenic acid, which is also responsible for the slight rancidity of the soy oil (◘ Table 2.3). In Germany, it is used for margarine production, in the USA also for the production of edible oils. Soy oil contains up to 3% lecithins, which are used as emulsifiers in the food sector as well as for technical purposes. The press cake produced during soy oil extraction, soy meal, contains almost all proteins and carbohydrates and is used in the form of soy flour, soy milk and soy quark (tofu) as food for humans, but is also used as concentrated feed for animals. After dissolving in alkali, the soy protein can also be spun into threads which, after flavoring, produce artificial “soy meat”.

The high content of linoleic acid is crucial for the technical use of soy oil: Lacquers, varnishes, lubricants, resins, plasticizers and paints are produced with soy oil. In recent years, soy oil-based polyols have increasingly been discussed as starting materials for biopolymers (polyester, polyurethanes, ► Chap. 19).

2.2.6 Linseed Oil from Flax Plants

Flax belongs botanically to the large family of Linaceae, but only the *linum usitatissimum* (translated: the extremely useful linen) has gained importance as a cultivated plant. The fruit of the flax forms a spherical or oval capsule

Fig. 2.10 Soy plant (© chungking/Fotolia)

containing the linseeds (◘ Fig. 2.11). Flax can be divided into oil flax, oil fiber flax and fiber flax, with the linseed oil content decreasing and the fiber content increasing in this order. The fabric of the flax fiber is called linen.

Linen was already known to the Sumerians and Egyptians 5000 years ago, and also in Europe, linen was already cultivated in the younger Stone Age. Fiber flax needs relatively much water for its growth; the oil flax prefers drier, warmer regions with temperatures around 20 °C. Linseed has an oil content between 30 and 50%. As ◘ Table 2.3 shows, linseed oil obtained by grinding, pressing and/or extraction contains high proportions of linolenic acid (50–60% C18:3) in addition to oleic acid (C18:1) and linoleic acid (C18:2). However, the key figures for linseed oil are sometimes subject to very strong fluctuations, especially the iodine value (BOX: Quality Criteria for Oleochemists).

The high proportion of triple unsaturated fatty acid leads to the fact that linseed oil gradually polymerizes in the air by reactions with atmospheric oxygen and finally becomes solid: Several fatty acid molecules combine to form a large, branched molecule. An oil with this behavior is also called “drying oil“. These drying oils are excellently suited for the production of ecologically compatible lacquers, paints, printing inks and varnishes. Further applications can be found in the paper, leather and oilcloth industries and in the production of linoleum floor coverings (► Sect. 4.2.2.5). The name “linoleum” already refers to the name of the main raw material, linseed oil (lat. *oleum lini*).

Fig. 2.11 Flax plants (© Janine Fretz Weber/Fotolia)

2.2.7 Castor Oil

Castor oil (*Ricinus communis*) belongs to the Euphorbiaceae family and comes from the tropics of Asia and Africa. Today, India, China, Brazil and Thailand are the main growing areas;

Fig. 2.12 Seedpot of the castor plant (© LianeM/ Fotolia)

in Europe, for example, the plant is cultivated in Romania and Spain. The plants grow up to 2 m high, have large leaves up to 40 cm long and form inflorescences with up to 20 fruits (**Fig.** 2.12). The spiny, red-green fruits contain seeds with an oil content of approx. 50%.

The special feature of castor oil is the high content (87%) of triglycerides of ricinoleic acid, which we already got to know in **Fig.** 2.2: Like oleic acid, it is a cis-C18:1 acid, but with an additional OH group in the C12 position. In addition, castor oil contains small amounts of oleic acid (7%) and linoleic acid (3%) as well as a few saturated acids. However, the castor oil plant also contains some toxic substances, such as the protein ricin and the alkaloid ricinine, which remain in the press cake after pressing. However, by physical or chemical methods, e.g. by short heating to 140 °C and/or by treatment with bases, the toxins can be eliminated and thus the press cake can also be used as animal feed.

