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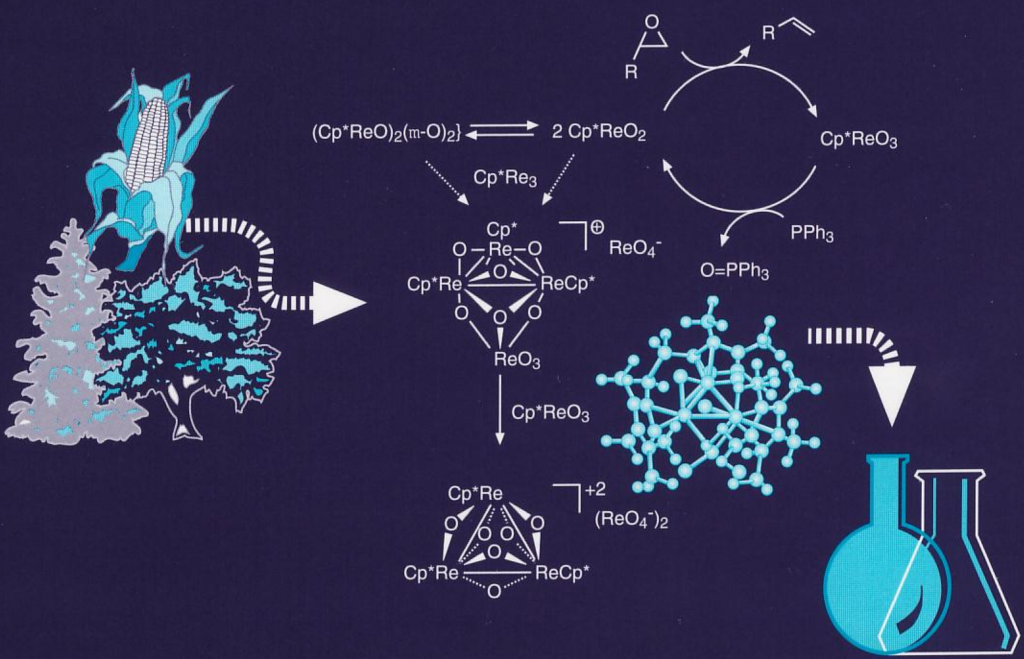
Feedstocks for the Future

Renewables for the Production of Chemicals and Materials



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Renewables for the Production of Chemicals and Materials

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Chapter 2

Sustainable Development and Renewable Feedstocks for Chemical Industry

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The principles of the United Nations Conference on Environment and Development (UNCED), held in June 1992 in Rio de Janeiro, the World Summit on Sustainable Development, held in August 2002 in Johannesburg, and Agenda 21, the comprehensive plan of action for the 21th century, adopted 12 years ago by more than 170 governments, address the pressing problems of today and also aim at preparing the world for the challenges of this century. The conservation and management of resources for development are the main focus of interest, to which the sciences will have to make a considerable contribution. The encouragement of environmentally sound and sustainable use of renewable natural resources is one aim of Agenda 21. In this contribution we investigate innovations in chemistry for such a development focusing exemplarily on chemical uses of fats and oils as renewable feedstocks. Since base chemicals are produced in large quantities and important product lines are synthesized from them, their resource-saving production is especially important for a sustainable development. New processes based on renewable feedstocks are significant here. Most products obtainable from renewable raw materials may at present not be able to compete with the products of the petrochemical industry, but this will change as oil becomes scarcer and oil prices rise. In the long run, renewable resources could replace fossil raw materials. The competition of the cultivation of food and of feedstocks for industrial use can be met by a global program of reforestation of areas wasted in historical time by human activities.

Introduction

First of all, we should have a thorough and very precise understanding what **sustainable development** may be. In principle that is quite simple; in practice it is much more difficult (*1,2*).

For example: may the international space station contribute to a sustainable development of mankind as claimed by the German ministry of Science and Technology? "One key principle of German space-programme policy is that space programmes should be seen and used as important means of developing sustainable policy world-wide." (*3*)

Will the creation of the "carbon sequestration leadership forum" and the stimulation of world wide research into how CO_2 produced through burning fossil fuels can be captured at source and stored deep underground promote sustainable development (*4*)?

