POSITION PAPER

Change in the Raw Materials Base

Produced and sponsored by a temporary work group consisting of:
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Gesellschaft für Chemische Technik und Biotechnologie e.V. (DECHEMA)
(Society for Chemical Engineering and Biotechnology)
Deutschen Wissenschaftlichen Gesellschaft für Erdöl, Erdgas und Kohle e.V. (DGMK)
(German Society for Petroleum and Coal Science and Technology)
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Gesellschaft
Deutscher Chemiker

DECHEMA

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Frankfurt, August 2010

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1. Summary

Driving innovation throughout various fields, the chemical industry is the basis of numerous value chains and exerts a strong influence in almost all areas of our economy. Thus, ensuring the supply of raw materials at reasonable prices represents one of the greatest challenges for the chemical industry in the 21st century. Due to ever increasing population growth and the demand for raw materials in emerging countries in Asia, there are shortages in the raw material supply. Even though this situation has relaxed somewhat during the creation of this position paper, in the long term one can expect that important raw materials will be more expensive and in shorter supply. Most of all, the chemical industry, which especially depends on the availability of organic and inorganic raw materials, must devise strategies for guaranteeing the raw material supply. According to the German Chemical Industry Association VCI, raw materials and energy represented 30% of the gross value for German chemical companies in 2007.

Living nature and the largest fraction of the value chain of the chemical industry are based on carbon compounds. Over the geological eras and via biomass as the intermediate, all fossil raw materials originating from atmospheric carbon dioxide have been generated from the sun’s energy and promoted by biocatalysis. Consequently, the chemical industry can only access three carbon sources:

- **Fossil raw materials such as coal, natural gas and petroleum;**

- **Biomass as a source for renewable raw materials;**

- **Carbon dioxide/carbonates.**

With petroleum-based raw materials as the backbone for many products in the chemical industry, it is likely that their supply will be depleted first; thus, alternative resources need to be developed. In order to ensure the supply of raw materials, broadening the base of raw materials is essential for guaranteeing the worldwide competitiveness of Germany in the field of chemistry. The following core scenario is expected for the change in the raw materials base:

- For the mid-term, petroleum will remain the leading carbon-containing raw material for the chemical industry; however, it will be gradually supplemented and replaced by other raw materials.

- Natural gas will play an increasing role in the production of short-chained olefins as important basic products via the intermediate of synthesis gas. Whereas the indirect synthesis via methanol has already reached technical maturity, numerous questions still need to be addressed regarding the selective olefin production from synthesis gas according to the Fischer-Tropsch method. This increasingly applies for the direct conversion of natural gas into aromatic compounds or functionalized products.

- Coal – because of its high reserves and availability in important industrial countries – could play a long-term, more significant role as raw material for the chemical industry. Nonetheless, a great amount of carbon dioxide results from the chemical exploitation of coal. One solution might be capturing carbon dioxide and storing it underground (CCS, Carbon Capture and Storage).

- Taking into account the further growing world population, the demand for raw materials for the chemical industry must not be reached at the expense of producing foodstuffs or feed. There are two time frames regarding renewable raw materials upon disregarding markets artificially created by subsidies: In the mid-term, one can expect a further development of cooperative production with the foodstuff and feed industries in which cost-effective side streams can be used for manufacturing chemical products. From a long-term perspective, the integrative processing of non-food biomass will predominately emerge in the union of energy, biogas, fuels and chemicals. Also feasible is the application of biogenic methane that can be exploited as a material similar to natural gas.

- Further in the future, renewable hydrogen produced from water without creating carbon dioxide will be significant as a raw material. Its possible basis will be electrolysis in connection with solar energy, photovoltaic, wind farms, electricity generated by nuclear power, high-temperature circuit processes as well as chemical or biological photocatalysis. Hydrogen produced by such means would be the key for the environmentally friendly conversion of coal, carbon dioxide and biomass into valuable products for the chemical industry.

Here, a bridge will span between fossil and renewable raw materials by linking them to the existing, highly efficient value chains. This will allow the usage of existing infrastructure with integrated resource-conserving production and energy systems and the chemical process know-how accumulated over many years. Thus, considered in parallel to an energy mix, the future supply of raw materials will be expectedly marked by diversification and a raw-material mix (biotechnological-petrochemical hybrid chemistry).

With all due considerations, it should not be forgotten that research still needs to be continued with regard to the fossil fuel exploration and production of petroleum, natural gas, oil sand and oil shale. For example, should success be attained in increasing the degree of deoiling (currently at 30-40%) of petroleum deposits, the oil reserves could be stretched by many years. Moreover, the reserves could be clearly augmented by new exploration and production (E&P) techniques.

Furthermore, one should recognize that the time scale for the material exploitation of fossil raw materials will be broadened through success in significantly reducing the competition in energy use. This can be realized, for example, by battery-operated automotive drives, energy-efficient construction of homes or energy-efficient process optimization. Regarding concepts for using carbon-containing wastes, the thermal use should be considered equal to the material recycling with the latter being primarily used where recycled materials are qualitatively just as valuable as ‘virgin’ material.

For metal or mineral raw materials, work should be devoted to improve the techniques for the production, increase in the recycling quota and substitution of dwindling raw materials with more available ones.

The active design of this change in raw materials, however, can only work by rapidly and drastically promoting research in the following areas:

- **Intensive fundamental research** in the field of material conversion for improving existing and creating new value chains, e.g. on the basis of synthesis gas, methane or lignocellulose;

- **Development of large-scale usable techniques** for producing hydrogen without formation carbon dioxide;

- **Priority-setting** with respect to catalysis, biocatalysis as well as reaction and process engineering with the aim for higher energy- and resource efficiency; and

- **Transfer of research results** to new economically and ecologically sustainable products and technologies as well as their increased pilot-scale testing.

This must be accompanied by the following activities:

- **Improving the availability of raw materials** by increasing the degree of exploitation reservoirs (further development of production techniques), decreasing the competing energy use as well as improving the recycling techniques for mineral raw materials; and

- **Creating public acceptance** through good quality and environmental compatibility of the new products and technologies.

The objective of this paper is to highlight the necessity and urgency of these research activities and to sensitize political actors to create reliable framework conditions necessary for this change in raw materials. As an industrial country deficient in raw materials, Germany, in particular, depends on actively exploiting the opportunities linked with this change in the raw materials base in order to maintain and strengthen its competitiveness.

2. Introduction

2.1 MOTIVATION

For an industrial country such as the Federal Republic of Germany, the supply with raw materials at economically reasonable prices is essential and secures the competitiveness of its industries. Consequently, strategies for securing the availability of raw materials and, hence, also to guarantee and develop the foundations of life and standard of living constitute the greatest economic and technical-scientific challenges. Whereas alternative raw materials already carry a high priority in the public perception as well as in research politics with respect to the topic of our future energy supply, up to now a comprehensive consideration is missing regarding the future raw material supply of the chemical industry. There are, however, the products of this industry that create the foundations for competitiveness and innovative potential of the processing industry, and thus create the core areas of our economy. Just consider the development of plastics from basic applications to highly valuable products.

The chemical industry utilizes carbon-containing and mineral raw materials, whereby the carbon-containing ones are economically far more significant. These raw materials represent the backbone of the chemical industry. Another difference is that the fossil – carbon-containing – raw materials petroleum, natural gas and coal meet each other in the carbon sink CO_2 and thus, are finite, at least from today's point of view. By contrast, the mineral raw materials are subjected to a different degree of distribution; thus, recycling is principally feasible and is already being performed. Yet due to the constantly growing degree of distribution, the mineral raw materials, too, are ultimately finite.

With regard to mineral raw materials, selected materials are presented in this paper to illustrate their future availability and security of supply.

The supply with carbon-containing raw materials for material use is tightly linked to the availability of energy resources. Because of their dwindling supplies change in the raw materials base distinctively shows on the horizon. Besides the availability and the price of raw materials, possible supply difficulties have to be taken into account that may result from a monopoly of single suppliers or from the reserves existing in regions of global tensions.

This situation cannot be comprehensively described within the scope of this position paper. Instead, this paper will illustrate – based upon selected characteristic examples – the raw material availability, the change in raw materials and research needed for effectively developing and using raw materials for the chemical industry.

The following raw materials will be analyzed:

- **Fossil raw materials** (Chapter 3)
  Petroleum, natural gas, coal

- **Renewable resources** (Chapter 4)
  Oils and fats, sugar and starch, 'non-food' biomass, carbon dioxide

- **Inorganic raw materials** (Chapter 5)
  Noble metals, indium, lithium, fertilizers

- **Hydrogen from** CO_2**-free production** (Chapter 6).

It is an objective of the chemical expert societies and of the chemical industry to highlight the challenges of this change of the raw materials base and to describe the need for action by industry, politics as well as science and research. This current position paper thus follows the example of the position paper from 2007 entitled "Future Energy Supply – the Contribution of Chemistry" of the coordinating group Chemical Energy Research comprising the chemical organizations involved in this present paper as well as the "Deutsche Bunsen-Gesellschaft für Physikalische Chemie" (DBG) (German Bunsen Society for Physical Chemistry) and the "Gesellschaft Verfahrenstechnik und Chemieingenieurwesen" (VDI-GVC) (Society for Chemical and Process Engineering).

2.2 IMPORTANCE OF CHEMISTRY

Because of their multidisciplinary nature, chemical products penetrate almost all sectors of industry. Thus, the chemical industry holds a key position and pacesetter role. Chemical innovations will also mark the future; in particular, chemistry will essentially contribute towards satisfying the basic needs of people, e.g. for nutrition, health, clothing, habitation, energy, communication and the environment. In order to improve the quality of life, chemistry is researching and developing resource-conserving and energy-saving technologies for household, industry and mobility. Without chemistry, there are no novel working materials; without chemistry, it will be impossible to feed the constantly growing world population. By improving its technologies and products, chemistry has already contributed significantly towards reducing CO_2-emissions.

With around 442,000 employees and a turnover of over 175 billion Euro in 2008, the chemical industry belongs to the largest industrial sectors in Germany. Having chemistry exports of almost 140 billion Euro in 2008, Germany is the world's leading chemicals exporter. In 2008, the German chemical industry generated an export surplus of around 43 billion Euro. In order to maintain its international competitiveness, the German chemical industry is extensively investing in introducing new products and processes. In 2008, the chemical industry spent a total of 9.1 billion Euro for Research & Development (R&D). Thus, it belongs to the most research-intensive industrial sectors in Germany. Upon international comparison, the research of the German chemical industry ranks in a top position. One-tenth of the R&D expenditures for chemistry in the OECD and every fifth chemistry patent originate from Germany.

Around 20% of all industrial product innovations are only made possible by R&D investments of the chemical industry.

In order to further ensure the development of the chemical industry in Germany, the chemical industry must diversify and effectively improve the possibilities of raw material usage also by continuously promoting R&D for securing the raw materials base.

2.3 SITUATION IN GERMANY

Since in Germany no notable natural resources are available for the national chemical industry, almost all raw materials have to be imported. This high dependency on imports makes the chemical industry vulnerable. Hence, strategies and efficient technologies for ensuring the raw material supply with carbon-containing and mineral raw materials and their processing represents a particularly important challenge for the German chemical industry.

During the formation of the chemical industry in the 19th century, coal played an essential role as a raw material. In the mid-20th century, petroleum and natural gas replaced coal that, today, is no longer significant as a chemistry raw material. The future will show whether coal experiences a possible renaissance in Germany and Europe in light of oil and gas shortages that do not affect coal to the same extent. In countries such as China and South Africa, coal is already being increasingly used as a raw material in chemistry.

The current chemical industry applies cost-effective materials streams from the petroleum-processing industry so as to produce basic chemicals. Whereas naphtha (light naphtha gasoline) predominates in Germany and Europe, ethane and propane rather serve as raw material in other parts of the world. Here, it is notable that in Germany, around 15% of the mineral oil and worldwide, only 10% of the total consumed petroleum is used by the chemical industry, whereby the prices are extensively determined by use for energy.

Natural gas contributes at present 8% to the raw materials of the chemical industry. Even though natural gas is considered as an alternative, raw materials basis because of its reserves and resources, there are currently no economically viable technologies to produce ethylene, propylene, C4-olefins, benzene and xylenes, which altogether make up 90% of basic chemicals, from methane – the main component of natural gas (the so-called 'methane challenge').

In Germany, the costs for carbon-containing raw materials and energy expenses in 2006 amounted to almost 30% of the gross value of the chemical industry, whereby depending on the respectively considered value chain, there is a varying influence of raw material costs. In particular, this fraction is clearly higher in the production of basic chemicals and polymers. Here, regions with petroleum reserves clearly enjoy cost advantages and, hence, a competitive edge. On the contrary, downstream of the value chain such as plant pesticides or pharmaceuticals, the fraction of raw material costs is clearly lesser.

The third pillar of the raw material supply for chemistry in Germany consists of renewable resources holding a market share of about 10%. Numerous, renewable resources are used, whereby fats, oils, starch, sugar and cellulose play the largest role in terms of quantity.

In Germany, various possibilities for mitigating CO_2-emissions are being discussed in order to protect the climate and natural resources. Hopes are resting on biomass that is neither used as animal feed, nor foodstuffs nor for producing food. One option is combining the energy and material utilisation of biomass in biorefineries that produce the basic chemicals for the chemical industry and, simultaneously, can make available energy carriers according to principles long established in petroleum refining. Exemplified by lignocellulose (such as wood, straw), Chapter 4.3 illustrates how material and energy use can be linked.

This is also handled by the "Status Report on Possible Potentials of Biorefineries for Research and Supply of Raw Materials for the Chemical Industry" (Position Paper of VCI and DIB, November 2009).

A change in the raw materials base towards renewable resources offers chances to increasingly use indigenous plants and, thus, to contribute towards securing our raw material supply. However, the limited availability of areas of arable land – yielding excess biomass not used for food – restricts these possibilities. Moreover, a change from oil and gas to biomass requires new and efficient technologies. There is a fundamental need for research here.

Naturally, the exploitation of biomass for chemicals production needs to orient itself towards sustainability criteria including ecological, economic and social aspects. Technical feasibility and cost-effectiveness remain the prerequisites for the successful use of renewable raw materials. The general worldwide availability of renewable raw materials at competitive prices must be ensured. This has already been pointed out in the position paper "Application of Renewable Raw Materials in the Chemical Industry" (DECHEMA, GDCh, VCI, DGMK, Frankfurt 2008).

Metallic and mineral raw materials are less in the focus of public perception. Regarding metallic raw materials, the whole demand in Germany has to be covered by imports. Analogous to fossil raw materials, guaranteeing the raw material supply depends on numerous parameters such as geological availability, political stability or the monopoly position of the producing countries.

The example of noble metals which can last from 150 to 200 years, shows that supply shortfalls occur for political or socioeconomic reasons. Thus, a high recycling quota can contribute considerably to long-term availability.

Lithium is also handled in this position paper, because it has currently assumed great importance mainly for producing lithium batteries. Such batteries seem to be the best candidates for converting conventional automotive drives to electric-powered drives. In other sectors, they can also contribute importantly towards energy storage.

Because the targeted use of fertilizers is indispensable – essentially increasing the yield and quality of agricultural products – phosphates and potassium salts (phosphorus, potassium and nitrogen are the main plant nutrients) were selected for this position paper, in order to point out their long-term availability.

In this position paper, hydrogen and carbon dioxide are also considered as potential raw materials for chemistry. Carbon dioxide represents an almost unlimited source of carbon. However, since it is a very stable compound, considerable amounts of energy have to be expended for using it as a raw material. This only makes sense when this energy stems from regenerative sources, from solar or nuclear energy. Up to now, the material use of carbon dioxide is limited to only a few chemicals such as urea, methanol or carbonates. If inexpensive hydrogen were available, the hydrogenation to methanol could be economically viable, and methanol, as feedstock, could be used for numerous subsequent products. This would span a bridge to today's petroleum-based chemistry. Nevertheless, even for large-scale applications, the quantitative potential of this regenerative source would amount to only a few percent of the anthropogenic CO_2-emissions, so that the CO_2-problem (climate change) could not be resolved in this way. The possibilities to use CO_2 by the chemical industry are presented in the papers "Utilization and Storage of CO_2" by DECHEMA and VCI as well as in the "Discussion Paper on Utilization and Storage of CO_2" by DECHEMA (www.dechema.de/ studien).