Castor oil has been cultivated and used for a long time, including 6000 years ago in ancient Egypt. In the pharmaceutical industry, it is used as a laxative and in cosmetics for the production of bath oils, lipsticks and shampoos. In technology, the good lubricating properties and high viscosity of castor oil are used for the production of lubricating oils. Due to its unusual functionality for fatty substances, ricinolic acid is also increasingly used as an oleochemical reactive component in the production of paints, lacquers, inks, foams and polymers (► Sect. 19.2.2).

2.2.8 Olive Oil

The olive tree (*Olea europaea*) has also been native in our culture for a long time: It has been known to the Sumerians and Egyptians for about 5000 years and was planted in Homer's time in Greece. The ancient medium-high shrub forms a tree that can grow up to 20 m high and whose trunk can grow up to 4 m thick. Due to its intensive root system, the olive tree is very undemanding and requires only little water. The stone fruits, the olives (**Fig.** 2.13) can grow up to 2.5 cm thick and are green, reddish, purple or black, depending on the variety. Olive oil is obtained by pressing ripe, whole or pitted fruits. At a first pressing under moderate pressure and temperatures up to 25 °C, the almost colorless *oleum virgineum* forms; at higher pressing pressure and higher temperatures, yellow to brown oils are formed.

The main components of olive oil are triglycerides with oleic acid (84%), palmitic acid (9%), linolenic acid (4%) and arachidic acid (1%). It is an excellent edible oil, but is also used for skin care, for the production of soaps and for technical purposes, e.g. for machine oils. Because of its high-oleic acid content, it is an important raw material in oleochemistry, and we will encounter oleic acid and its derivatives even more frequently in ► Chaps. 3 and 4.

Fig. 2.13 Fruit and leaves of the olive tree (© Maceo/ Fotolia)

2.2.9 Safflower Oil

The safflower (*Carthamus tinctorius*) belongs - like the sunflower - to the family of daisies. It is a thistle plant which was originally cultivated as a color plant. The red dye from the petals was used in the Middle Ages to dye textiles (◘ Fig. 2.14).

The seeds of the safflower contain up to 37% oil and are also very rich in protein (20–55%). The viscous oil is golden to reddish yellow and roughly comparable to linseed oil: It contains 70–80% linoleic acid and up to 20% oleic acid, is therefore highly unsaturated and can therefore be used as drying oil in the paint industry like linseed oil. It does not darken and is therefore also suitable for light colors and lacquers. However, its shelf life is very limited: It can only be stored for up to 12 months if cooled. Because of its nut-like taste, safflower oil is also valued as an edible oil and is also used as a dietary food.

◘ Fig. 2.14 Flowering of safflower (© Dr. R. Kaiser-Alexnat, Institut für Färbepflanzen, Michelstadt)

2.2.10 Jatropha Oil

The jatropha (*Jatropha curcas*) belongs to the spurge family (*Euphorbiaceae*) and is native in tropical and subtropical areas. The special feature of this plant is that, due to its frugality and robustness, it also grows in dry savannahs, where food plants cannot survive. It is therefore ideal for growing oil plants in desert-like and erosion-endangered areas. The jatropha shrub can grow up to 8 m high and forms plum-sized fruits that contain several seeds. These seeds consist of up to 60% oil (◘ Fig. 2.15). Although the press cake contains up to 60% crude protein, it is unsuitable as food for humans or animals because it contains toxic substances, the phorbol esters, which cannot yet be removed.

Jatropha oil contains about 75% unsaturated fatty acids, especially oleic acid (42%) and linoleic acid (35%), and only small amounts of saturated fatty acids such as palmitic acid (14%) or stearic acid (6%). However, the composition of the jatropha oils varies considerably. In recent years, jatropha oil has attracted special attention because it can also be used as diesel fuel ("biodiesel") due to its high cetane numbers (approx. 60). Parts of South America, Africa and Asia have therefore seen a sharp increase in the cultivation of jatropha. However, this plant will not be able to solve the energy problems of the industrialized countries.