Can the global energy consumption, increasing continuously by more than 50% from 2001 to 2025 be sustainable? And can the distribution of the energy consumption expected in 2025 - 1 billion people in the industrialized countries consume 50%, 8 billion people in the developing countries 50% as well – be assigned as sustainable? (*5*)

And finally: Could it be possible that the results of synthetic organic chemistry performed with fatty acids obtained by saponification of the seed oil of some plants eventually become a contribution of chemistry to a sustainable development (*6,7*)?

Sustainable Development

Sustainable development is being understood as the implementation of the Rio process, as developed in the Rio Declaration and Agenda 21, (*8*) including its on-going advancements such as the Johannesburg Declaration and Plan of Implementation of the World Summit on Sustainable Development in 2002 (*9*). Science as well as industry will best contribute to promote sustainable development being devoted to the implementation of the Rio process. The 27 principles of the Rio Declaration were made concrete in the forty chapters of Agenda 21, the comprehensive plan of action for the 21st century which was adopted by more than 178 governments in Rio. We should keep in mind that these documents should be our compass to assess sustainability (*10*). Here we want to discuss some of the many unsolved problems on the way to a sustainable development outlined in Agenda 21 and some aspects of renewable feedstocks for the chemical industry exemplarily referring to Chapter 4 "Changing Consumption Patterns" focusing "on unsustainable patterns of production and consumption" and "national policies and strategies to encourage changes in unsustainable consumption patterns" (*8*).

In 1995, the energy consumption in Germany was about 14 exajoule. That is approximately the same as in 2002. The chemical industry used 1.7 exajoule, about 12 % of the total and 45 % of the energy consumed in all manufacturing processes. The main energy consumption was invested in the production of the organic chemicals. Approximately 51% of the total energy was used as feedstock for chemical products - the non-energetic consumption - and 49 % as process energy. A potential saving of about 15% of the total energy was identified by reduction of the process energy (*11*).

"Reducing the amount of energy and materials used per unit in the production of goods and services" is an important aim of Agenda 21. However, a reduction factor of 4 (*12*) or even 10 (*13*) is thought to be necessary on the way to a sustainable development. In addition to the demand for food, the demand for other goods will grow substantially with an increasing adoption of the standard of living in developing countries. That is a real challenge for chemists and chemical engineers to realize this goal in chemical processes and products. What can chemists do?

Chemistry can contribute to the conservation of resources by the development of

- more efficient and environmentally more benign chemical processes to reduce the energy consumed in chemical industry.
- chemical products that are environmentally more benign and enhance significantly the efficiency of production processes and products in the other manufacturing areas; to reduce the energy consumed in all manufacturing processes and finally and most important
- products that allow the consumer to use resources more efficiently to reduce the energy consumed in daily life (*14*).

Base chemicals

Base chemicals, chemicals that are each produced worldwide in more than one million tons per year, are most important to discuss with respect to the conservation of resources. A large part of the energy in chemical industry is used for base chemicals and most energy may be saved by potentially improving their production processes. The gross energy requirements – the requirements of fossil energy – used for the production of some important base chemicals are given in Figure 1. It is evident that all petrochemical base chemicals have a much higher gross energy requirement – the sum of process energy and feedstock energy – than base chemicals derived from biomass such as ethanol and rape seed oil having zero feedstock energy. Here, the differences in the fossil resource consumption are so high that it can be assumed that products based on renewables must clearly be more sustainable than petrochemical products. Most interesting is the fact that the GER of ethanol derived from corn is only one third of that of petrochemical ethanol. Thus, clearly, we should begin to substitute petrochemical base chemicals by renewables. Let us consider in more detail and exemplarily propylene oxide, the base chemical with the highest GER.