Hydrogen is also used in multiple chemical processes, for example, in the numerous hydrogenations conducted industrially. How cost-effectively hydrogen might be generated in the future is treated in Chapter 6.

Against the backdrop of competition between material and energy use of fossil raw materials (natural gas, petroleum and coal) and with renewable raw materials raw material diversification is also expected in chemistry. Such a "feedstock mix" is exemplified in Fig. 1. Synthesis gas (mixture of CO and H_2) as well as methanol would be examples for universal building blocks from which all carbon-containing compounds may be produced.

The necessary technologies to exploit alternative side streams on an industrial scale principally exist. However, the scientific and technological basis has to be further developed which should be reflected in a correspondingly designed funding of research.

This position paper aims to sensitize decision makers in politics and industry as well as public experts for the change in the raw materials base in the chemical industry as well as to point out research fields as well as the need for further research and development for effectively utilizing these resources. In particular to promote long-term developments, scientists at universities and non-academic research institutes should be addressed, for they are challenged to devise the foundations for future developments. Last but not least, concepts in teaching should be re-examined and accordingly changed to meet this challenge.

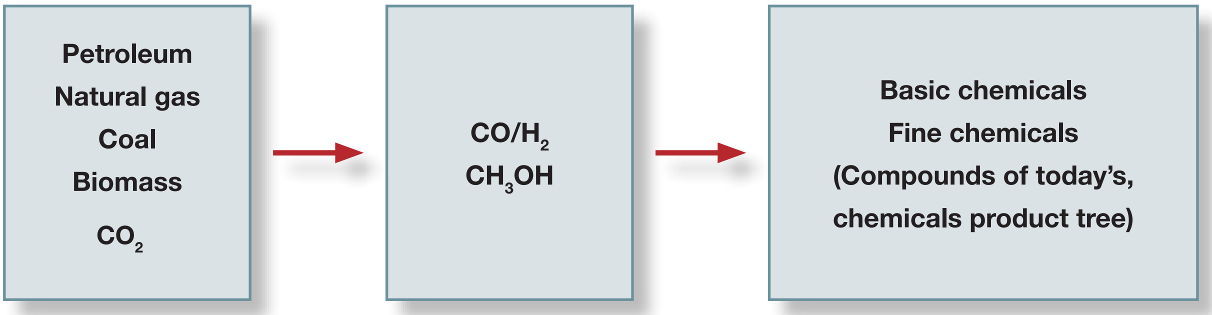

Fig. 1. One option for the 'raw material mix' in the chemical industry

3. Fossil Raw Materials

The second half of the 19th century was considered to be the cradle of the chemical industry, because the chemists learned to exploit the raw material coal. At first it was coal tar that allowed numerous new dyes as well as dyes known from nature to be produced. The pronounced alliance of science and industry in Germany allowed coal chemistry a fast breakthrough. Supposedly in 1800, when it was not yet understood how to exploit coal for chemical purposes, about 500 organic substances were known. When the first edition of Beilstein's Handbook of Organic Chemistry appeared in 1882, already 20,000 organic compounds were cited in the first compilation; this, of course, was also attributed to the isolation of natural substances from plant and animal organisms. Thirty years later, 150,000 organic compounds were known. Today, over 50 million chemical compounds have been registered.

Whereas the enormous potential of petroleum for chemistry was first recognized starting from the USA, in Germany autarky efforts led to a sophisticated chemistry of coal. Following the destruction and dismantling of processing plants with and after World War II, a new beginning took place in Germany with the feedstock petroleum. The C2- to C4-olefins gained from petroleum and natural gas as well as the aromatics benzene and xylene formed the basis for mass products such as polyethylene, polypropylene or polystyrene.

3.1 LONG-CHAIN HYDROCARBONS: PETROLEUM

Present Situation and State-of-the-Art

In this study, higher hydrocarbons comprise conventional petroleum and the unconventional fossil raw materials heavy oil, oil sand and oil shale. Nowadays, petroleum is by far the most important raw material for producing chemical products. At the same time, it is also the raw material for manufacturing gasoline, diesel fuel and jet fuel as well as heating oils for heating buildings and fueling power plants. An estimated 10% of the worldwide supply of petroleum is applied as a raw material for chemicals in the chemical industry, while 50% is used as raw material for fuels, 20% is used for heating oils and 20% for various other purposes. Heavy oils, oil sands and oil shale are currently being used only to a small extent (mainly Canadian oil sands). However, they are considered to be substitute raw materials for petroleum if petroleum shortfalls occur in the coming decades.

Today, the global consumption of petroleum amounts to 3.95 gigatonnes annually which corresponds to a calorific value of 165 exajoules/year or 36% of the primary energy consumption on Earth. Germany consumes 2.6% thereof and needs to import about 97% of its demand because of its lack of domestic oil reserves. The worldwide reserves – surely proven reserves and deposits of conventional petroleum that are economically exploitable with today's available production technologies – are currently figured to be 164 gigatonnes (corresponding to 6,850 exajoules). By dividing the reserves by the global consumption, one can calculate a depletion point of petroleum lasting 41.5 years. By also considering the reserves of unconventional raw materials heavy oils, oil sands and oil shale amounting to a total of 66 gigatonnes (corresponding to 2,760 exajoules; source "Reserves, Resources and Availability of Energy Raw Materials in 2007, State: Dec. 31, 2007", German Federal Agency for Geosciences and Raw Materials (Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, 2008), these reserves increase to 230 gigatonnes (corresponding to 9,610 exajoules). Furthermore, by assuming a constant consumption of long-chain hydrocarbons of 3.95 gigatonnes per year, for the near future the depletion point of these reserves is figured at about 60 years.

Obviously, such lifespan calculations for the raw material petroleum, based on very simplified assumptions, are linked to considerable uncertainties. Pessimistic scenarios predict the oil production to peak in the 2020s - thus linked to resulting supply shortfalls and skyrocketing prices of this raw material. Since the majority of the most important petroleum producing countries is located in politically unstable regions in the world, the production and distribution policies of such countries are uncertain. On the other hand, the discovery of new large petroleum reserves, e.g. at great depths of the oceans or in the Arctic might lead to a longer availability of the raw material petroleum for the chemical industry. From today's point of view, however, one notable limitation here is the fact that petroleum production in such areas is technically extremely difficult. Another development which might contribute to stretching petroleum as a raw material for chemical products is the introduction of gasoline- and diesel-saving automotive drives or of construction measures that save heating oil.

From a chemical perspective, petroleum is a highly complex mixture of hydrocarbons and other organic compounds containing heteroatoms such as mainly sulfur, oxygen, nitrogen as well as the metals vanadium and nickel. The boiling range of petroleum extends from ambient temperature to far over 500 °C. In refineries, petroleum is first rectified to yield various fractions having different boiling temperatures. These individual fractions are subsequently upgraded to fuels and heating oils that meet the specifications, mostly by applying catalytic processes. The most important interfaces to chemistry, in which petroleum fractions are converted to basic products of organic chemistry, are the steam cracking of light gasoline (C5- and C6-hydrocarbons, boiling range of ca. 30-80 °C) and the reforming of heavy gasoline (C7- up to ca. C9-hydrocarbons, boiling range of ca. 80-180 °C). With respect to the former petrochemical technique, the hydrocarbons are cracked in the presence of steam at high temperature (ca. 850 °C) without a catalyst. Target products are the light olefins ethylene and propylene. The resulting by-products are hydrogen, methane, a mixture of C4-hydrocarbons and the so-called 'pyrolysis gasoline' which is rich in aromatic hydrocarbons such as benzene, toluene and xylenes ("BTX-aromatics"), which can be produced in pure form from pyrolysis gasoline. Reforming of heavy gasoline represents the second source of aromatic hydrocarbons. Here, BTX-aromatics are produced on platinum-containing catalysts and hydrogen in considerable amounts is formed as a very desirable by-product without the concomitant production of carbon dioxide. This hydrogen is needed in the refineries for removing the heteroatoms sulfur, nitrogen and oxygen by using the catalytic hydrotreating technique. The olefins and aromatics produced during steam cracking and reforming represent the basic chemicals, originating from petroleum, of the value chains that yield a broad variety of organic chemistry products.

Needs and Opportunities

A relatively small fraction of the globally produced petroleum is used as a raw material for producing petrochemicals for the chemical industry. Even so, petroleum is by far the dominant raw material for manufacturing organic chemical products besides regenerative resources, natural gas and coal. The aforementioned value chains are thus vulnerable when there is a prolonged shortage in petroleum as raw material and/or significant increases in cost.

Consequently, the development target is to produce the basic compounds of today's value chains, i.e. low molecular-weight olefins and aromatic hydrocarbons, from other fossil fuels that have a longer projected lifespan. Obvious options are methane from natural gases, ethane, propane and butane from wet natural gases, coal and heavy oils and crude oils from oil sands and oil shales. Another possibility is to directly manufacture organic chemical products from the relatively non-reactive light alkanes methane up to butane. Finally, a long-term development target is to generate hydrogen without forming CO_2 by means of photocatalytic cleavage of water by harnessing sunlight. A new industrial organic chemistry would evolve from the hydrogen generated in this way together with suitable carbon sources.

Scientific and Technological Challenges

Heavy oils and oil sands have a composition similar to that of conventional petroleum. However, they contain clearly smaller low-boiling fractions and greater fractions of the heteroatoms sulfur, oxygen, nitrogen, vanadium and nickel. Thus, an increased exploitation of such heavy oils to produce chemistry raw materials requires intensifying the implementation of cracking techniques and so-called 'hydrotreating' methods that use hydrogenation to remove sulfur, oxygen, nitrogen and metals. On the one hand, these techniques need large amounts of hydrogen, which needs to be generated cost-effectively without simultaneously producing corresponding amounts of the greenhouse gas carbon dioxide. On the other hand, the currently available catalysts used for the hydrotreating of heavy oils are unsatisfactory: their activity (reducing the reactor volumes), their stability (decreasing the high operation pressures) and their capacity for the uptake of metals (increasing the running time) have to be clearly bolstered and their production costs have to be decreased. Low molecular-weight alkanes of natural gas can be converted by steam reforming or by partial oxidation into synthesis gas ($CO + H_2$), which can serve as raw material for certain chemical products. The conversion of synthesis gas to olefins and aromatic hydrocarbons, the fundamental compounds of today's value chains, is not yet working satisfactorily. The direct conversion of low molecular-weight alkanes to organic chemical products is especially challenging and, up to now has succeeded only in a few special cases. This difficulty is attributed to the thermodynamic stability of low molecular-weight alkanes, especially methane, and to their low reactivity.

Solution Approaches

Catalysis is a key technology for solving the problems connected with the change of the raw materials base. Improved catalysts are necessary for exploiting heavy oils as raw materials to produce organic chemicals and facilitating the removal of the heteroatoms sulfur, oxygen, nitrogen, vanadium and nickel as well as for cracking techniques to convert heavy oils into lighter hydrocarbons. A completely different approach, which is especially significant in the exploitation of heavy oil reservoirs, is increasing the degree of their de-oiling by using chemicals during oil recovery. The further development of these so-called tertiary petroleum production techniques can contribute significantly to stretching the petroleum supplies. From the known petroleum deposits that are typically exploited to only 30-40%, attempts are generally being made to recover a higher share by implementing new technologies.

Also denoted as 'enhanced oil recovery', this tertiary petroleum production consists principally of three methods that will help to improve the exploitation of petroleum reserves. By means of special production methods, i.e. the injection of gas (e.g. CO_2) or of chemicals, the pressure in the oil reservoir is increased, thereby improving the flow properties of the oil and thus enhancing the recovery rate. Concerning the injected chemicals, on the one hand surfactants are used to reduce the surface tension, thereby improving the mobility of the oil drops. On the other hand, water-soluble polymers are used to facilitate the pressing of the oil out of the pores in the rock formations by increasing the viscosity of the flooding water.

For the improved exploitation of oil sands, fundamental investigations are necessary regarding the agglomeration and segregation behavior of particles in organic, highly viscous surroundings. Moreover, methods have to be developed to separate the oil from the sand in an energy-efficient and environmentally friendly way. To better utilize oil shales, the approach is to selectively grind them so that they can be processed to fuels. In general, economical upgrading processes have to be found.

Various approaches are elucidated in Section 3.2 concerning utilization of low molecular-weight alkanes from natural gas.

Need for Further Research

Ensuring the raw materials base for the production of organic chemical products is decisively linked to discovering and developing improved catalysts. Examples for developments that require much more research have been cited. Moreover, further research should be conducted in the necessary improvement of the yields of current petroleum deposits, increasing the degree of de-oiling of heavy oil reserves and the necessary exploitation of oil sands and oil shale (see Solution Approaches).

As a whole, international efforts will ultimately boost progress in the area of the production of raw materials for industrial organic chemistry. Germany can assume a leading role here because of its high status in catalysis research. Prerequisites for this are the further intensification of research efforts, the bundling of existing know-how and a close collaboration of research institutes and the chemical industry. An important objective remains the increase of efficiency in the processing of petroleum, namely in refineries, e.g., by improving heat integration.

3.2 NATURAL GAS AND NATURAL GAS CONDENSATES

Present Situation and State-of-the-Art

Natural gases mainly contain the hydrocarbon methane. These natural gases occur as pure gas deposits or together with petroleum. In the latter case, besides methane, the recovered natural gas consists of other hydrocarbons, i.e. mainly ethane, propane and butane. These compounds in low concentration can remain in the natural gas, thus raising its heat value; otherwise, they can be separated from them, whereby they are called ‘natural gas condensates’.

Currently, Germany ranks fifth among the countries with the highest natural gas consumption; in 2007, this amounted to 96 • 109 m^3 annually (based on a temperature of 0 °C and 1.013 bar) which corresponds to about 3.2% of the worldwide consumption. Unlike for petroleum, Germany has significant indigenous supplies of natural gas available. About 19% of the natural gas consumption is currently met by national production; the remaining ca. 80 % has to be imported – the largest share originates from Russia and Norway. Additional supplies of natural gas could possibly come from North African Mediterranean areas or perhaps from natural gas-rich areas in the Middle East. In Germany, natural gas is used mainly for heating buildings and for combustion in power plants, whereas a smaller fraction is used as motor vehicle fuel as well as raw material in chemistry. The chemical industry consumes roughly 11% of the natural gas supply in Germany (8% and 3% thereof for energy and material utilization, respectively). The ethane extracted from natural gas can be used as a raw material for generating ethylene by steam cracking (see Section 3.1); this use, however, plays only a subordinate role due to the lack of ethane-rich natural gases in Europe. Propane and butane are the components of liquid gas (LPG), principally used for heating purposes at remote sites. Moreover, these compounds are used as raw material for producing olefins in steam cracking or for generating synthesis gas or hydrogen by steam reforming (see below).

Natural gas is considered to be an environmentally friendly fuel, because it is rich in hydrogen (pure methane shows an atomic ratio of $n_H/n_C = 4$ as opposed to that of $n_H/n_C \approx 2$ for petroleum and that of $n_H/n_C \leq 1$ for coal). Thus, when natural gas is combusted, lower amounts of CO_2 are emitted with respect to the amount of heat generated. Natural gas can be transported safely and cost-effectively through pipelines over land as well over moderate distances over water bodies. However, for its intercontinental transport over oceans, natural gas has to be first liquefied (liquefied natural gas (LNG)), then transported by ships in special tanks and once the ships dock, be again evaporated. Altogether, this type of transport consumes a considerable fraction of the energy contained in the natural gas and it requires sophisticated safety measures.