◘ Fig. 2.15 Jatropha seeds (© Prashant ZI/Fotolia)

BOX: An Oil that Is not an Oil at All

The jojoba plant (*Simmondsia chinensis*) with its gray-green, leathery leaves also loves the sun: It comes from the Sonora desert between California and Mexico and is now also native in dry locations in Argentina, South Africa and South Australia. The jojoba plant can be planted - like jatropha - on land that is no longer suitable for food production. By the way, the name is of Indian origin and should actually be pronounced "Ho–Ho-Ba".

The yellowish oil obtained from the seeds of the evergreen jojoba bush is by our definition not an oil at all, but a wax! Oils are defined as triesters of glycerol (■ Fig. 2.1), but waxes are monoesters of fatty acids with primary alcohols. However, since jojoba oil is a wax with a very low melting point (7 °C), it is still often included in the list of oils. Jojoba oil consists of esters of the unsaturated fatty acids eicosenoic acid (C20:1) and docosenoic acid (C22:1) with unsaturated C11 and C12 alcohols. It is thus very similar to sperm oil, which was formerly obtained from the sperm whale. However, since whaling has been severely restricted, sperm oil is hardly available today.

The seeds of the jojoba plant are very similar to the olives (■ Fig. 2.16).

Jojoba oil is mainly used in cosmetics such as skin creams and lipsticks, but also as a wax coating for citrus fruits or sweets. Jojoba is also used for pharmaceutical purposes, e.g. to cure skin diseases and burns. Since it almost maintains its viscosity at high temperatures, it is also used as a lubricant for high-speed engines. Some also consume jojoba oil as cooking oil: Since there are no enzymes in the human body that can break down the monoester, this trick allows you to enjoy very fatty foods without getting thicker. However, we do not recommend this "reduction diet", as the oil that has not been degraded remains in the intestine and can then cause diarrhea.

■ **Fig. 2.16** Seeds of the jojoba bush (© Roman Dean/Fotolia)

2.2.11 Other Fats and Oils

Since a textbook has only a very limited scope, we hereby end the description of the most important oil plants. Poppy, peanut, cottonseed and walnut oils, sandalwood and pumpkin seed oils and many others are therefore not explained here. Hemp oil will be presented in ▶ Chap. 7. Altogether, there are about 1400 species of oil plants, of which about 20 are commercially cultivated. At the end of this chapter, however, we will take a look at some important fats of animal origin:

- **Grease** is a collective term for spreadable animal fats. Typical representatives are grease from pigs, geese and butter. Important fatty acids of grease are oleic, palmitic and stearic acid (◘ Table 2.3).
- **Tallow** is a solid, granular fat mass that is usually less suitable for human consumption. For this reason, tallow is also relatively inexpensive. The most important representatives of tallow are beef tallow and mutton tallow. They also contain odd C number fatty acids, e.g. margaric acid (C17:0), trans-fatty acids such as elaidic acid (◘ Table 2.2) and branched fatty acids. Triglycerides of oleic, palmitic and stearic acid also dominate in beef tallow - as in grease.

BOX: The Healthy Eskimo

Fish oils are obtained from herring fish or from fish processing waste. Characteristic for fish oils is the very high content of polyunsaturated fatty acids, PUFA, with four to six C=C double bonds, e.g. arachidonic acid (◘ Table 2.2). These have a special nutritional significance for humans: They have a beneficial effect on the prevention and treatment of arteriosclerosis and cardiovascular diseases. This effect has been found in the Eskimo people, which, despite their very high caloric and high-fat diet, including fish, are hardly prone to heart disease.

2.3 Some Numbers

The **worldwide production** of fats and oils has increased enormously in recent decades, especially for the production of food fats. The development in the last four decades shows ◘ Fig. 2.17: The total consumption of fats and oils has increased from 41 million tons in 1970 to about 200 million tons in the market year 2014/15 and has thus increased fivefold during this time! Similar growth rates are also expected in the future.

◘ Figure 2.18 shows once again in more detail how the world production increases for the individual oils have developed over the last decade. For a long time, soybean oil was the most important oil worldwide; in the meantime, it has been overtaken by palm oil due to constantly new oil palm plantations in the Asian region. The order of the most important oils today is therefore: Palm oil > Soybean oil > Rapeseed oil > Sunflower oil > Tallow > Palm kernel oil > Coconut oil.