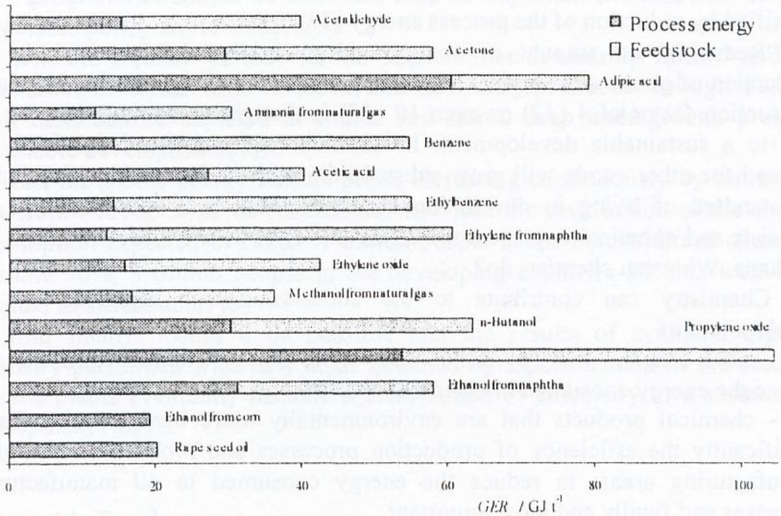


Figure 1. Gross energy requirements (GER) for important base chemicals. Data are taken from Ref. 11.

Propylene oxide is one of the top 50 chemicals. More than 4 million t/a are produced worldwide. It is reacted via polyetherpolyols to form polyurethanes and via propylene glycol to form polyesters (*15*). Obviously, the polyol and diol functionalities are used to form with diisocyanates derived from diamino compounds polyurethanes and with diacids polyesters, respectively. These functionalities are available from renewable feedstocks: carbohydrates, oils and fats, proteins and lignins.

Without any doubt, alternatives to propylene oxide and also to other oxidized base chemicals should be possible to be developed based on renewable feedstocks. We want to focus on the examples of a possible contribution of synthetic organic chemistry to a sustainable development given on vegetable oils, the renewable feedstock we are working with (*5*). Vegetable oils can easily be epoxidized (Figure 2). That is a well known industrial process. Obviously, this process should be much improved i. e. by direct catalytic oxidation using oxygen from the air (*1*).

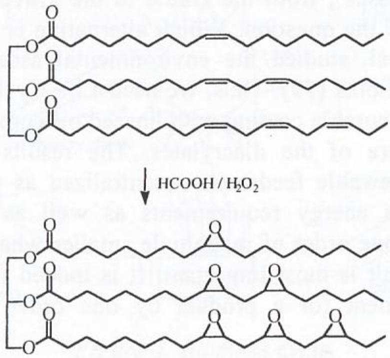
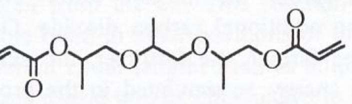
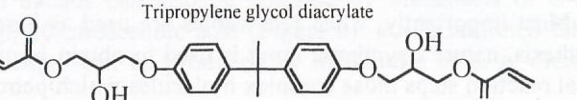


Figure 2. Epoxidation of a vegetable oil.

We introduced a UV-curable coating with linseed oil epoxide as binder that has the additional advantage that it is processed free of organic solvents thus avoiding VOCs (*1*). The initiator of this cationic curing process is, for example, a sulfonium hexafluoroantimonate (*16*). The best green as well as most economical solvent is no solvent at all in chemical reactions and especially in the processing of chemical products mostly performed by the non-chemical industry (*17*).



Tripropylene glycol diacrylate



Bisphenol A diglycidether acrylate

Figure 3. A mixture of tripropylene glycol diacrylate and of Bisphenol A diglycidether acrylate is an important petrochemical UV-curable coating (1).

However, there are of course also petrochemical UV-curable coatings available - for example a 1: 1 mixture of the diacrylates given in Figure 3 Tripropylene glycol diacrylate is produced from propylene oxide (*15*).

Agenda 21 calls for "criteria and methodologies for the assessment of environmental impacts and resource requirements throughout the full life cycle of products and processes", from the cradle to the grave. In other words, we have always to answer the question: Which alternative is greener *(18*) or more sustainable? Patel et al. studied the environmental assessment of bio-based polymers and natural fibres (*19*). Thus, we used Life Cycle Assessment (LCA) and compared the UV-curable coating with linseed oil epoxide as binder with an often used 1:1 mixture of the diacrylates. The results showed clearly the advantages of the renewable feedstock – centralized as well as decentralized processing. The gross energy requirements as well as the CO_2 and other emissions are almost one order of magnitude smaller when linseed oil epoxide was used.(*1*) This result is most important: It is indeed feasible to reduce the gross energy requirement for a product by one order of magnitude using renewable feedstocks.

Thus, the encouragement of the environmentally sound and sustainable use of renewable natural resources is an important aim of Agenda 21.