The current (state: 2007) worldwide consumption of natural gas is 3 • 1012 m^3 annually which corresponds to a heating value of 115 exajoule per year or 26% of the primary energy consumption on Earth. The proven natural gas reserves, that can be economically exploited with currently available technologies, amount to 183 • 1012 m^3 (corresponding to 6,954 exajoule) and thus slightly exceed that for conventional petroleum (see Chapter 3.1). Since the natural gas consumption is about 30 % below that for petroleum, a correspondingly higher depletion point of 60.5 years can be calculated for natural gas. Hence, even if the demand for natural gas moderately increases, the proven natural gas reserves can meet needs extending into the second half of this century.

Upon discussing the lifespan of natural gas, one also has to consider the resources. In contrast to the reserves, these resources deal with – from today's perspective – uncertain, probable or supposed supplies that have not yet been technologically and/or cost-effectively exploited. Nonetheless, great hopes are being placed in unconventional resources of natural gas: i.e., natural gas in dense reservoirs, coal seams, natural gas in porous, brine-containing rock formations (aquifers) as well as methane hydrates in the oceans. The German Federal Agency for Geosciences and Raw Materials in Hannover estimates these resources to total 1,533 • 1012 m^3 (corresponding to 58,250 exajoule); however, some literature sources cite speculations that the reserves of gas hydrates alone could be much higher.

For utilization as a chemical feedstock, in general natural gas today is converted at first to synthesis gas, a mixture of carbon monoxide and hydrogen. This takes place either by steam reforming with water vapor at 850 to 900°C on nickel catalysts or by partial oxidation with oxygen at temperatures of up to approx. 1,200 °C. The generated synthesis gas is then cooled down and further processed to the desired product. Examples of established processes of this kind are the methanol synthesis, the Fischer-Tropsch synthesis resulting in a mixture of n-alkanes of higher molecular weight, as well as the hydroformylation (oxo synthesis) in which the synthesis gas is reacted with an olefin such as propylene to produce aldehydes and alcohols of higher molecular weight. Furthermore, synthesis gas is an important source for hydrogen that, for example, is needed for ammonia synthesis and many other kinds of hydrogenations. In order to produce hydrogen, synthesis gas is catalytically reacted with steam in the so-called 'CO-conversion', whereby CO_2 and H_2 are yielded and the carbon dioxide is then separated.

In a few large-scale units e.g. in South Africa, Malaysia and Qatar, high-quality diesel and aviation fuels (so-called Gas-to-Liquids, GTL) are produced from natural gas as raw material. First, synthesis gas is produced from the natural gas. By using the Fischer-Tropsch synthesis, this is further processed to long-chained waxy n-alkanes from which the liquid fuels are yielded by mild hydrocracking. Alternatively, olefins of low molecular weight – constituting a basic chemical – can be produced from natural gas (or coal) likewise in three processing steps. Again, the first step involves the production of synthesis gas that is then converted to methanol in the second step. In the third step, the resulting methanol is converted to propylene according to a new technique using the zeolite catalyst H-ZSM-5 (the so-called Methanol-to-Propylene process, MTP). Alternatively, by using the zeolite catalyst H-SAPO-34, methanol can be converted to a mixture of ethylene and propylene (Methanol-to-Olefins, MTO). Through direct conversion of methane, the chemical industry produces acetylene according to an autothermal method as well as hydrocyanic acid by ammonoxidation and chloromethane via chlorination.

Needs and Opportunities

Compared to petroleum, natural gas plays a subordinate role as a raw material for the chemical industry; e.g. in Germany, approx. 8% of the organic chemical products is produced from natural gas. In perspective, natural gas might become more significant as a petroleum substitute should petroleum shortages clearly arise in the coming decades. Besides its comparatively long lifespan and secure availability, another advantage of natural gas as a chemical raw material is its high hydrogen content. A large disadvantage of natural gas is that its main component methane, up to now, can only be converted to a small range of chemical products by means of efficient techniques – essentially this represents hydrogen and the subsequent products of synthesis gas. In particular, for both large groups of the basic chemicals of organic chemistry, i.e. olefins and aromatics, there are currently no single step techniques available that based on methane. The development of such new methods is an especially worthwhile aim of modern chemistry, catalysis and processing engineering.

Likewise attractive is the development of new techniques for directly converting ethane, propane and butane from natural gas condensates to valuable chemical products, without needing to chemically detour via the pathway of olefins.

A considerable deficit that hampers the reliable planning of the future raw material situation is the large uncertainty regarding the resources and the exploitability of unconventional sources of natural gas. This mainly applies to gas hydrates – no other fossil raw material shows such a wide span of estimated values for the recources. Furthermore, still no convincing technologies exist as yet for the exploitation of the gas hydrates and the transport of the natural gas yielded from them to consumer countries. A reliable survey of the supplies of natural gas in the form of gas hydrates and other unconventional resources as well as the development of economical and environmentally sustainable methods for producing natural gas from such sources represent long-term aims of high priority.

Scientific and Technological Challenges

The increased utilization of natural gas as a chemical feedstock represents one of the largest challenges for modern chemistry, catalysis and process engineering. From a current perspective, three essential development lines have to be differentiated:

1. New or improved routes via synthesis gas: the generation of synthesis gas from natural gas by steam reforming and partial oxidation has proven itself in numerous units worldwide. The procedures, however, are energy-intensive and expensive because of the high reaction temperatures. The cost effectiveness might be clearly improved by reducing the costs of synthesis gas through further process engineering optimizations and/or scale enlargements. The process routes from the raw material natural gas to basic chemicals are still too long (olefins via MTP or MTO in three process steps); thus, they are either costly or do not yet exist, e.g. for aromatics. There is a great demand for new methods that would decrease the number of process steps. One example would be a modified Fischer-Tropsch synthesis by which synthesis gas can be converted to olefins and/or aromatics in one process step.

2. Direct conversion of methane to industrial chemicals: thermodynamically, methane is unusually stable and kinetically inert. Consequently, its direct reaction to basic compounds of the organic-chemical value chains, by avoidance of the step of synthesis gas, represents a particular challenge. Target products of such reactions would be, e.g., olefins, aromatics or methanol.

3. Direct reaction of ethane, propane or butane to industrial chemicals: the direct conversion of the hydrocarbons occurring in the natural gas condensates to yield valuable products of organic chemistry, by avoiding detours via olefins or synthesis gas, has succeeded only in a fewl cases as yet, e.g. in the oxidation of n-butane to maleic acid anhydride. New routes of synthesis through direct conversion of alkanes of low molecular weight could contribute towards substantially increasing the efficiency in the utilization of natural gas condensates as raw material.

Solution Approaches

Catalysis plays a key role in solving these illustrated problems. Already known catalysts for the described conversions of the hydrocarbons, found in the natural gases, to valuable substances have to be further developed, and totally new catalyst formulations have to be tested in reactions of natural gas components.

Initial approaches for catalysts by which the Fischer-Tropsch synthesis can be directed, under suitable reaction conditions, towards unsaturated hydrocarbons, are already cited in the scientific literature. The yields of olefins of lower molecular weight or of aromatics must still be increased.

Reactions for the direct conversion of methane or also ethane, propane and butane can be divided in two categories, namely oxidations, preferably with the inexpensive oxidative agents air or oxygen, as well as dehydrogenations. Examples are the direct oxidation of methane with air to methanol on, e.g. iron molybdate catalysts or the direct aromatization of methane to benzene that runs on molybdenum-containing H-ZSM-5-zeolites. The oxidation reactions are exothermic and are not limited by the position of equilibrium. What is problematic and reduces the yield here is the excessive tendency of the target product, e.g. methanol, to undergo undesired consecutive oxidation reactions to create the worthless products carbon monoxide and carbon dioxide (‘total oxidation’). For this, fundamentally improved catalysts are needed, in which the target products, after being formed, can be immediately released from the catalyst surface before total oxidation can set in. The dehydrogenation reactions involve quite different problems: these reactions are endothermic, and the position of equilibrium mostly limits the attainable yields. Here, increasing the reaction temperature is favorable regarding the equilibrium position — a measure that nevertheless can only be applied when no unwanted side reactions take place at such high temperatures. If this is the case, one opts for favorably shifting the of equilibrium by process engineering measures. In the chosen example of the aromatization of methane to benzene, a membrane reactor, through whose wall hydrogen could be selectively withdrawn from the reaction mixture, could be used in order to shift equilibrium towards the desired product.

Need for Further Research

The barriers hindering an increased use of natural gas as a raw material for the chemical industry can be overcome by significantly advancing catalysis. Efforts should be directed towards improving the already known catalysts as well as formulating novel ones. Examples for reactions that are especially attractive in the context of a stronger material use of natural gas have been cited in this chapter. Equally, it has been exemplified for the conversions of natural gas components via dehydrogenation, that a considerable increased value can be reached for the future usage of this raw material through close linkage of the relevant research in catalysis with research in process engineering regarding new reactor concepts.

3.3 COAL: PROCESSING TECHNIQUES AND SUBSEQUENT PRODUCTS

From the beginning of the chemical industry until the mid-20th century, coal was the principal raw material that was rapidly replaced by less expensive materials starting from petroleum. From a worldwide perspective, coal is still an important raw material for the chemical industry. Many compounds, in particular, multinuclear aromatic compounds, are practically completely produced from coal tar. In contrast to its rather insignificant supplies of petroleum and natural gas, Germany has substantial deposits of hard coal and lignite that are currently being used for energy (generating electricity) as well as for producing iron and steel. The mining of hard coal in Germany today depends on subsidies. By contrast, lignite mining is internationally competitive. By taking into account the shrinking petroleum deposits, coal is a main focus of attention as a raw material besides natural gas and biomass. The carbon content of coal amounts to about 65% for lignite and can exceed 90% for hard coal. Complementarily, the hydrogen content decreases from around 5% to 2%. The remainder consists of heteroatoms and mineral components. If it is used as a fundamental raw material, coal need significant amounts of energy to fuel the required conversion processes and yields considerable amounts of CO_2. Thus, the art of process engineering is to reduce both the amounts of needed energy and CO_2-emissions as well as to attain high degrees of effectiveness so as to be able to best exploit the content of carbon as raw material from coal.

As shown in Fig. 2, there are essentially three primary techniques for producing fuels and chemicals from coal: hydrogenation, gasification and pyrolysis (degasification):

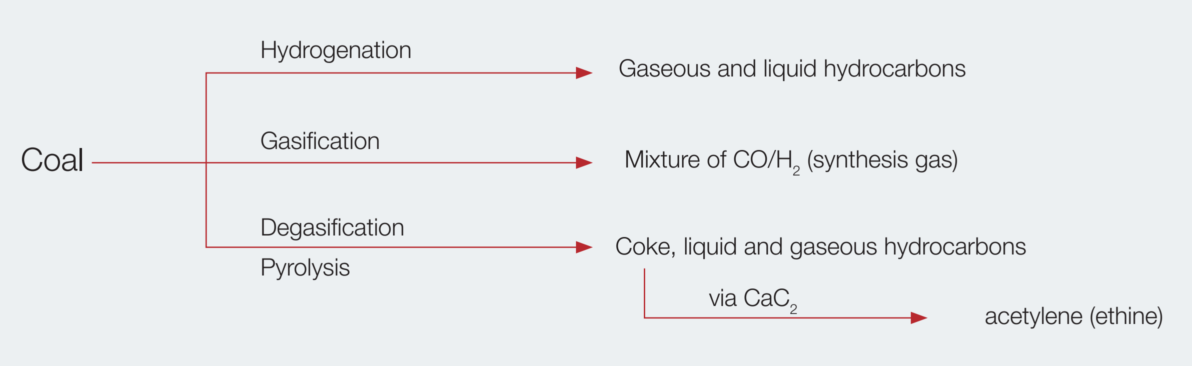

Fig. 2: Primary techniques for producing fuels and chemicals from coal

In addition, there are secondary processes for generating products from coal tar. To select suitable primary processing techniques, knowledge of the origin of the coal, its moisture, its content of mineral substances (ash content) and undesired heteroatoms (eg. S, Cl) is of importance.

The products (gas, tar, coal oil) from the primary coal refinement, with the exception of coke, have to be processed for further usage in secondary processes to yield the desired basic chemical substances.

Following tar and dust separation, the gas resulting from pyrolysis or gasification is a mixture of C1- to C4-hydrocarbons, CO, CO_2, H_2O, H_2 and impurities such as H_2S, NH_3 or halogens. For utilization as a raw material for chemical syntheses, the gas first has to be carefully cleaned and converted to a purely CO/H_2-containing gas in the desired ratio. Known syntheses are the Fischer-Tropsch synthesis to produce fuels, paraffine and lubricating oils; the methanol synthesis which leads to numerous base materials used in chemistry; the oxo synthesis for producing alcohols, aldehydes and organic acids as well as the ammonia synthesis. The syntheses are also denoted as indirect coal liquefaction processes. The reactor design and the selection of suitable catalysts hereby dictate the quality and quantity of the desired products, for which considerable know-how is required.

In principle, all basic organic chemicals can be produced from coal, whereby economical and ecological issues have to be clarified.

3.3.1 Coal Gasification and Downstream Chemistry

Present Situation and State-of-the-Art

Synthesis gas mixtures of hydrogen and carbon monoxide are required as energy sources and feedstocks in industrial processes, coal-based fuel production and electricity generation. The production of synthesis gas via coal gasification is a proven technology. In 2007, 45 coal-based gasification plants with over 200 gasification units and a synthesis gas capacity of more than 30 gigawatt (thermal) were operated worldwide. By the end of 2010, the capacity is expected to have increased by 5 gigawatt due to the start-up of new gasification plants.

Around half the world's coal gasification capacity is employed in the generation of feedstock for fuel plants (in South Africa), while about 32% is used for the coal-based production of chemicals mainly in China. The remaining capacity supplies power plants (11%) and gas-production units (8%).

Coal-based motor fuel production amounts to almost 10 million tonnes annually. This is about 0.5% of global fuel production.

Ammonia and methanol are in terms of their quantities, the most important chemical products manufactured from coal. The worldwide production of ammonia is about 150 million tonnes/year, 15% of which originates from coal-based synthesis gas. A similar proportion of the 40 million tones of methanol produced annually throughout the world is also made from coal-based synthesis gas. Other chemical products based on coal, such as dimethyl ether or acetic acid, are in comparison less significant. The market for gasification plants has soared in recent years in particular in China with increased exploitation of the enormous coal reserves there for manufacturing basic chemicals and fertilizers. In addition, a few Fischer-Tropsch units are currently being planned there for motor fuel production. In India there is also interest in such developments. Even though the USA has the largest coal reserves in the world, there are only a few coal-based chemical plants in operation. However, there are numerous strategic coal-based fuel generation projects.

The synthesis gas resulting from gasification has to be further processed in a complicated manner in a series of downstream steps (dedusting, desulfurization), whereby it is of especial importance to adjust the desired CO/H_2 ratio (conversion). What all techniques have had in common up to now is that the energy needed for the gasification is supplied by the combustion of feedstock coal which leads to corresponding CO_2-emissions. In the past, some research effort in Germany has been directed towards meeting the energy requirements of coal gasification with heat from nuclear plants.

Key Statements on Availability of and Change to Coal-Based Technology

Regarding its availability, there are good long-term prospects for the use of coal in the chemical industry. At current rates of consumption known reserves of coal will last some 200 years, a figure which is far higher than those for oil and gas.