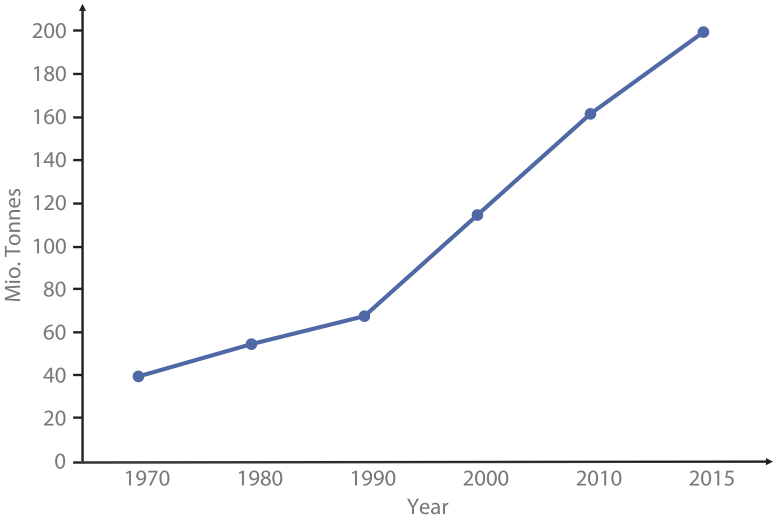
A brief look at the average **oil prices** in Europe for the four most important oils in June 2017 (source: ▶ www.oilworld.biz):

- Palm oil 0.69–0.72 $ kg^{-1}
- Soybean oil 0.67–0.82 $ kg^{-1}
- Sunflower oil 0.72–0.78 $ kg^{-1}
- Rapeseed oil 0.83 $ kg^{-1}.

Finally, some statistical data from the “Fachagentur Nachwachsende Rohstoffe” on the special situation of fats and oils in Germany is presented:

- In 2013, 1.2 million tons of fats and oils were used (Table 1.3).
- These 1.2 million tons are divided into almost 20% animal fats and 80% vegetable oils, in particular rapeseed oil, linseed oil, sunflower oil, palm oil, soybean oil, coconut oil and castor oil.
- The domestic industrial plants were cultivated on 153,000 ha of arable land. These include rape (140,000 ha), sunflower (9000 ha) and linseed oil (3500 ha). Please note that the field of energy crops is not included in these figures: Rape is still being planted on a further 616,000 ha in Germany to produce biodiesel (▶ Chap. 20).

Fig. 2.17 Global consumption of fats and oils. From 1970 to 2014/15, *source* ► www.oilworld.biz