Renewable Feedstocks

The biomass cycle (Figure 4) shows the advantages of renewable feedstocks. Biomass is formed by photosynthesis; extraction gives renewable feedstocks such as vegetable oil, starch and others. These are processed to give the renewable base chemicals such as fatty acids, glycerol, glucose etc. Further processing gives the useful products that, after utilization, can be biologically degraded to give again carbon dioxide and water. That is the ideal type of biomass cycle giving no additional carbon dioxide. Of course, some process energy is needed for the farmer, the fertilizer, the extraction and processing. However, the chemical energy accumulated in the product comes completely from the sun. In contrast, petrochemicals are derived completely from fossil feedstocks. Most importantly, when renewables are used as base chemicals for organic synthesis, nature's synthetic input is used to obtain in one or only very few chemical reaction steps those complex molecules which petrochemically are only accessible in multistep reaction sequences, thus reducing the process energy as well.

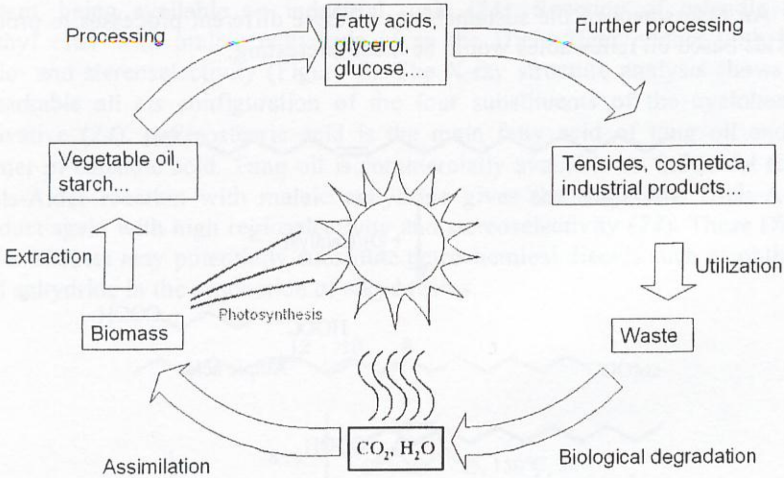


Figure 4. Biomass cycle

Dicarboxylic Acids Derived from Renewable Feedstocks

Adipic acid is a base chemical that is produced from benzene in 2.3 million t/a worldwide with a GER of about 80 GJ/t. There are important alternatives based on renewables for the production of dicarboxylic acids available.

Ozonization of oleic acid gives azelaic and pelargonic acid (*20*). However, ozone is much too expensive and energy consuming. It should be a real challenge for chemists to develop a catalyst that enables this reaction to proceed quantitatively with oxygen from the air. This reaction applied to unsaturated fatty acids with the double bond in other positions of the alkyl chain will open access to diacids of different chain length, such as adipic and lauric acid from petroselinic acid. Tridecane diacid will be obtained from erucic acid (Figure 5).

Long chain diacids can also be obtained by metathesis of ω-unsaturated fatty acids, e. g., 10-undecenoic acid (Figure 6). ω -Unsaturated fatty acids of different chain length can be produced by metathesis of e. g. oleic acid with ethylene (*7*).

Cognis developed a metabolically engineered strain of *Candida tropicalis* to oxidize a terminal methyl group of an alkyl chain. Reaction of fatty acids (e. g. oleic acid) gives the respective C 18 diacid (*21*). Remarkably, adipic acid can be synthesized in a combined biotechnological-chemical process via muconic acid that is hydrogenated to give adipic acid (*22*). One problem is that two molecules of the energy expensive hydrogen are needed for the hydrogenation step.

An assessment of the sustainability of these different processes to produce diacids based on renewables would be most interesting.

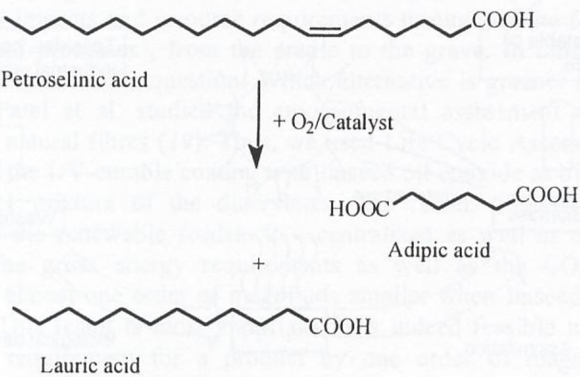


Figure 5. Oxidative scission of unsaturated fatty compounds.