The countries with the largest coal reserves are the USA, the Commonwealth of Independent States (CIS), China, India and Australia. To reduce its dependency on its greatly increasing oil and gas imports, China is already exploiting these coal reserves in grand style for chemical production. In other countries, there is only a slow movement towards implementing coal gasification, at least in part due also to the complexity and high capital cost of coal gasification plants, and the fact that the oil and gas based petroleum chemical industry is already very well established. Other factors which hamper the rapid spread of coal gasification are the price of imported coal and environmental issues around CO_2-emissions as well as the cost impact of instruments such as carbon trading or possible future CO_2 taxation.

If oil and gas prices stay at a high level, there will be increased interest in coal-based processes. The regions most profiting from this will be those where the long term price of coal is low. Furthermore the high efficiency and favourable CO_2 balance of IGCC power generation will make this a growth market of the future – particularly, if CO_2-sequestration is the goal. These power plants offer the option of a ‘CO_2-free’ operation in which the gas turbines are powered by pure hydrogen, the carbon having been removed from the fuel as CO_2 beforehand. The experience gained in operating such plants can be expected to advance the use of coal in the chemical industry.

In the future, the range of raw material used in gasification will widen. In addition to coal, renewable resources, that are unsuited for food production, as well as residual and waste materials will be increasingly employed for producing synthesis gas and fuel gas. In refineries, petroleum coke and petroleum residues are already being used in quite large quantities to generate hydrogen.

Scientific and Technological Challenges and Solutions

Gasification plants are technologically demanding and capital-intensive. Their use is economical only where inexpensive resources are available and large capacities are envisaged. Consequently, research and development are focused on reducing the complexity of the units on the one hand and, on the other hand, in quantifying or modelling the transport phenomena as well as the chemistry of gasification (e.g. slack formation) with the aim of optimizing process design. Furthermore, renewable resources unsuitable for food production as well as residual and waste materials are being examined for their applicability for gasification units. It is intended to supply such feedstocks to the gasifier alone or in combination with coal. In order to ensure a steady supply of material to the gasifier, which operates under pressure, these alternative feedstocks must have a similar flow behaviour to coal. Thus, mechanical and thermal pretreatment steps such as pyrolysis have to be developed.

It is also possible to directly gasify coal in seams by supplying air or oxygen. However, all the efforts to date have not been very successful.

Synthesis gas from coal gasification plants is used to produce fuels, synthetic natural gas, ammonia, methanol, dimethyl ether and acetic acid. In Germany, these kinds of coal-based processes are not used. However, it seems to be advisable that R&D in Germany again pays closer attention to these processes.

Need for Further Research

The operation of demonstration plants for the gasification of coal and residues is a prerequisite for the rapid attainment of research targets. Such units already exist in Germany and elsewhere in Europe. However, the goals being pursued in such units should be harmonized and deficits compensated by initiating new research programs, quite possibly in additional new plants.

The integration of gasification technology into existing chemical and refining industry structures requires the development of new or alternative processes for the conversion of synthesis gas (to olefins, aromatics and saturated hydrocarbons; see Chapter 3.2, Scientific and Technological Challenges).

3.3.2 Coal Hydrogenation

Present Situation and State-of-the-Art

Coal hydrogenation, based on the fundamental work of Friedrich Bergius from around 100 years ago, was brought to large-scale use by Matthias Pier. Between 1940 and 1944, about four million tonnes of coal based gasoline were produced annually in twelve hydrogenation plants in Germany.

For hydrogenating coal, grounded coal is suspended in a coal-originating oil and, in the presence of a solid catalyst based on transition metals, is reacted with hydrogen under high pressure at temperatures around 450 °C to form a liquid hydrocarbon mixture. For the first step of liquefaction of the coal particles in the liquid phase, inexpensive suspended disposable catalysts are used, because the recycling of catalyst from the hydrogenation residue is too complicated. An alternative method is the indirect hydrogenation, e.g. with tetraline. After separation of the residue by distillation, the resulting coal oil has to be further processed, because it contains large amounts of aromatics as well as sulfur- and nitrogen-containing compounds. This takes place by means of hydrotreating.

Scientific and Technological Challenges and Solution Approaches

Unlike coal gasification, there are much higher requirements placed by coal hydrogenation with respect to coal type and coal quality: only coal low-in-carbonisation such as lignite and so-called high-volatile hard coals (steam coal, open burning coal and gas coal) can be directly liquefied with hydrogen. Bituminous coal, forge coal and semibituminous coal as well as anthracite show little reactivity for this hydrocracking process. With the exception of the catalytically effective pyrite, the mineral content of the feed coal should be as low as possible.

The processing of coal oil to fuels of today's fuel grades or to produce raw materials for chemicals requires an enormous effort regarding subsequent refining technology (catalytic hydrotreating) which is attributed to the relatively high fractions of polycyclic compounds and compounds with the heteroatoms oxygen, nitrogen and sulfur. Altogether, significant amounts of hydrogen thus have to be made available in coal hydrogenation. The hydrogen costs can be reduced if the direct coal liquefaction is, for instance, combined with a large coking plant and the hydrogen in the coke-oven gas is utilized. For further processing of coal oil into fuels, the combination with a petroleum refinery would be an option.

Compared to the indirect coal liquefaction by coal gasification and subsequent Fischer-Tropsch synthesis or via the methanol route, the direct coal liquefaction has thermodynamic advantages, ultimately reflected by a higher efficiency.

Need for Further Research and Development

A key for improving the coal hydrogenation technique is in the development of novel catalyst systems for increasing the selectivity. However, up to now the catalysis researchers have not paid sufficient attention to this, probably due to the complexity of selectively hydrogenating an extremely inhomogeneous mixture.

To address this challenge, the following options exist:

- Development of novel catalyst systems with significantly higher selectivity, whereby these catalysts can be separated from the liquid phase (e.g. via their unusual density or magnetically);
- Devising integrated processing concepts; and
- Optimization of catalysts for the further processing of coal oil to marketable products.

3.3.3 Pyrolysis

Pyrolysis is a purely thermochemical process in which, under the influence of temperature only, exclusively volatile and gaseous products evolve from the feed coal and solid coke remains.

Starting Situation and State-of-the-Art

Pyrolysis, also called coal degassing or coking, is the oldest technique to refine lignite and hard coal. The coking of hard coal still assumes greater importance nowadays in producing raw basic materials for chemistry. Here, volatile components, i.e. the so-called 'coking-oven gas' is formed at high temperature and under absence of air. After separation of aromatic components, mainly benzene, and recovery of the coal tar for further processing, the coking-oven gas is typically combusted for coverage of the energy demand of the coking process. The coke remains as the main product of coal degassing and is used mainly as a reducing agent in the steel and iron production.

Currently, there are five coking plants in operation in Germany. The technology is far advanced and well mastered. Each year, 450 million tonnes of hard coal are processed worldwide into coke. Moreover, there is another primary technique denoted as hydropyrolysis that involves the thermal treatment of powdered coal in a hydrogen atmosphere at temperatures of 500 to 900 °C.

Coal tar from hard coal is formed in great quantities of about 17.5 million tonnes worldwide a year during coal degassing/coking. This tar has always represented a significant resource for the chemical industry, in particular, for the production of aromatic compounds such as naphthalene and anthracene derivatives. Furthermore, coal tar pitch is the starting material for carbon products such as soot and graphite electrodes. Historically, the processing of coal tar pitch has been based in Germany; however, the scientific-technical worldwide leading know-how is currently allocated only on the company Rütgers Chemicals in Castrop-Rauxel. Compounds such as aromatics, phenols, naphthalene, anthracene, cresols, pitch, resins and pyridine can be separated via many procedural steps. These compounds are then used as base material for paints, plastics, pharmaceuticals, solvents, electrodes and special oil. The required process chains are state-of-the-art.

The electrothermal reaction of lime and coke results in calcium carbide which, when further treated with water, yields acetylene. Each year, 14 million tonnes calcium carbide are produced, 95% of which is produced in China. In Germany, acetylene is produced utilizing natural gas as source. Application areas of acetylene are: welding in metal industry, production of acetylene soot and calcium cyanamide as well as the manufacture of some valuable chemical products, e.g. butanediol. Historically, the acetylene chemistry on the basis of coal was very important for producing compounds such as vinyl chloride, acrylic acid and –ester, acrylonitrile, chloroprene, acetaldehyde, acetic acid, ethanol and vinyl acetate. Petroleum chemistry has almost fully supplanted the coal-based acetylene chemistry. Only in China, a certain renaissance for the production of PVC exists.

Scientific and Technological Challenges and Solutions

The future of coal degassing/coking in Germany is directly linked to the development of the iron- and steel manufacture. Currently, one can assume that the coal degassing/coking of hard coal will continue on a large scale. Thus, the by-product coal tar will continue to be available as a raw material for chemicals. At the present, the conversion of coal in coking-oven processes is worldwide about ten-times larger than that via coal gasification. Even though coke-free iron smelting is being discussed, a time scale cannot be foreseen for the substitution of the established methods.

Need for Further Research and Development

In recent years, there have been developments regarding the construction of large coking reactors and optimization for two-products only coking plants (focus on gas and coal, no tar). Besides improving the environmental sustainability, predominate targets are further optimizing the energy demand by recycling and widening the choice of feed coal. The development and construction of coking plants is also an important export factor for German companies.

The R&D demand for processing coal tar is not considered to be of priority, because it is very well established. However, there is a need for further R&D in the development of methods for converting aromatic hydrocarbons all of which is generally considered a task field of chemistry and catalysis. Also the selective hydrogenation of coal might be of interest in producing aromatic compounds as well as feed material for soot production.

A coal-based acetylene chemistry has certain potential; thus, the carbide route could gain some interest in the future. However, for reasons of economy and environmental relevance, no research is needed with respect to the classic calcium carbide route. Instead, new approaches are needed which will lead to an essential reduction in energy consumption and environmental pollution. Hence, there is a demand for the development of technologies with autothermal reaction control, alternative metal carbides with a closed metal circuit or developments that integrate the calcium carbide synthesis into energy-generation processes.

4. Renewable Resources

'Renewable resources' denote carbon-containing raw materials that can be regenerated within foreseeable time. These so called sustainable resources are based on biomass but also include carbon dioxide, mainly formed during the combustion of fossil fuels.

From the advent of modern chemistry up to the beginning of the 20th century, the renewable raw materials, derived from plant and animal biomass, belonged to important starting materials for the production of chemicals such as ethanol, acetic acid, formic acid or acetone. As coal and petroleum became more important, conversely, raw materials originating from plants and animals became less significant. What remained was a stable fraction of ca. 10% renewable raw materials, essentially due to the economical and technical advantages gained through making use of nature's capacity to synthesize special molecular structures. This applies to numerous oleochemical products as well as to those based on starch and cellulose. In addition, sugar is used as a raw material for fermentations in the field of biotechnology as well as glycerol, also resulting from the substantial increase in biodiesel production.

Demands for an intensified use of renewable raw materials are currently being voiced. Motivations for this include: the sometimes very high oil price; the desire to reduce dependency on oil and gas imports, thus ensuring future energy and resource supply; the reduction in CO_2-emissions from fossil carbon sources in order to contribute towards climate protection; and the economic development of rural areas hoping to reduce agricultural subsidies. In this context, however, many further aspects have to be considered: the prices for renewable resources have also increased in many cases in parallel to the oil prices. Moreover, the available arable land is limited, and there is a competition of use between the production of food and animal feed, on the one hand, and the production of biofuels and chemicals on the other hand. Furthermore, there is a risk that excessive fertilizer input leads to additional greenhouse gas emissions and that changes in land use can trigger the loss of carbon sinks. Because of these risks, many people hope for the increased utilization of lignocellulose biomass, i.e., essentially using wood as a forestry product and straw as an agricultural waste.

Besides 'non-food biomass' as a promising renewable resource, the other important regenerative resources for the chemical industry will also be presented in the following sections.

4.1 OILS AND FATS

Present Situation and State-of-the-Art

Fats and oils are esters of the trivalent alcohol glycerol with three predominately different, even-numbered and non-branched aliphatic monocarboxylic acids, the so-called fatty acids. The esters with glycerol are called 'triglycerides'. Fats and oils primarily imply a substance mixture from various fatty acid triglycerides of either animal or plant origin.

In 2004, the worldwide demand for fats and oils amounted to about 131 million tonnes, whereby 83% and 17% of this was produced from plant and animal basis, respectively. Of this 131 million tonnes, 81% was used for food, 11% for the chemical industry, 5% for animal feed and approx. 3% for the generation of biofuels and energy. For 2008, the worldwide consumption of fats and oils was cited at 165 million tonnes with an analogous use distribution as given for 2004 except that approx. 9% of these resources was used to generate biofuels and energy.

In the production of biodiesel (fatty acid methyl ester), 100 kg glycerol result per tonne product yielded. Besides its traditional uses as antifreeze, surfactants or emulsifiers, it is a great challenge to establish glycerol as a platform chemical, e.g. for producing acrolein, propanediol or epichlorohydrin. However, there are also other possible processes such as hydrocracking in which diesel oil is produced without compulsorily yielding glycerol.

In 2006, plant oils and animals fats, making up 50%, were the most important renewable raw materials used by the chemical industry. The respective use of other renewable raw materials was as follows: starch (11%), cellulose (14%), sugar (12%), fibers (7%) and other natural components (4%). Historically, the industrial use of plant oils and animal fats has developed, in a time in which no one needed to consider the competition between food production. About one-third of the industrially processed plant oils and fats are used to produce surfactants. Not only are oils and fats needed for detergents and cleaning agents but they are also needed in the pharmaceutical, cosmetics and textile industries. Moreover, fats and oils are important raw materials for biolubricants and -oils, polymers and polymer additives as well as varnishes and paints.

Whereas rape-seed oil, beet oil, linseed oil and sunflower oil are produced from indigenous plants in Germany, castor-, palm-, soybean- and coconut oil are all imported (total consumption of plant oils in Germany in 2006: 5.93 million tonnes; OVID, Verband der Ölsaaten verarbeitenden Industrie in Deutschand). The imported oils contain special fatty acids which are not available in native oils but are valuable industrial raw materials. They mainly comprise of fatty acids with medium chain lengths used in synthesizing products for technical uses, such as saturated and unsaturated fatty alcohols. Representing main raw materials, fatty alcohols, depending on their chain length, are used in technical, cosmetics and pharmaceutical applications. The technical applications include their use as softeners, surfactants and lubricants (C_6 to C_{14}). In the cosmetic and pharmaceutical industries, the fatty alcohols (C_{12} to C_{22}) are utilized as surfactants or as regulators of melting point or consistency. Fatty acids of medium chain length are mainly derived from coconut and palm kernel oils.

Sources of mono- and polyunsaturated long-chained fatty acids, which are principally applied in foods and feed, are oils from rape seeds, soybeans, sunflowers, linseeds and olives, for example.

In 2004, the shares of the worldwide demand for fats and oils is given as follows: soybean oil 23%, palm oil 23%, animal fats 17%, rape-seed oil 11%, sunflower oil 7%, lauric oil 5% and others 14%.

Key Statements, Theses and Development Aims

Economic aspects have strongly influenced the use of natural fats and oils. Thus, within the last three decades, the ratio has totally reversed with regard to the origin of fatty alcohols: whereas in 1980, 60% of these fatty alcohols originated from synthetic sources and 40% from natural ones, nowadays 60% stem from natural sources.

If one differentiates the demand for plant oils of the EU-25 member states during the period 2002/03 until 2006/07 according to their use in food or as industrial raw material, one recognizes that the consumption of these resources as foodstuff remained stable or slightly increased from 12.1 to 12.7 million tonnes. However, over the same period, the demand for plant oils for industrial applications has tripled from 2.5 to 8.2 million tonnes.

This increased demand is primarily explained by an increased consumption of rape-seed oil being processed to biodiesel. At the same time the rise in consumption of soybean- and palm oils is attributed to biodiesel production. The increasing use of plant oils for producing biofuels basically leads to a shortage of supply and thus to increased prices - also of oils for food production. Recently, there has been a strong volatility in prices observed for fats and oils, whereby the prices greatly rose in 2008 but fell in 2009 with the beginning of the economic crisis. A long-term trend cannot be predicted currently.