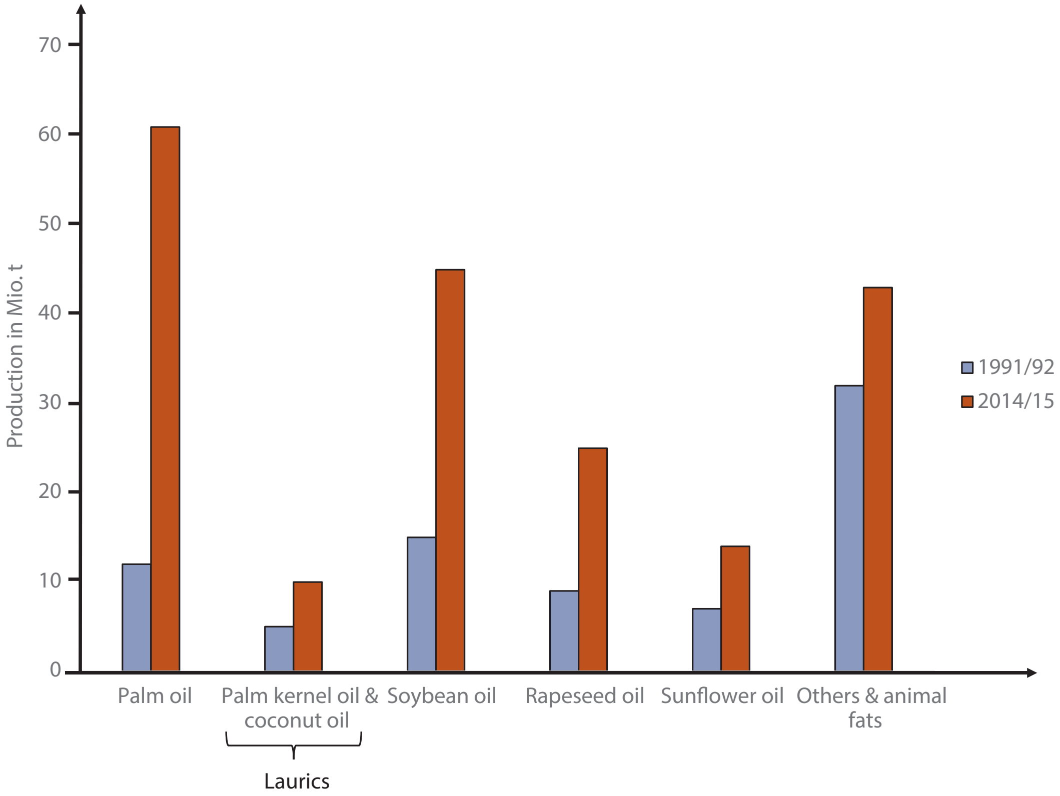


Fig. 2.18 World production of various fats and oils. *Source* ► www.oilworld.biz

Summary (*Take-Home Messages*)

- A distinction is made between **vegetable fats** with predominantly short fatty acid chains (C12–C14) and fats with predominantly longer chains (C16–C22).
- The **laurics** include coconut oil and palm kernel oil. They play an important role as raw materials for the production of oleochemical surfactants.
- The **extraction of oils** from seeds and nuts was explained using the example of coconuts: these are crushed, heated and pressed out in screw presses. The cloudy oil is then filtered. The remaining press cake can still be extracted with hydrocarbons or supercritical CO_2.
- The old **rapeseed oil** contains erucic acid (C22:1) and is therefore unsuitable for human consumption. The new rapeseed oil with high content of oleic acid (C18:1) and linoleic acid (C18:2) was created by new breeding.
- The oil of the old **sunflower** contains a lot of linoleic acid, similar to soy oil. The newly bred high-oleic sunflowers, on the other hand, contain almost exclusively oleic acid. Oleic acid is also the main fatty acid of olive oil.
- **Linseed** is used to produce linseed oil, which contains a high proportion of linolenic acid (50–60% C18:3). This polyunsaturated fatty acid (PUFA) can polymerize in air to a solid layer. Linseed oil is therefore also called drying oil. **Safflower oil** also contains a higher proportion of PUFA and is therefore used similarly to linseed oil in the paint and varnish industry.
- The main fatty acid of **castor oil** is ricinoleic acid, a C18:1 acid with an additional hydroxy function in the C12 position. The oil has good lubricating properties, but because of its alcohol group it can also be chemically converted in many ways.
- **Jatropha oil** can become more important in developing countries because it is also growing in arid areas. Due to its high cetane number, it can be used as “biodiesel”.
- **Jojoba oil** is not a fat but a wax, i.e. a monoester of a fatty acid with a long-chain alcohol. Jojoba oil is used in cosmetics, pharmaceuticals and as a lubricant.
- Important **animal fats and oils** are grease, tallow and fish oils. Grease and tallow contain high levels of oleic and palmitic acid; fish oils contain the four to sixfold unsaturated fatty acids that are important for nutrition.
- In the market year 2014/15, the worldwide **production of fats and oils** amounted to approx. 202 million tons. The world’s most important oils in terms of quantity are palm oil, soybean oil, rapeseed oil and sunflower oil.
- In Germany, about 1.2 million tons of fats and oils are currently used each year in chemical industry.