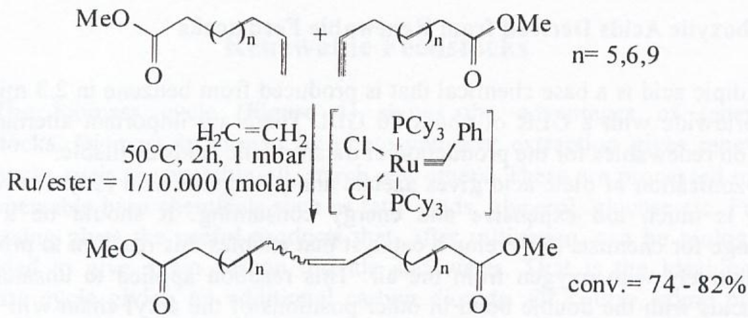


Figure 6. Metathesis of ω-unsaturated fatty esters to give long-chain diacid diesters.

Increasing the Agricultural Biodiversity

We can expect that the increasing usage of renewable feedstocks will also enlarge agricultural biodiversity. Petroselinic acid from *Coriandrum sativum* was already mentioned as a possible feedstock for adipic acid. *Calendula officinalis* offers a most interesting C18 fatty acid with a conjugated triene system, being available on industrial scale (*23*). Reaction of calendic acid methyl ester with maleic anhydride gives the Diels-Alder adduct with high regio- and stereoselectivity (Figure 7). The X-ray structure analysis shows the remarkable all *cis* configuration of the four substituents of the cyclohexene derivative (*24*). α-Eleostearic acid is the main fatty acid of tung oil and an isomer of calendic acid. Tung oil is commercially available on industrial scale. Diels-Alder reaction with maleic anhydride gives the respective Diels-Alder product again with high regioselectivity and stereoselectivity (*24*). These Diels-Alder adducts may potentially substitute petrochemical diacids such as phthalic acid anhydride in the production of alkyd resins.

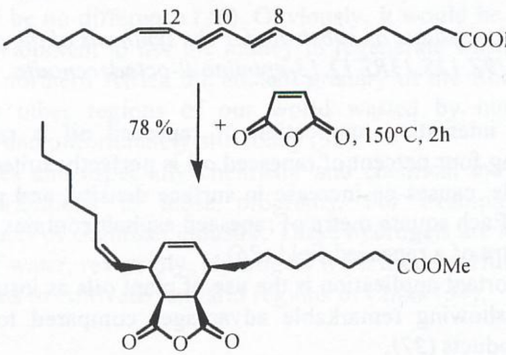


Figure 7. Diels-Alder reaction of calendic acid methylester and maleic anhydride and X-ray structure analysis of the product.

Vernonia oil is a naturally occuring epoxidized vegetable oil containing the chiral enantiomerically pure vernolic acid, thus offering most interesting synthetic possibilities. *Vernonia galamensis* originates from tropical and subtropical Africa. Nowadays it is cultivated in Zimbabwe, Kenya, Ethiopia and in parts of South America. As an example, the synthesis of an enantiomerically pure fat derived aziridine is given (Figure 8). In the first step, nucleophilic attack of azide gives the azido alcohol and an interesting fat derived pyrrol. The azido alcohol can be reduced to give the enantiomerically pure α-aminoalcohol. Reaction with triphenyl phosphine gives the aziridine (*25*).

Biodiesel, Rapeseed Asphalt, Insulating Fluids

The production and consumption of biodiesel in Germany will reach more than one million tons this year. In the European Union 2.2 Million tons are expected in this year. Biodiesel can be used as chemical feedstock as well .

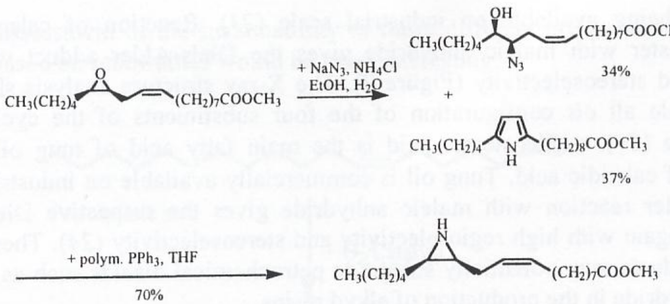


Figure 8. Methyl vernolate as substrate for the synthesis of the aziridine methyl (9Z,12S,13R)-12,13-epimino-9-octadecenoate.

A new and interesting application of rapeseed oil is rapeseed asphalt. Asphalt containing four percent of rapeseed oil is perfectly suited for the surface treatment of roads, causes an increase in surface density, and prolongs service life of the roads. Each square metre of rapeseed asphalt contains the rapeseed oil of one square metre of a rapeseed field (*26*).

Another important application is the use of plant oils as insulating fluids for electric utilities showing remarkable advantages compared to the respective petrochemical products (*27*).

Industrial Use of Renewables and Food Production.

One could ask which quantities of oils and fats and of other renewable feedstocks are available to displace petrochemicals. In 2002 the chemical industry in Germany used approximately 900,000 t of oils and fats and $1x10^6$ t of renewables such as cellulose, starch, sugar and others. That is about 8 % of total feedstock consumption of about $20x10^6$ t petroleum equivalents (*1*). This percentage could be doubled or even tripled considering the above mentioned increasing consumption of biodiesel in Germany and in the European Union. The 'Biomass Technical Advisory Committee' presented the 'Vision for Bioenergy and Biobased Products in the United States' (*28*). In 2030, 25% of the production of organic chemical products is expected to come from renewable feedstocks. However, it seems to be most difficult to substitute a higher percentage or finally the total of fossil feedstocks because an important problem most narrowly connected with the industrial use of renewables is the competition of the cultivation of food on the limited available agricultural area

(*29*). Also food demand and consumption will increase dramatically. The world population will rise from the present 6 billion to about 9 billion in 2050 (*30*).

For this reason, the UN programs to combat deforestation and desertification are most important. In short, "efforts should be undertaken towards the greening of the world", to enlarge the terrestrial biosphere (*8, 9*). Unfortunately, very little has been done to implement these programs, especially because the industrialized countries have evidently not been interested in contradiction to their obligations accepted in Agenda 21 (*31*). They have been more interested in other things, for example in the planet Mars! However, there is nothing new on Mars as one can see comparing the images taken in 2004 with the first image taken in 1976. It can be assumed that in a hundred or a thousand years there will be no difference (*10*). Obviously, it would be much better for a sustainable development to use the money to regenerate wasted areas on earth, for example in northern Africa the ancient granary of the Roman Empire or in Sinkiang or in other regions of our world wasted by human activities in historical times and unfortunately still today (*32*).

The sciences and especially chemistry and chemical industry could make enormous contributions to those programs. For example, hydrogels are important products of chemical industry. These hydrogels are able to bind a four hundred fold of water, reversibly. Hydrogels were used by Hüttermann (*33*) and Chinese scientists to cultivate semiarid regions in China (*34*).

CO_2-Sequestration

The UN programs to combat deforestation and desertification face another problem. The capture and storage of CO_2 is becoming necessary with the upcoming coal based economy in the coming decades of this century (*35*). A respective program was called in Germany COORETEC (CO two reduction technologies) and in the U.S. Future Gen. We mentioned already the international program to establish "a carbon sequestration leadership forum" (*4*) The costs for separation of CO_2 are estimated to 18 – 60 €/t and for transport and deposition to 10 – 24 €/t. However, the most efficient system of CO_2 sequestration, validated over millions of years, is the terrestrial biosphere. Costs for sequestration of CO_2 by reforestation are estimated to be 1 – 5 €/t. Important additional advantages of a reforestation would be the generation of sufficient biomass for chemical and energetic use, the improvement of the global climate and the improvement of water retention. Furthermore employment would be generated in many developing countries (*36*).

Conclusions

In conclusion, we can see that the CO_2 sequestration program is obviously non sustainable as is the international space station, and global energy consumption and distribution. In contrast, synthetic organic chemistry with biomass as renewable feedstock including fats and oils may contribute eventually to a sustainable development. A global reforestation program of areas wasted by human activities in historical time would give sufficient biomass as renewable feedstock for chemical and energetic use without competition to food production. The greening of the world can be realized if we want to do that.

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