However, for the case of fats and oils, it is important to critically analyze the increasing material use and, in particular, energy use of ‘foods’ and arable land, relative to their potential available quantities. Future challenges will result, among others, from the increasing consumers’ desire for increasingly ‘greener’ products from renewable raw materials (material use by the chemical industry), whereby the sustainability aspect, and indeed for the entire value chain, will simultaneously be increasingly significant for the end consumer.

Scientific and Technological Challenges

In order to allow a rising standard of living for a growing world population, it is important to develop various and substantial sources of raw materials. These new sources should also satisfy the demand for fatty acids of medium chain-length (C_{10}, C_{12}, C_{14}) for industrial application. Furthermore, the search for new innovative and sustainable products as well as for ever more efficient processes based on the applied raw material is an important research field. Here, it concerns the identification, breeding, optimization and cultivation of ‘new’ oil plants such as jatropha (oil content of ca. 30%). Such new plants should grow on barren soils so that no arable land is lost for their cultivation. Moreover, such plants should have a high oil content and a spectrum of fatty acids, suitable for industrial applications.

Furthermore, the use of genetically modified plants has to be considered in order to attain better qualities and yields. These plants can be engineered in a way that they adapt to barren conditions of a site and also form industrially relevant product spectra such as short-chained fatty acids that rarely occur naturally in plants.

Further approach is the evaluation and optimization of microorganisms such as microalgae and prokaryotes for the production of fats and oils as well as the aforementioned technical uses, along with the food supplements such as polyunsaturated fatty acids. The exploitation of microbes can lead to novel products and processes, for example, the synthesis of a biosurfactant directly by the organism without the detour via an isolated fatty acid.

Further Need for Research

Chemical process- and product development have to continue to be promoted to create an improved product spectrum. The aim must be to ease the competition to food production.

There is further need for research in the field of screening plants and microorganisms in order to create an exploitable industrial product spectrum. This may concern the synthesis of oils and fats or concern products directly produced from these raw materials. Subsequently, further steps should be taken to optimize the cultivation of production organisms and plants. Hereby, plants would be adapted to growing on barren soils and microbes would be fitted to work in corresponding reactor systems.

Depending on the product group and consumer acceptance, the possibility of genetically improving the organisms should be examined and, if needed, the corresponding methods applied or developed where necessary (also see Chapter 4.3. “Non-Food Biomass”).

4.2 SUGAR AND STARCH

Present Situation and State-of-the Art

Sugar: Sugar is a collective term for mono- and disaccharides. The most important sugar is sucrose – a disaccharide consisting of glucose and fructose. Colloquially, the term ‘sugar’ signifies sucrose. Sugar and starch belong to the carbohydrates and are the most important energy and storage sources in metabolism. For humans, they serve as foodstuffs. All green plants manufacture carbohydrates by means of photosynthesis. Among indigenous plants, the sugar beet is the most important sucrose-producing plant; it has been cultivated in Germany since the 18th century. Elsewhere in Europe, sugar beet is grown in France, Poland, Turkey and Ukraine. Abroad, this plant is also used in the USA, Canada and other overseas countries. However, sugar cane is cultivated in South America (Brazil), Africa and Asia (India, Thailand, Indonesia). In 2007/2008, worldwide production of sugar (sucrose) amounted to 168.9 million tonnes raw value (ca. 21% thereof from sugar beets). The sugar production in the 27 EU countries amounted to 17.3 million tonnes in 2007/2008 (Germany: 4.3 million tonnes).[1] In 2006/2007, the total volume of sugar traded worldwide was approx. 53 million tonnes, i.e. 69% of the produced sugar was consumed by the producing countries.

Availability and Development: The supply-to-consumption ratio amounting to 49% for sugar lies considerably above that for comparable crops (wheat 19%, corn 16%, 2007/08)[2]. The consumption of sugar is consistently increasing by ca. 2.8% per annum. Since the beginning of the sugar market regulation, Europe has evolved from a sugar exporter to a net sugar import market (1.3 million tones in 2007/08). The worldwide finance crisis has affected the sugar market on the short-term by slowing the expansion of capacities. India, the chief sugar producer last year, is expected to cultivate considerably fewer sugar crops due to the plummeting prices. However, stock market commodity prices for sugar in September 2009 were at the highest point worldwide since decades; with raw sugar cost at 340 Euro per tonne and white sugar at 400 Euro per tonne[3]. The prices for European raw- and white sugar are fixed respectively at 335 and 404 Euro per tonne for 2009/2010[4].

Co- and By-products: During the crystallization of sugar, the by-product molasses is formed as syrup, mainly used for animal feed and yeast production. In 2006/2007, the molasses production was 656,000 tonnes[5]. Also the chopped sugar beet remains are marketed as animal feed. In the processing of sugar cane, the so-called bagasse, formed as the fiber fraction, is burned to generate energy for bioethanol production.

Industrial Use: Sugar is mainly applied in the food industry; i.e. the German chemical industry or fermentation industry utilized 295,000 tonnes sugar as a raw material[5], only about 22% of the total German turnover in sugar.

The chemical industry uses sugar and its by-products as starting material for chemical syntheses and fermentation. Sucrose, itself, is mainly applied in the form of polyetherpolyols for manufacturing polyurethane foams. Moreover, sucrose is utilized as a starting material for the sweetener isomalt and for biodegradable surfactants (esters of fatty acids). Functionalized with fatty alcohols, glucose is employed as a surfactant (alkylglucoside); in hydrogenated form, it is used as a sweetener (sorbitol) and in oxidized form, as a sugar acid for various industrial applications (e.g. as a corrosion inhibitor). Furthermore, sugars and enzymatically degraded starch are, by far, the most important raw materials for industrial fermentation processes that, in turn, yield products for the chemical and pharmaceutical industries (‘white biotechnology’). Quantitatively, the mostly important products, besides bioethanol (see below) are: amino acids, organic acids, dextranes, vitamins as well as fragrances, aromas and sweeteners for the food- and feed industries. Globally, about two million tonnes of feed additives such as L-lysine, L-threonine and L-tryptophane are produced via fermentation processes. Moreover, numerous pharmaceutical products (e.g., antibiotics, hormones, growth factors as well as therapeutic products and antibodies) are produced by biotechnological fermentation based on sugars. Especially to be mentioned are enzymes that are likewise produced by fermentation techniques and are used in multiple applications ranging from stain removal in detergents to auxiliaries e.g. in the food industry or as biocatalysts in the production of fine chemicals. White biotech products show a growth rate significantly higher than that of classically produced products of the chemical industry, whereby the worldwide market volume of such biotechnology products is estimated at 55 billion Euro annually. In 2004/2005, biotech products accounted for four to six percent of turnover

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[1] F.O. Licht’s Int. Sugar & Sweetner Report, Vo. 141, 30

[2] F. O. Licht’s Sugar and Ethanol Brazil 2009, March 2009, Sao Paulo; 11th European Sugar Conference, June 2008, Brussels

[3] New York #11 (raw sugar, spot), London #5 (white sugar, spot)

[4] Council Regulation (EC) 318/2006 on the common organization of the markets in the sugar sector

[5] *Zucker in Zahlen* (Sugar in Numbers), *Wirtschaftliche Vereinigung Zucker*, Bonn, October 2008

in the chemical industry and corresponded to a production value of 3.5-4.3 billion Euro. Experts guess that the world market for biotechnology products will grow further at double-digit figures (Deutsche Industrievereinigung Biotechnologie (DIB), Frankfurt/Main).

Because of its enormous use as a fuel component, ethanol is, by far, the most important product from biotechnological manufacturing and is produced by fermentation of sugar- and starch-containing plant parts. The choice of the applied crops depends on the regional availability and prices - in Germany, mainly grains and sugar beets are used (36% from sugar beets in 2008). Whereas Brazilian ethanol producers use sugar cane, those in the USA use corn. The worldwide largest producer of bioethanol is the USA with 27.7 million tonnes in 2008, followed by Brazil (19.1 million tonnes) and the EU (2.2 million tonnes). In the ethanol manufacture from corn or wheat, the starch fraction is first hydrolyzed to sugars that are then fermented to ethanol and carbon dioxide. The bioethanol production in Germany amounted to 0.46 million tonnes in 2008, and was principally used for the reaction with isobutene to produce ethyl tertiarybutylether (ETBE), an anti-knocking agent for gasoline. According to the German Biofuel Quota Law, as of 2008, bioethanol, in a maximum fraction of 3.08% (v/v), may be added to gasoline (Bundesverband der deutschen Bioethanolwirtschaft, Berlin).

Starch: Starch consists of linear and branched chains of glucose as monomeric units. For industrial applications, the branched form (amylopectin) is more valuable than the linear form (amylose). Even though the two forms can be separated from one another, it involves a considerable energy expense. Thus, recently, starch plants that almost exclusively produce amylopectin have been developed, in particular, by genetic engineering methods.

About 50 percent of starch is produced from corn; other important sources are wheat and potatoes. For technical applications in Germany, starch is mostly produced from potatoes (3 million tonnes), followed by wheat (0.9 million tonnes) and corn (0.6 million tonnes). In 2006, about 0.26 million tonnes of starch was applied by the chemical industry. It was used partially in chemically unchanged form, and in part, in modified or degraded forms. Starch is principally used because of its specific properties (e.g. its swelling ability). Modifying starch is easier than modifying cellulose, because even with low degrees of substitution, improved functional properties can be attained. Starch and starch derivatives are used in the paper- and textile industries as well as in food production. Dextrines can be made by partial hydrolysis, and cyclodextrines can be produced by enzymatic treatment, whereby their ability to enclose organic molecules is increasingly being exploited. Compared to native starches, esters in the form of acetates or phosphates and ethers - mostly as hydroxyethylethers - show a clearly changed solubility profile and are important auxiliaries in the textile- and paper industries. Moreover, cationic and oxidized starches are economically important. Upon addition of softening agents and copolymers (e.g. polyvinyl alcohol), starch compounds can be manufactured by extrusion and applied as biodegradable plastics e.g. in plastic bags and agricultural foil systems. Further areas of application are the fermentative production of basic chemicals (e.g. tensides, stabilizers, organic acids), binders and adhesives, the production of biopolymers (after fermentation to polylactic acid, PLA, or polyhydroxybutyrate, PHB), of filling agents and foams (e.g. for the packaging industry) as well as the use in pharmaceuticals.

Besides sugar from sugar beets or sugar cane, starch plants are an important source of glucose. Hereby, the starch, extracted from the grains, is completely hydrolyzed via enzymatic techniques.

Needs and Opportunities

Sustainability: Regarding the aspect of sustainability, it is to be noted that products based on sugar or starch do not contain fossil carbon. Nonetheless, it has to be specifically ascertained to which extent fossil resources are used in producing such products. This consideration begins already with the cultivation of the starting plants on fields; here, the known sugar- and starch plants by all means pose different demands. From a physiological point of view, sugar beets depict a high efficiency with respect to energy, fertilizer and water consumption as well as high dry mass production, connected to considerable binding of carbon dioxide and release of oxygen.

Both the sugar beet cultivation and sugar industry act as exemplary models through the utilization of all products resulting from sugar production as well as by the integration of the corresponding processes to create a closed economic circuit. This is also true for sugar cane.

With regard to the production of bioethanol, its ecological assessment is not always advantageous and depends on the type of cultivated areas, the agricultural production techniques used and the heat management during processing of fermentation products and by-products. Moreover, another increasingly critical issue is the competition between the use of crops for biofuel or food production.

Political framework conditions: The sugar market in the European Union has been regulated by the common organisation (ZMO) since 1968. The relatively high price for industrial white sugar on the European market, as compared to world market raw sugar prices, has been disadvantageous from the perspective of international competition. Thus, the EU sugar market regulation is to be amended until 2015 with the aim of reducing sugar production, and in the expectation of future decreasing tariffs, to adjust the sugar prices to world market levels. Within the scope of the European market reform, a retroactive fixed annual import contingency was introduced for the fermentation industry resulting in considerable uncertainties for industrial production planning.

The price for bioethanol strongly depends on the regulations and mixing quotas in individual countries. Brazilian bioethanol costs during the period from 2006 to 2009 on the average 40% of European bioethanol (CEPEA, ICIS). Subsidies such as the partial exemption of biofuels from mineral oil tax distort competition, since products going into tax-promoted applications become too expensive for other industrial sectors. Within the course of the sugar market-control reform, alternative marketing options become more important. The production of bioethanol for the fuel market and the use as raw material for the chemical industry are feasible options. However, regarding the world market prices up to now, the German as well as the European bioethanol production is not competitive. A possibility would be higher-yield genetically engineered plants. However, such developments are being restrained by the EU-Commission and national governments blocking cultivation of such plants by arguments which are not entirely substantiated scientifically.

Scientific and Technological Challenges

In recent years, there has been an increasing number of approaches to produce bulk chemicals and biopolymers using industrial biotechnology. In Brazil, several companies are planning the large-scale production of polyethylene from bioethanol. Moreover, bioethanol is also replacing fossil based ethanol in the production of C_2-componds such as ethyl amines. In these catalytic processes, it is important to carefully remove catalyst poisons such as sulfur compounds. In principle, all C_2-compounds can be produced directly, such as the oxidation product acetic acid, or indirectly via ethylene as intermediate. Researchers are also working on manufacturing isoprene, as the starting material for synthetic rubber (Genencor/Goodyear) as well as manufacturing fuels (Votorantim/Amyris) on the basis of sugar and starch. Further examples are 1,3-propanediol (DuPont) or methacrylic acid (Perstorp), polylactic acid (Purac) and polyester from succinic acid (DSM/Roquette).

Carbon dioxide is produced as a co-product in fermentation processes in the same amounts as the desired main product. Because it can easily be separated, some fermentation plants are using this CO_2 for the beverage industry or for technical applications (see Chapter 4.4, Material Utilization of Carbon Dioxide).

Need for Further Research

There is a need for further research in the field of processes of white biotechnology. Targets hereby are to improve fermentation processes through molecular biology research in strain development in order to develop new routes of synthesis, to raise product yields and moreover facilitate the processing of the fermentation broth by increasing the concentration of the value product. Further research is also needed in the areas of enzyme catalysts, reaction technology and processing techniques. Today fermentation processes often result in products of low concentrations or salts in aqueous solutions. The objective of modern processing techniques thus must be to achieve high yields and low energy input without water evaporation used for isolation. Furthermore, often only the so-called platform chemicals are accessible through fermentation processes, and the desired target products are obtained by further catalytic reactions. In order to promote raw material and energy efficiency, these process steps should be integrated in the highly efficient overall procedure.

The industrial biotechnological production can only compete with chemical processes based on fossil resources if, by optimizing the biotechnological processes, improving microbial strains for higher biomass production as well as by more efficient techniques for its conversion allow to achieve the same price level.

Besides sugar and starch, lignocellulose is becoming an increasingly important hydrocarbon source, which will be illustrated in the following chapter. Here, industrial biotechnology can contribute significantly by creating tailored enzymes for the hydrolysis of cellulose. Thus, an enzyme has been developed which can catalyze the hydrolysis of cellulosic components from various resources such as straw, bagasse or wood chips to sugar followed by fermentation to ethanol.

4.3 “NON-FOOD” BIOMASS

Present Situation and State-of-the-Art

So-called ‘non-food’ biomass primarily denotes wood, agricultural and forestry remains such as straw, waste from the food- and animal feed industries as well as grass. Its use as raw material for the chemical industry avoids the competition with food production. Moreover, non-food biomass can be generated from areas that are unsuited for cultivating crops. The economical and environmentally friendly utilization of non-food biomass for chemicals production, however, requires innovations in creating new plant strains and cultivation techniques, in the logistics and processing of plant raw materials as well as new approaches in the further processing in biorefineries or gasification plants.

The development of biorefineries represents the key for an integrated production of feed as well as of chemicals, materials and fuels. The availability, the quality and the market price of biomass will play a decisive role for the industrial exploitation of bioresources as well as for the choice of the refinery concept. The key component of non-food biomass is lignocellulose, the combination of lignin (the macromolecule which causes the woodiness of the plant cell wall), hemicelluloses (polysaccharides, which together with cellulose serve as a supporting and skeletal substance of the cell wall) and cellulose. In the lignocellulose biorefineries (LCF), the raw materials are separated into cellulose, hemicellulose, lignin and extracts. From these components, chemical or enzymatic processing techniques yield sugar, fats/oil and refined products of lignin. These intermediates are subsequently fermented to produce such platform chemicals as ethanol or lactic acid and polymers such as polyhydroxybutyrates. The remaining residues can then be used as a raw material by thermal treatment via gasification and Fischer-Tropsch synthesis to yield second-generation biodiesel or the residues can be fermented to biogas. Minerals can be utilized for the sustainable fertilization in biomass cultivation.

Another biorefinery concept follows the use of wet biomass such as grass, clover or lucerne. This results in additional process streams containing amino acids and proteins.

Lignocellulose has been used for a long time and on an extensive scale for producing paper: in the pulp plants about 280 million tonnes of wood are being processed worldwide. The pulp produced essentially consists of cellulose together with fractions of hemicelluloses and smaller fractions of lignin residues. 97% of this pulp is used in the paper industry. Pulp qualities of higher purity are used in the form of regenerative cellulose for producing fibers for the textile industry or as chemical cellulose for producing cellulose acetates and other derivatives.

The so-called ‘black liquor’ of the cellulose process essentially contains lignin as well as fractions of hemicelluloses and degradation products. The latter comprise acetic acid, furfural, methanol, and other chemical products. In general, this black liquor, however, is incinerated for covering the energy needs of the pulp plants. In some plants, valuable products are separated previously; e.g., furfural with a worldwide annual production of approx. 150,000 tonnes and vanillin with a worldwide annual production of approx. 5,000 tonnes. A small fraction of the lignin is utilized in the form of lignosulfonates as flow aid in the production of concrete, as an additive for pesticide formulations or for making pellets of animal feed.

Recently, the pulp factories are aiming to reach higher value by separating the hemicelluloses. The sugars resulting from the hydrolysis thereof are expected to be used for fermentations.

Needs and Opportunities

The fuel sector and the chemical industry are tightly interwoven via the processing of the raw material petroleum in refineries. The current petrochemical product lines and the product trees are the result of over 70 years of development. In complex value chains, the chemical industry produces an extraordinary wide spectrum of products beginning with petroleum-based platform chemicals ethylene, propylene, benzene, toluene and xylenes leading to numerous, subsequent intermediate products such as ethylene oxide, styrene and vinyl chloride, ex-

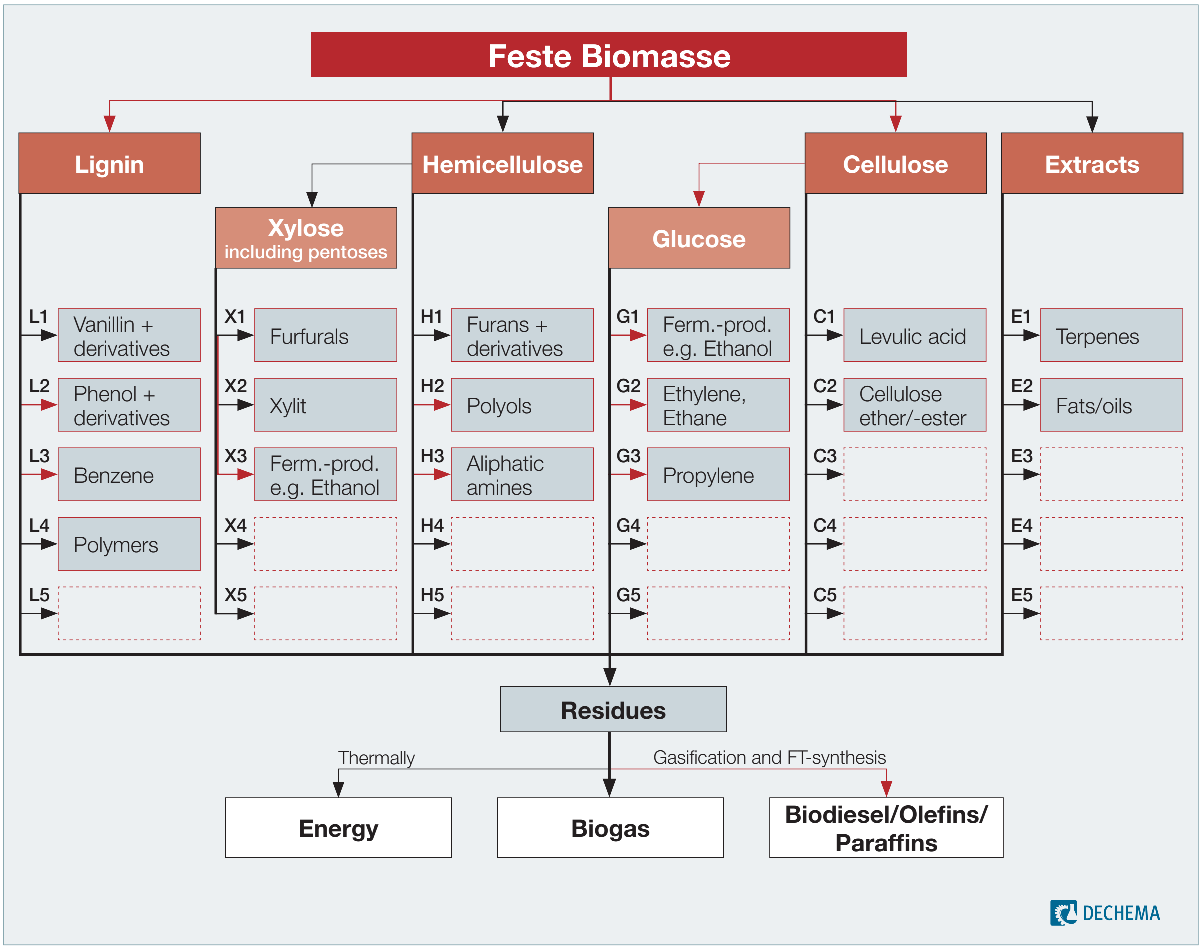

Fig.3: Processing scheme for lignocellulose biorefinery

tending to high-value products such as pharmaceuticals and plant protection products. These basic chemicals are referred to as 'eternal' because of the efficient, highly integrated production systems based on petroleum.

For further development of the biomass-based chemistry, it is thus reasonable to create links to existing value chains via suitable interfaces. Thus, ethylene can be attained from ethanol by dehydration, and the established subsequent petrochemical process chains can follow. Glycerol can also be considered as another platform chemical which results from the production of first-generation biodiesel from oils (see Section 4.1) and which might serve as the basis for today's products created from propylene. In this way, the chemical industry can flexibly exploit the amounts of and prices offered for petrochemical and native raw materials.

This concept, however, can also be achieved via the gasification of biomass to synthesis gas and its conversion to short-chain olefins such as ethylene and propylene. Methods for this are the Fischer-Tropsch synthesis and the MTO-process (Methanol-to-Olefins). Even though these methods are principally known, the olefin selectivity should be improved.

Precursors for biorefineries, namely, units for the complete hydrolysis of cellulose and hemicellulose by separating lignin and utilizing its energy, have already existed since the beginning of the 20th century. Here, diluted or concentrated mineral acids were used. The sugar solutions were fermented for producing ethanol and feed yeast. Operations were terminated in Germany in the 1950s, not only because of the high waste water contamination but mainly because of the competition by fossil raw materials; in the former Soviet Union, such plants still existed up into the 1980s. Recently, there are numerous research projects involving the hydrolysis of lignocellulosic materials either with acids or purely enzymatically in order to produce bioethanol. This applies in particular to the USA. Currently, however, there are only pilot plants for this having a production capacity of several thousands of tonnes per year.

Plant biotechnology can deliver tailored contributions for increasing the biomass yield for biorefineries and optimizing the components. Thus, it is important to mobilize the entire arsenal of modern plant breeding including genetic engineering.

The comparatively low energy density of non-food biomass leads to high logistics and transport costs. The large capacities of chemistry plants that are necessary for them to operate cost-effectively moreover require long transport routes. However, by means of decentralized fast pyrolysis, it is possible to produce pyrolysis oils that could be transported comparatively cheaper and could be used in central gasification plants. This option is being followed in the Bioliq-process with the aim to process almost all kinds of dry lignocellulose. Primarily used are residues and co-products from agriculture and forestry such as forest wood residues or straw. In this process, synthesis gas is first generated and, from this, synthetic fuels and basic chemicals are produced. Electricity and heat are formed as by-products with which the energy demand of a part of the processes can be covered.

For generating synthetic fuels and basic chemicals, the gasification of black liquor from pulp plants or LCF-biorefineries comes into consideration.

Scientific and Technological Challenges

One of the greatest challenges for the refining particularly of lignocellulosic biomaterial and for a high-yield material conversion in well-usable chemicals is the development of catalysts or the search for enzymes, yeasts or other microorganisms.

Thus, numerous chemicals could be produced, for example, on the basis of the hemicelluloses and from the resulting C_5- and C_6-sugars by using suitable microbes analogous to industrial biotechnology today based on glucose. Another idea is to graft or cross-link hemicelluloses, that do not exhibit a high degree of polymerization, in order to produce plastics ('xylophane').

Need for Further Research

For solving these challenges, it is important to develop new biorefinery-platform technologies such as:

- Lignocellulose feedstock conversion (LCF-biorefinery, i.e. LCF-pretreatment for effectively separating the LCF into lignin, cellulose and hemicellulose);
- The further development of thermal, chemical and mechanical processes such as new digestion methods, gasification (synthesis gas) and liquefaction of biomass;
- The further development of biotechnological processes (biosynthesis, lignin-, starch- and cellulose-hydrolyzing enzymes);
- The combination of biotechnological and chemical-catalytic conversion processes for coupling to the value chains of the chemical industry;
- Development of product strains based on furfural (hemicellulose line) and hydroxymethylfurfural as well as levulinic acid (cellulose line) for direct linking to the current petrochemical product lines;
- Handling of solids for digestion and component separation;
- Testing of the whole process in pilot plants.

4.4 UTILIZATION OF CO_2 AS A FEEDSTOCK

Present Situation and State-of-the-Art

The anthropogenic emission of CO_2 through the use of fossil fuels has been estimated at around 29 gigatonnes/year in 2006 (International Energy Annual 2006, Update December 8, 2008). Because of carbon dioxide's contribution towards climate warming, currently numerous measures have been discussed to mitigate its emission, including the separation of the large resulting quantities of CO_2 from stack gases and subsequent sequestration. This requires the development of a new infrastructure for transporting the CO_2 via pipeline networks to the collection sites where it would be safely stored. Because of the high connected costs and possible problems of public acceptance, it is being discussed whether CO_2 can be partially utilized materially (also see "Utilization and Storage of CO_2," DECHEMA/VCI, 2009). Another aspect here is the saving of carbon-containing raw materials such as petroleum.

The energy industry causes the largest fraction of total CO_2-emissions making up 45% of this sum, followed by the transportation industry with 24%, steel production with 6%, cement production with 4%, the refineries with 3% and the chemical industry with 2%. Because of the low CO_2-concentrations, it is basically difficult and costly to separate the CO_2 from the stack gases – the lower the concentration, the higher the effort. Depending on the type of use, contaminants such as sulfur compounds also have to be removed from the CO_2.

In the chemical industry, almost pure CO_2 is formed during large-scale production processes. Examples are the hydrogen production for ammonia synthesis and oxidation processes such as the production of ethylene oxide. The currently utilized CO_2-streams originate almost exclusively from these processes, whereby excess amounts are released into the atmosphere.

In contrast to the CO_2-emissions, only a minimal fraction in the per mille range is used physically as an industry gas or for chemical syntheses. 20 megatonnes of carbon dioxide were used as an industrial gas in 2002 for which the important application areas are the tertiary petroleum extraction, the beverage industry and use as a cleaning agent or extractant. As a chemical raw material, carbon dioxide is mainly applied for synthesizing urea by reaction with ammonia for which approx. 107 megatonnes of CO_2 were used in 2008. Besides being used as a fertilizer, urea is applied for condensation resins with formaldehyde, partially via the intermediate step of melamine that, in turn, shows an extensive subsequent chemistry. Moreover, about two megatonnes CO_2/year are employed for producing methanol from hydrogen-rich synthesis gas. Not only is methanol a fuel component but it is chemically used mainly for manufacturing formaldehyde, methyl tertiarybutylether (MTBE) and acetic acid.

Furthermore, there are still other chemical processes based on CO_2, nevertheless with lower amounts used: the synthesis of cyclic carbonates by reaction with epoxides (around 40 kilotonnes per year) as well as the production of salicylic acid by reaction with sodium phenolate (around 25 kilotonnes per year).

Needs and Opportunities

In order to positively contribute to climate protection, the following aspects have to be considered in the material utilization of CO_2 as C_1-carbon source for fuel- and chemistry raw materials:

Firstly, CO_2 is the energy end product from combustion processes. In the reaction (reduction) of carbon dioxide to, for example, fuels more energy has to be put in, with regard to thermodynamics, than being released by means of combustion. Thus, exploitation of CO_2 is only sensible in combination with renewable energy resources or, at least, with available CO_2-free energy resources. Even though the photocatalytic pathway would be interesting, it is still in the stage of fundamental research and is not a technical option in the foreseeable future. Alternatively, the CO_2-reaction with hydrogen can take place, whereby this, in turn, has to originate from renewable or CO_2-free processes. If these conditions cannot be fulfilled, the balance of the material utilization of CO_2 leads to an increase in CO_2-emissions.

Secondly, one has to address the question of quantity ratios: Even if the majority of polymers and other basic chemicals were produced from CO_2, the worldwide emissions of CO_2 would only be reduced by less than 1%. To reduce CO_2 emissions by the power of ten, fuels for mobility have to be produced but with the corresponding amount of available H_2 and energy from renewable sources.

The chemical utilization of CO_2 can take place by reaction with energy-rich compounds such as alkene oxides to create cyclic or polymeric alkene carbonates. Another strategy is the reaction with reducing agents such as hydrogen, methane or carbon to yield carbon monoxide or subsequent products.

Scientific and Technological Challenges

Kinetically, carbon dioxide is extremely inert. Thus, most reactions have to be activated by heterogeneous, homogeneous and biological catalysts. A key reaction is the water-gas shift reaction. This reaction is used on a large scale in order to produce hydrogen from synthesis gas, whereby CO is reacted with water to form CO_2. Today, large quantities of ammonia are produced by this route on the basis of coal under massive emission of CO_2.

Solution Approaches

Quantitatively, the greatest potential lies in the production of synthesis gas, i.e. mixtures of CO and H_2. Three possibilities exist: dry reforming of methane with CO_2 (catalytic high-temperature technique), reduction of CO_2 with hydrogen (reverse of the water-gas-shift reaction) and the addition of CO_2 to hydrogen-rich synthesis gases as is already today the case with methanol synthesis.

Interesting for large-volume applications is the dry reforming in which the CO_2 is reacted with methane to create synthesis gas.

The concept raises a possibility for exploiting remote natural gas fields upon production of methanol or of GTL (Gas-to-Liquid) products. Principally, a purified biogas could be used. The currently known catalysts based on noble metals, however, are too expensive and tend to produce coke.

Currently, the water-gas shift reaction is used for producing hydrogen from CO with release of CO_2. The reverse of this reaction – such as, generally, reactions of CO_2 with hydrogen – is thus only sensible if cheap energy is available from CO_2-free sources. The hereby produced synthesis gas can be used via the Fischer-Tropsch synthesis to produce fuels (diesel, gasoline) or chemistry raw materials (olefins, paraffins).

Carbon dioxide can also be used as a sole carbon source for methanol synthesis, besides its current application in hydrogen-rich synthesis gases.

Methanol, as a subsequent synthesis gas product, has potential in the fuel field, among others, in the form of derivatives such as methyl tertiarybutylether (MTBE), dimethyl carbonate (DMC) and dimethyl ether (DME). Moreover, chemistry raw materials such as ethylene or propylene (MTO-techniques) and alkyl aromatics can be produced via dehydration reactions catalyzed by zeolites.

Dimethyl carbonate is produced by the oxidative carbonylation of methanol or by methanolysis of ethylene carbonate and is increasingly replacing phosgene in the production of polycarbonates. An efficient synthesis directly from CO_2 is not yet known. The replacement of the highly toxic phosgene by derivatives of carbonic acid such as dimethyl carbonate or urea would also be interesting for the synthesis of isocynanates.

Formic acid is the industrial chemical that is chemically most closely related to CO_2. The hydrogenation of CO_2, for example, is possible by homogeneous noble metal complexes under basic conditions leading to formiates from which formic acid first has to be released by thermal cleavage. This has not yet been solved. Likewise by hydrogenation of CO_2, methyl and dimethyl formamide can be produced, whereby here the problem of processing is easier to solve.

Upon keeping the C=O or COO-functionality, further interesting target products are: carbonic acids, esters, lactones, polyesters, polylactones, polycarbonates, cyclic carbonates as well as urea derivatives. Polycarbonates, based on the reaction of alkene oxides with carbon dioxide are already commercial; they are used as packaging foils because of their high elasticity and transparency.

In nature, CO_2 is used to create biomass by means of photosynthesis. The formation of biomass is accelerated by increasing the CO_2 concentration; this is technically exploited in greenhouses in which exhaust gas from natural gas-operated heating units is directed into the greenhouses. On a pilot scale, the separation of CO_2 is being tested using green algae; these can then be used as valuable products as is described in Chapter 4.3 “Non-food Biomass”. Also being investigated is if the use of C_4-plants – which are plants having C_4-componds as the first product of carbon dioxide fixation – leading to increased efficiency of CO_2-fixation as opposed to the use of C_3-plants.

Need for Further Research

More energy-efficient techniques have to be developed for separating CO_2 from the stack gases of power plants, whereby the gas also has to be practically free of substances that act as catalytic poisons. The CO_2-reaction to fuel components and chemical raw materials is particularly challenging in the field of catalysis and chemical engineering. For example, in the dry reforming, still unsolved problems are the high catalyst costs, the too low residence time and the coking of the catalysts. In the production of DMC from methanol and carbon dioxide, the essential tasks are to develop more active catalysts as well as possibilities for separating product water from the reaction mixture. Suitable membranes that shift the equilibrium might achieve this. In the hydrogenation of CO_2 to formic acid, the product processing and the catalyst separation have not been satisfactorily solved for large-scale production.

The material utilization of CO_2 represents a strategically important concept which – on the long term and in combination with cost-effective CO_2-free methods for H_2-generation and the use of renewable resources – can lead to novel technologies for ensuring the raw material supply. Quantitatively, the application of carbon dioxide for fuels is ten times greater than its use for chemistry raw materials.

5. Inorganic Raw Materials

In the first part of this position paper, the various sources of carbon-containing raw materials have been presented. Besides them, numerous other elements are of high importance as raw materials for the chemical industry. This applies for metals (such as noble metals, alkali metals, alkaline earth metals) as well as non-metals (such as sulfur, phosphorus) as well as the semiconductor elements (such as silicon, germanium). In this context, it should also be mentioned that the chemical industry plays a decisive role for supplying the raw materials of the semiconductor industry.

Many of these elements are strategic for the production of chemicals and fertilizers, because either they cannot be replaced or it is difficult to substitute them. Recently, a number of studies have described the dependency on very few supply countries as well as, in a few cases, the relatively short depletion point resulting from small natural supplies of these elements (e.g. study of the FhG-ISI, “Rohstoffe für Zukunftstechnologien: Einfluss des branchen-spezifischen Rohstoffbedarfs in rohstoffintensiven Zukunftstechologien auf die zukünftige Rohstoff-nachfrage” (“Raw materials for future technologies: Influence of the sector-specific raw material demand in resource-intensive future technologies on the future resource demand”)). This study specifically cites gallium, neodymium and indium as critical elements.

Already in the past there have been supply shortfalls due to increased demand for elements that resulted in drastic price increases (e.g. for rhodium or platinum). In these cases, alternatives were usually developed by means of chemical innovations. Another means to compensate for these shortfalls is recycling which can and must be more extensively applied in the future.

A very current example is indium. The material ITO (indium tin oxide) is used extensively as a transparent, electricity-conducting layer in flat-screens. But, much greater amounts of indium would be needed upon the market introduction of CuInSe-solar cells (CIS). Because an increased production of indium seemingly could not be realized due to limited reserves of this element, Sharp terminated the development of CIS-solar cells because of this expected supply deficiency.

A complete analysis of the inorganic materials applied in chemical production is beyond the scope of this paper. Thus, the following handles a few important inorganic raw materials as examples.

5.1 NOBLE METALS

A few representatives of the noble metals are of considerable strategic importance for the chemical industry - beyond the large number of applications in the jewelry industry as well as in electrical engineering and electronics industries. Automotive exhaust catalysts represent the most important chemistry related product: each catalyst contains about three grams of noble metal – mostly platinum, palladium and rhodium – as a thin layer on a ceramic honeycomb. Noble metals are just as important for large chemical processes for producing bulk chemicals (e.g. the ammonia oxidation on platinum nets for producing nitric acid or the homogeneously catalyzed hydroformylation at rhodium catalysts for producing butanal from propene). Noble metals likewise play an important role in the hydrogenation and dehydrogenation processes in the petroleum oil processing and in chemistry. Numerous soluble noble metal complexes are applied in homogeneous solution for manufacturing fine chemicals.

Availability

The most important producer countries for noble metals that are very important for catalysis are South Africa (79% for platinum (Pt), 34% for palladium (Pd), 87% for rhodium (Rh); Russia (12% for Pt, 51% for Pd, 9% for Rh) and North America (5% for Pt, 12% for Pd, 2% for Rh). Altogether, the world mine production amounts to 220 tonnes Pt, 215 tonnes Pd and 25 tonnes Rh per year. In addition, there is gold, important for jewelry and as a currency metal with a worldwide mine production of 2,500 tonnes per year as well as silver, important for jewelry, photography (with a clearly decreasing trend) as well as in electronics with a yearly production of 20,000 tonnes. Besides the production from ores, recycling is playing an increasing role. The recycling quota for technically applied catalysts is > 90%, and for automotive exhaust catalysts, > 50%; in addition to this, there are noble metals recycled from electronic wastes. Whereas gold and silver are stored in great amounts (as jewelry and as reserves of central banks) and are thus relatively easily mobilized upon increasing demand, this does not apply for platinum group metals that are important raw materials for catalysts. In the past this temporarily caused a pronounced market imbalance with strongly rising prices for palladium, when its demand for diesel exhaust catalysts was estimated to be very high.

The mine production has been extended as a consequence of the significantly rising prices from past years up to the beginning of the worldwide financial crisis. Nonetheless, mines cannot quickly react to strong increases in demand. At the same time, it has to be emphasized that today, the reserves of Pt, Pd and Rh that are exploitable at a value that corresponds to 1.5-times the value of these reserves a decade ago yet amount to 150- to 200-times the current consumption. With regard to the supply security, one has to take into account, however, that there are countries which can apply as safe supply countries only with restrictions.

Scientific and Technological Challenges and Solutions

The availability of noble metals may be raised, in particular in the case of automotive exhaust catalysts, as the result of R&D efforts by reducing the metal loading (about half of the yearly consumed Pt and Pd as well as over 80% of Rh go into the latter application). Further efforts focus on substituting these noble metals with other, better available metals.

Need for Research

Opportunities for catalysis research are the replacement of noble metals by non-noble metals and the reduction in the use of noble metals by optimizing the catalysts. There is a need for further research for techniques which allow for a better exploitation of the reserves, i.e. new extraction techniques in order to raise the mine production. Furthermore, the recovery rate of noble metals should be increased in technical applications such as in electronics and computer wastes by improving recycling processes.

5.2 LITHIUM

Inorganic lithium compounds, among which lithium carbonate, lithium hydroxide and lithium chloride are economically the most important, are found in a variety of applications. Lithium carbonate is used as starting material for the production of lithium-ion batteries. Today, these batteries are predominately used in electrical devices such as mobile telephones, notebooks and electrical tools. For the future, the more important use will be to power electric cars. In the aluminum industry, lithium carbonate is used as an additive in the aluminum electrolysis for an improved process by reducing the emissions and decreasing the energy demand. In the glass industry, lithium carbonate improves the thermal stability, e.g. of Ceran cooking stove elements. As an additive in the production of enamel surfaces, lithium salts increase the flow behavior, decrease the melting point and improve the resistance to chemicals. In the construction industry, lithium carbonate is used as an accelerator for fast-hardening building components such as tile adhesives or industrial floors. Moreover, a number of further lithium salts are produced from lithium carbonate for various industrial applications. As a pharmaceutical active ingredient, lithium carbonate is also used to treat manic depression.

Lithium hydroxide increases the thermal stability of high-performance lubricants and is applied in the CO_2-absorption in submarines, in the aerospace as well as in mining industries.

Lithium chloride is primarily important as a starting material for the electrolysis for producing lithium metal which represents the basis for the entire metallo-organic lithium chemistry. Organic lithium compounds are used in the synthesis of polymers, pharmaceutical products, in agricultural chemistry and in other application fields of organic synthesis. Moreover, highly pure lithium metal is applied as anode material in small high-performance primary batteries, for example, in heart pacemakers.

Raw Materials Base

By far, the greatest part of the worldwide demand for lithium salts is covered from the South American salt lakes. The worldwide largest reserves lie in the Chilean Atacama Desert. Other reserves that are partially exploited or are being explored lie in bordering Argentina and Bolivia. About 60 % of the world demand is currently met from South America. Plants for extracting lithium from salt lakes are also found in China, Tibet as well as in Nevada, USA. The largest mineral reserves are found in the USA, Australia, China and Canada.

For extracting the raw material, there are principally two technical methods that are based on different starting materials. First of all, lithium is found as lithium oxide in minerals, mainly in spodumene that is mined in strip- and underground mines and is further processed in several steps to lithium carbonate. In these processes, great quantities of ore rocks have to be processed under an enormous energy input so that the 1.5% to 7% lithium oxide contained in the ore can be extracted.

The second method for extracting the raw material involves using brines from the salt lakes. Generally, these lakes are dried up on the surface and the salt-containing brine is pumped from deep below. In artificially setup evaporation ponds, the dry and warm desert climate is exploited for this purpose. At the end of the evaporation, the contained lithium is concentrated from a concentration of 0.16% at the beginning to that of 6% after 18 to 24 months. The further processing takes place in a chemical plant in which subsequent process steps remove the contaminants boron or magnesium. At the end of the process, lithium carbonate results as a white powder.

The production of lithium salts by means of evaporation takes place with only minor input of energy. The resulting process by-products such as sodium-, potassium- and magnesium salts are ecologically safe. The use of energy is only necessary in later steps of the value chain, for example, in the electrolysis to lithium metal.

Middle- and Long-term Availability

In the past years, the consumption of lithium salts has increased by about six to eight percent per year due to new applications. Resulting from the market introduction of electric and hybrid cars with lithium-ion batteries, a significant increase in consumption is expected in the second half of this decade. Currently, the lithium-ion technology has no competitors regarding the further development of electromobility. The leading producers will adapt to market demand and make the necessary amounts of lithium carbonate available. Moreover, with regard to the future expected demand, numerous projects can be observed that exploit lithium reserves in salt lakes or on the basis of lithium-containing minerals.

The worldwide known and exploitable reserves are running at around 28 million tonnes lithium which corresponds to about 150 million tonnes lithium carbonate. With a current consumption of about 23,000 tonnes lithium (corresponding to 122,429 tonnes lithium carbonate) per year, these reserves are figured to last 1,217 years. According to calculations of a leading lithium producer on the basis of the future need of the automobile industry (with various scenarios of the future market penetration), the utilized resource basis in Salar de Atacama in Chile with 6.9 million tonnes reserves will suffice even for the highest calculated prognosis. Considering the current cost fraction of lithium carbonate of clearly under one percent in the lithium battery, from a current perspective, unprofitable raw material sources can also be used. Theoretically, the largest amounts of lithium are found in seawater, but in a low concentration (0.000017 percent by weight).

Scientific and Technological Challenges

The actual technical challenges consist of optimizing the process yield in the existing plants for raw material production. Also the topic of recycling will be increasingly interesting: lithium, for example, is not consumed in lithium-ion batteries and can be recycled at the end of a battery's life. Already today, lithium compounds, mainly after the use as catalyst in chemical processes, are recycled and again used in the same processes.

Need for Further Research

The research in lithium chemistry is concentrated on new applications in the fields of energy, the environment and efficiency of chemical processes. In the case of lithium-ion batteries, the development of more powerful battery cells is the focus of attention. New cathode materials as well as environmentally friendly conducting salts and additives such as lithium-bis-oxalatoborate (LiBOB) should contribute towards powering the electric car of the future. With effective lithium reagents, new chemical processes ought to produce less waste and consume less energy. The development of new lithium metal alloys will enable the construction of more stable and lighter materials. Because of its unique physical properties, lithium should further assume high priority worldwide in R&D laboratories of universities and industry.

5.3 FERTILIZERS

5.3.1 Potassium Salts

Potassium salts are primarily used as fertilizers. The term 'potassium salt' generally denotes a mixture of various salt minerals having a high concentration of potassium compounds. The most important components of raw potassium salt are halite (NaCl), sylvite (KCl), carnallite ($KMgCl_3 \bullet 6\,H_2O$) and kieserite ($MgSO_4 \bullet H_2O$). From these salt minerals, only potassium chloride and magnesium sulfate are economically used.

Occurrence

The largest deposits are found in North America (Canada and USA), Russia, Germany, the Ukraine and Belarus. Depending on the main component, one differentiates among kieseritic, sylvitic and carnallitic potassium salt. Most of the mined deposits worldwide are pronounced sylvinitic or carnallitic raw material. Extensive kieserite deposits in Germany are found in the areas of Braunschweig-Hanover in Lower Saxony, in Magdeburg-Halle in Saxony-Anhalt as well in South Baden and in the Werra-Fulda region in Hesse and in Thuringia.

Considering today's state-of-the-art technologies, only a small fraction of the geological reserves (ten billion tonnes K_2O of about 200 billion tonnes K_2O) are exploitable. Yet even those reserves that can be currently exploited will last around 170 years (consumption: 58 million tonnes per year). Of the enormous supplies in the Commonwealth of Independent States (CIS) and in Canada, only insignificant amounts have been mined as yet. The recently discovered and not yet fully developed deposits in Thailand/Laos, Argentina and China also have geological potential and will be increasingly important in the respective regions.

Processing to Fertilizers

There are various qualities of fertilizers depending on the desired product and refining process. Generally, the product applied in agriculture has a purity of about 93% KCl. Further processing is necessary, because the mined raw salt only has an average concentration of 20-35% KCl. On above-ground plants, the applied processing techniques are flotation, hot-extraction or electrostatic separation. Depending on the processing technique, the product is then dried and formulated (e.g. granulated).

Application

Potassium salts are so important as fertilizers, because potassium is a main element of the plant nutrition and is crucial for metabolic processes. It is essential for the conversion of sugar to starch as well as in the synthesis of proteins. This promotes the growth of plants and the quality of the products in a sustainable manner. Moreover, the K^+-ion concentration increases the osmotic pressure and regulates the water household of the plants. Sufficient potassium fertilization improves the ability of plants to adapt to arid conditions and frost as well as to utilize their other nutrients. Thus, the stability of the plants is indirectly increased.

Highly pure potassium chloride is used in the chemical industry, in polymer production, in the food industry as well as in medicine.

Estimated Trends of Consumption and Supply Security

The worldwide population growth, the changed consumption habits, the increasing economic strength mainly in Asia and the increasing use of bioenergy all are leading to intensified land use. Consequently, up to 2013, there is an expected increase of three to five percent in the annual demand for potassium fertilizers, whereby already in 2007 the production fell behind the demand. The North American and CIS producers reported that they would increase production. The extension of production capacity depends greatly on the price development, since considerable investments are necessary. It is expected that on the middle term, there will be continued shortfalls in the potassium supply, because increasing capacities can only be realized slowly. However, in general, the supply of potassium is not endangered, and especially Germany is in a good position.

5.3.2 Phosphates

The most important applications of phosphates are for fertilizers (> 80 %), detergents, as well as animal feed and foodstuffs. For this, the mostly insoluble phosphate ores are extracted and converted to phosphoric acid or soluble phosphate salts.

Occurrence

Phosphates are derived from minerals such as apatite, $Ca_5[(PO_4)_3(OH,F,Cl)]$. The main deposits lie in northern Africa (Morocco, Western Sahara), Florida, Russia (Cola Peninsula), South Africa and China. The geological reserves of 56,000 million tonnes (source: British Sulphur, 2005) are expected to last for ca. 300 years relative to current consumption. There are two types of phosphate deposits: sedimentary raw phosphate is mined in North Africa, the Middle East, China and Florida, whereas magmatic raw phosphate is mined in Russia and South Africa.

The raw phosphate qualities of the deposits are very different. They are defined by the phosphate content as well as the concentration of the undesired fractions. Examples for this include insoluble components such as SiO_2 or heavy metals such as cadmium or uranium that interfere in the processing, storage or use of the phosphates. Typical concentrations are: 30-40% P_2O_5, 2-10% SiO_2 as well as 5-100 ppm Cd. Magmatic raw phosphates are especially valuable. Nonetheless, the processor companies often apply a mix of raw phosphates from various sources, in order to ensure an optimal output via a constant product quality. Moreover, as phosphate ores also often contain uranium, uranium-rich potassium deposits are also exploited to produce uranium.

The worldwide raw phosphate production is currently around 170 million tonnes per year (International Fertilizer Industry Association, IFA, 2007), of which approx. 32 million tonnes are exported annually. The largest phosphate producers are China and the USA, followed by Morocco and other North African countries. Morocco, the remaining North African states as well as the Middle East are simultaneously the most important exporting regions.

Processing to Fertilizers

Raw phosphates are poorly soluble and can hardly be used as a fertilizer. Thus, they are digested with mineral acids, mostly with sulfuric acid, in large fertilizer plants. The by-product calcium sulphate is separated (→ phosphogypsum). The mixture consisting of calcium dihydrogenphosphate and gypsum is denoted as 'super phosphate' and is a common P-fertilizer 'Triple super phosphate' or 'double super phosphate' are produced from raw phosphate and phosphoric acid and show a higher phosphorus concentration. Water-soluble phosphates are partially converted in soil to poorly soluble compounds which are subsequently slowly re-dissolved by organic acids in the plant root, thereby making themselves available for the plant. Nitrogen-containing phosphorus fertilizers such as diammonium phosphate or monoammonium phosphate are produced from ammonia and phosphoric acid.

Super phosphates and ammonium phosphates can be processed with N- and K-containing components to create mixed fertilizers in almost any desired nutrient ratio. The technically better alternative is to mash the nutrient carriers together and then granulate them to NPK-fertilizers. The NPK-compound fertilizers do not show the typical problems of blends such as demixing upon scattering or incompatibility of the components.

The digestion with nitric acid according to the ODDA-technique (Odda is a place in Norway, where the technique was developed) avoids the production of gypsum. The resulting calcium nitrate can either directly be used as a nitrate fertilizer or can be converted with ammonium carbonate to produce ammonium nitrate and lime. Hence, by means of the ODDA-process, NPK-fertilizers (from the processing acid) and calcium ammonium nitrate, an important N-single-fertilizer, can be produced.

Raw phosphates as feedstocks for the mineral fertilizer production have to fulfill numerous requirements. The P_2O_5-performance of the units – i.e. the phosphoric acid that can be further processed to P-fertilizers – is limited by non-digestible ballast in the raw phosphate. Nitric acid yields nitrogen oxide as the result of reducing agents such as organic components. Secondary components and trace substances can impair the granulating behavior. During the digestion, heavy metals remain in the NP-acid and thus enter the end products. Because the heavy metal content is legally regulated in most countries, its content in raw phosphate may not exceed certain limiting values. Moreover, because of the danger of smouldering of ammonium-nitrate-containing fertilizers, which is enhanced by the presence of impurities such as transition metal ions or chlorides, the concentration of such impurities via the raw phosphate has to be restricted.

Alternatives to Fossil Raw Phosphate

In principle, recycled products are considered as alternatives. However, sewage sludge, liquid manure or meat wastes are unsuited, because they, due to their high organic C-content, are incompatible with mineral fertilizers. The $Mg(NH_4)PO_4$ (struvite), precipitated from sewage sludge, cannot be used as a raw phosphate substitute to produce phosphoric acid, but it can be considered as a blend component for mixed fertilizers. Even though sewage sludge ash does not contain any organic carbon, it consists only of a little P_2O_5 and a high fraction of transitional metals, e.g. iron. It can then only limitedly be used to replace raw phosphate. By contrast, Ca-apatite from animal meal ash is well suited as a replacement but is only available in small amounts. The earlier usage of Thomas ground basic slagl, a by-product of iron ore mining, is ruled out for health reasons because of its high contamination with chromium.

Use

Mineral fertilizers have enabled enormous gains in agricultural productivity. Mineral phosphate fertilization, however, can also lead to an enrichment of metals in soils and, via plants, also in the food chain. Thus, limiting values have been introduced for the concentrations of cadmium, uranium and other metals in fertilizers. Phosphate is hardly present naturally in surface water bodies; however, an increased P-influx results in the growth of algae and water plants and, hence, to eutrophication of the water bodies. Since fertilizer phosphate is mostly bound in soil, the leaching out of phosphate from clay soils, however, can be practically disregarded. A bigger problem is the washing off of soil via erosion as well as the improper use of agricultural fertilizers such as liquid manure.

In Europe, the use of phosphate in detergents, e.g. in the form of pentasodium triphosphate as a water softener, has been mostly banned because of the possible eutrophication of water bodies.

Various phosphates are approved as food additives and serve as preservatives, acidifying agents, acid regulators and emulsifiers. Phosphates and phosphoric acid are applied for non-alcoholic beverages, aromatized drinks, sterilized and ultra-heated milk, thickened milk, milk powder and low-fat milk powder and as a technical auxiliary. Phosphates also play a large role in the meat industry and are components of the melting salt for soft cheeses.

Furthermore, phosphates are used in animal feed, corrosion-protection agents (phosphatization), flame-retardants as well as buffers in the neutral pH-range.

Scientific and Technological Challenges

Cost-effective techniques to separate heavy metals and other undesired by-products should be developed in order to expand the basis of use of raw phosphates.

Need for Further Research

The input of raw phosphates can be reduced through new processes for utilizing phosphate from, as yet, unsuitable recycling streams such as sewage sludge, sewage sludge ash or struvite.

6. Hydrogen for the Chemical Industry – Carbon Dioxide- and Climate-Neutral Production Methods

Motivation

Hydrogen is extensively needed to convert raw materials on the basis of coal, renewable resources and carbon dioxide to produce valuable products. As the following presents, the current techniques for producing hydrogen are linked, with few exceptions, to the emission of considerable amounts of carbon dioxide. The exceptions concern the water-electrolysis in connection with carbon dioxide-free methods (regenerative/nuclear) for generating electricity.

If the refining of the cited raw materials ought to occur in a sustainable manner and without additional emissions of greenhouse gases, economical, carbon dioxide-free methods for producing hydrogen must be developed. Such methods deal with ‘exotic’ processes that, up to now, have only been demonstrated on a laboratory scale and have shown an extremely low degree of efficiency. Because of the aforementioned potential, the efforts in this area have to be bolstered.

There are many options to produce hydrogen in a carbon dioxide-free or climate-neutral way:

- Cleavage of water
- From carbon-containing raw materials with CO_2-capture and sequestration (CCS)
- From biomass
- Methane cleavage.

Present Situation and State-of-the-Art

Today, about 50 million tonnes of hydrogen are produced, requiring two percent of the worldwide energy use. About 95% of this amount of hydrogen is based directly on the fossil starting materials coal, petroleum fractions and natural gas, whereby roughly half is produced via steam reforming of methane. This method, with an energy efficiency of 70%, represents the benchmark for all discussed alternatives. In refineries, large amounts of hydrogen are formed by reforming techniques that are internally applied for petroleum processing.

Electrolysis processes produce approx. five percent of the hydrogen quantity. Here, the chloroalkali electrolysis is economically the most important technique in which hydrogen is yielded stoichiometrically as a co-product. Water electrolyses are less important. Indirectly, the electrolyses are carbon dioxide- and greenhouse gas emitters, insofar as the electricity consumed for these processes has been generated from fossil resources. Nonetheless, the electrolysis techniques (discounting the electricity generation) likewise show high energy-efficiencies that approach those of steam reforming.

The coal- and petroleum-based processes are less efficient and have considerably higher specific CO_2-emissions than electrolyses and the steam reforming of methane. In particular, coal is being discussed as a possible, relatively price-stable and long-term source of hydrogen. Here, the carbon dioxide formed during the production should be subsequently captured and stored in a suitable long-term reservoir. The technologies for this so-called ‘carbon capture’ will have been satisfactorily developed in a few years. Then, it will be clearer what kinds of efficiency losses this additional process step involves. Underground carbon dioxide sequestration remains an open question; already today the geological problems related to this have led to public reluctance in embracing this new concept.

Thus, the scenarios for a hydrogen economy for the next two to three decades are mainly based on two hydrogen sources: steam reforming from natural gas and water electrolysis. All other method suggestions for producing hydrogen are still in their infancy.

Needs and Opportunities

Many studies exist that give guidance for public funding for hydrogen synthesis. Their value depends on the ability to realistically assess the economic and technological viability of the different alternatives. Such a feasibility estimation might be improved if already known technology know-how and well-documented R&D experience were used. In this context, chemistry has an enormous wealth of knowledge that ought to be increasingly brought into the discussion.

In many future scenarios, hydrogen is the focus of attention as an energy carrier itself or as an input material for energy carriers (e.g. biofuels). This application field is mainly pushing the development of carbon dioxide-free hydrogen processes. Ultimately, the chemical industry will profit from these developments.

Scientific and Technological Challenges

The fact that hydrogen production requires enormous amount of energy is fueling the discussion about the future of hydrogen embedded in worldwide energy-efficiency strategies. In contrast, the chemical industry, as hydrogen consumer, is insignificant. Also optimistic scenarios with high growth rates of renewable energy forms do not assume that, within the next two decades, there will be free amounts of inexpensive energy from sources with a low carbon dioxide-footprint. Thus for the time being, hydrogen will not play a significant role as an energy carrier. In the following decades, this situation might change because of technical innovations in regenerative energies and increasing prices for fossil fuels.

Solution Approaches

There are two options to produce hydrogen without forming carbon dioxide:

- Hydrogen is produced from carbon-free substrates (whereby H_2 ultimately originates from H_2O).
- The carbon of the starting material is classified as ‘climate neutral’ and is excluded from the synthesis balance.

For the first option, the energy expended to cleave the water has to be generated carbon dioxide-free. Here, the criteria ‘carbon dioxide-free’ is limited to the pure energy production and excludes the energy consumption from the construction and maintenance of the units. The second option uses ‘climate-neutral’ biomass and techniques with subsequent capture and sequestration of carbon dioxide (CCS). One variant might be the cleavage of methane into carbon and hydrogen so as to store carbon and not carbon dioxide. All these pathways will only be successful via modern chemical-technical methods that enter, to a large part, new territory. The following new routes for producing carbon dioxide-free hydrogen are being discussed:

Combination of water electrolysis with electricity generated from carbon dioxide-free/renewable sources: This solution is already technically realizable today and shows, regarding the electrolysis, a high energy-efficiency. Research is needed regarding some methods for energy generation from carbon dioxide-free/renewable sources such as solar energy, photovoltaic and wind power, whereas as hydroelectric power and nuclear energy are mature technologies.

Hydrogen from biomass: Like from coal, hydrogen can also be produced from biomass. Since many technology components are applicable in both fields, the proponents of this route see that the aim can be reached early on. Moreover, hydrogen can be produced from biomass via fermentation. The corresponding carbon dioxide is considered to be climate-neutral and might also be able to be easily separated because of its high concentrations in the exhaust gas. Nonetheless, there are considerable ecological and process engineering limitations. Even if C_4-plants are used which show a higher photosynthetic energy yield than C_3-plants, the plausible total yield of hydrogen is very low. The often very high water consumption, the logistics, the effort expended for fertilizers and technical equipment altogether make the production of hydrogen from biomass difficult. Numerous open questions make it currently impossible to quantify the technical potential for hydrogen from biomass. A possibly decisive argument for biomass is the low price of plant photosynthesis against which other hydrogen production processes cannot compete.

Photobiological water cleavage with green algae and purple bacteria: The fundamental mechanisms of hydrogen formation (instead of carbon dioxide fixation) are established. Energy yields of about ten percent would be possible. However, the performance and stability of current laboratory organisms are far away from this possible optimum. Moreover, the reactor design and the total processing are only in rudimentary stages. A serious problem is the stoichiometrically formed (aggressive) oxygen. Thus, concepts are being followed to decouple the oxygen formation with respect to time/space.

Photo(electro)catalytic water cleavage: The cleavage of water can be obtained with inorganic as well as with (metallo)organic catalysts. Similar to biological systems, only a part of the sun's spectrum can be used. The task of research is to adapt the energy levels of the catalyst to both the processes, hydrogen formation and oxygen development, and to link the reductive two-electron step (H_2) with the oxidative four electron step (O_2). Principally, similar degrees of effectiveness as those of photovoltaic might be attained which would be more than double those of photobiological systems. Here, the process engineering is also in the developmental stage.

Thermal water cleavage: The development of this approach has stagnated, although there are known already about 400 systems to decompose water in regenerative cycles to oxygen and hydrogen, and research has been intensively conducted beginning decades ago. Here, the chemistry is based on well defined reactions, and the separation of both partial steps is already given depending on the reaction. Technical problems result from the partially very high reaction temperatures and the often very aggressive reactants. Solar energy and nuclear power plants might supply the thermal energy for this route.

Hydrogen and carbon from methane: A currently proposed route exploits the already well-examined cleavage of methane into carbon and hydrogen – an attractive option with regard to energy. Storing carbon ought to be technically easier than storing carbon dioxide. Because one assumes that enormous amounts of energy are stored in the form of methane hydrates, the 'petroleum era' might evolve into a long 'methane era'. At the same time, methane emissions from these warming natural sinks should be avoided in order to defuse another climate problem. As long coal is still mined and used for energy generation with resulting carbon dioxide emission, the sense of such a technique would have to be doubted. A more positive evaluation might be if the resulting carbon could be materially used, e.g. as a reducing agent in the steel production.

Need for Further Research

As has been presented, there is a considerable need for further research with regard to almost all climate-neutral techniques for producing hydrogen. Mainly the photobiological water cleavage as well as the photo(electro) catalytic water cleavage are still in the stage of fundamental research.

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