? Ten Quickies

1. Are there odd-numbered fatty acids in natural fats? Do you know an example?
2. Write down the abbreviations for cis-6-octadecenoic acid (petroselic acid), trans-9-octadecenoic acid (elaidic acid) and trans-13-docosenoic acid (brassidic acid)!
3. Name (at least) one fatty acid with a hydroxy group!
4. What are “laurics”? In which oils do these fatty acids occur?
5. Distinguish between MUFA and PUFA. Give examples!
6. You are offered the untreated press cake of the castor oil plant as dog food. How do you react?
7. Which oil plants are particularly undemanding?
8. Give examples of “drying oils”! Where did they get her name?
9. Which fats and oils contain a relatively high proportion of oleic acid?
10. Why is the extraction of oil plants with supercritical carbon dioxide particularly advantageous?

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The Basics of Oleochemistry - Basic Oleochemicals

A. Behr and T. Seidensticker, *Chemistry of Renewables*,
https://doi.org/10.1007/978-3-662-61430-3_3

Chapter Timetable

- You will learn several methods for splitting triglycerides into the basic chemicals fatty acids (or fatty acid esters, respectively) and glycerol.
- We will discuss the chemistry of the carboxy group of fatty acids, which leads us to fatty alcohols and fatty amines, among others.

This chapter describes the basic reactions of the chemistry of fats and oils, the so-called *oleochemistry*. They have been known for over a century and have long been used in industry. On the other hand, a great deal of research has been carried out in this field in recent years, and new types of reactions have been developed. We will get to know these in ► Chap. 4.

3.1 Production of Basic Oleochemicals

In the petrochemical industry, petroleum hydrocarbons are used to produce a large variety of chemical intermediates and end products. This process involves splitting the mixture of aliphatic and aromatic compounds contained in crude oil into smaller units in the steam cracker and the reformer before producing specific secondary chemicals. These smaller units are, for instance, ethene, propene, butadiene, benzene, toluene and xylenes. These are called "petrochemical basic chemicals".

In oleochemistry, too, only little chemistry is carried out directly with fats and oils, but triglycerides are often broken down into glycerol and fatty acids or their derivatives. There are several variants:

- As already described in ◘ Fig. 2.1, triglycerides can be broken down into free fatty acids and glycerol by **hydrolysis**, i.e. by reaction with water. This process is called *fat splitting*.
- Triglycerides can also be split into fatty acid (methyl) esters and glycerol by **transesterification**, e.g. with methanol.
- The third way is **saponification** of fats with bases, e.g. sodium hydroxide, resulting in glycerol and in the sodium salts of fatty acids, i.e. soaps, respectively. Soaps are usually no longer chemically converted, but used directly by the consumer as cleaning and washing agents.
- The fourth method, which has not (yet) been technically implemented, is the **direct-hydrogenation** of fats and oils into glycerol and fatty alcohols. Fatty alcohols can also be formed indirectly by hydrogenation of either fatty acids or fatty esters, respectively.

Fatty acids, fatty esters and fatty alcohols as well as the coproduct glycerol can be regarded as **basic oleochemicals** in analogy to basic petrochemicals. As we will see in this and the following chapters, these basic chemicals can be converted into numerous important derivatives. ◘ Figure 3.1 gives us an overview of the routes leading to the oleochemical basic products.

3.1.1 Fat Splitting

When one mole of triglyceride is split with three moles of water, three moles of fatty acids and one mole of glycerol are formed. Looking at the quantities, depending on the type of fatty acids, approx. 950 kg of fatty acids and 100 kg of glycerol are formed from one ton of fat. According to the equilibrium equation in ◘ Fig. 2.1, it is obvious that good space–time yields are obtained especially if

- water is in large surplus,
- one product is constantly removed from the equilibrium,
- the reaction rate is accelerated by the process conditions or by a catalyst.

There are several industrial processes for fat splitting that consider these three effects:

- The **Twitchell process** was developed as early as 1890: At ambient pressure, fats were heated in the presence of an aqueous sulfuric acid solution with the addition of organic sulfonic acids as catalysts. Mixing was carried out with superheated steam. However, this batch process, which was carried out in tanks coated with lead due to the sulfuric acid, has the major disadvantage of a very long reaction time of up to 24 h. Nevertheless, it is still occasionally carried out in small companies.
- The Twitchell process makes good use of the possibilities of influencing the equilibrium: