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Renewable Resources

Refining of Plant Oils to Chemicals by Olefin Metathesis

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Plant oils are attractive substrates for the chemical industry. Their scope for the production of chemicals can be expanded by sophisticated catalytic conversions. Olefin metathesis is an example, which also illustrates generic issues of "biorefining" to chemicals. Utilization on a large scale requires high catalyst activities, which influences the choice of the metathesis reaction. The mixture of different fatty acids composing a technical-grade plant oil substrate gives rise to a range of products. This decisively determines possible process schemes, and potentially provides novel chemicals and intermediates not employed to date.

1. Background

Today's chemical industry relies primarily on fossil feedstocks. Renewable resources[1,2] account for roughly one-tenth of the feedstock consumed. There are various motivations to increase this contribution. In view of the limited range of crude oil and natural gas, replacements are required on the long term. For the next several decades, crude oil and increasingly natural gas will very likely continue to predominate as a feedstock for the chemical industry, because hydrocarbons are simply very useful high-energy starting materials and petrochemistry is well established. At the same time, it is reasonable to assume that the importance of alternatives like coal and renewable feedstocks will gradually increase. More immediate arguments include reduced dependence on oil-producing countries, the volatility of crude oil prices, and the proven environmental risk associated with oil recovery from the deep sea and oil shale. On a different level, reduced carbon dioxide emissions are desirable in view of the potential irreversible impact on climate, but it is now generally accepted that renewable resources per se do not provide an advantage. Rather, the carbon footprint for each individual process and product must be determined (although most coal-based chemical syntheses are likely the worst option in this respect). A presumption of these and further discussions is that science and technology are able to provide solutions and put them into practice.

For the synthesis of chemicals, fatty acids are particularly attractive substrates.[3–5] Although they account for only about 2% of the biomass produced annually, roughly 35% of the renewable feedstocks currently utilized by the chemical industry are based on fatty acids.[5] About one-sixth of the natural oils and fats produced are consumed by the chemical industry.[6] In contrast to carbohydrates and most other biomass-derived feedstocks, fatty acids have substantially lipophilic character owing to the long hydrocarbon chain. This lipophilicity is the basis of the long-standing application of their metal salts as soaps, and amphiphilic properties are provided by the polar carboxylate head groups. Thus also in this regard the utilization as soaps reflects the specific molecular structure of the plant oil feedstock.

In many other instances, further functional groups in addition to the carboxylic groups of the fatty acids are desirable. The double bonds of unsaturated fatty acids lend themselves to this purpose. A well-known example is the epoxidation of triglycerides for the generation of multifunctional cross-linkers in polyurethanes.[7] While in these applications the fatty acid chain remains intact, cleavage reactions are also applied to unsaturated fatty acids. Typically, a monofunctional by-product is obtained along with the target difunctional product. Thus, ozonolysis or catalytic oxidation of the double bond yields α,ω-dicarboxylic acids and derivatives of medium chain length along with monofunctional oxygenates. Thermal rearrangement of ricinoleic acid affords undecenoic acid, which is further converted to nylon-11. In addition, heptanal is formed as a stoichiometric by-product. Treatment of ricinoleic acid with a strong base leads to C−C bond cleavage affording octan-2-ol and sebacic acid, which is utilized in corrosion inhibition and for the production of nylon-6,10. Other transformations applied to fatty acids industrially include hydrogenation, isomerization, fermentative ω-oxidation to yield linear dicarboxylic acids, and dimerization to yield branched products.[3,5]

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This repertoire can potentially be complemented by catalytic C–C linkage reactions. Olefin metathesis is an outstanding example, and it is also illustrative for general issues in the development of new concepts for the "biorefining" of renewable feedstocks to industrial chemicals by chemical routes.

Transformations of fatty acids and their derivatives have been studied broadly,[3,8] and olefin metathesis of these substrates is pursued in academia as well as industry.[9] Olefin metathesis is utilized, for example, for the synthesis of biologically active compounds and fine chemicals. Here, compounds generated from plant-oil-derived fatty acids may serve as substrates.[10] This Minireview focuses on issues specific to the implementation of olefin metathesis of plant oils for the generation of chemicals on a larger scale.

2. Metathesis Reactions of Unsaturated Fatty Acids

Olefin metathesis[11,12] was employed on a large scale already nearly 50 years ago. In the Phillips process, propylene was converted to ethylene and butenes (a procedure which is run the other way round today).[13,14] These transformations employ heterogeneous catalysts based on metals like tungsten and rhenium. A significant expansion of the synthetic scope of metathesis came with the advent of defined metal alkylidenes as catalyst precursors.[15] Perhaps the most significant potential of these catalysts is their functional-group tolerance.

Classical heterogeneous and in situ catalysts can convert unsaturated fatty acids and oils.[16,17] Their performance in these reactions has been suggested to be limited by their tolerance towards the substrate's carboxylic acid or ester groups.[18] For example, a turnover number (TON) of 500 was reported for the ethenolysis of methyl oleate.

Recent developments comprise the self-metathesis of fatty acid derivatives[19] as well as their cross-metathesis with functionalized olefins like acrylates, acrylonitrile, and allyl chloride,[20,21] and simple alkenes such as ethylene.[22–29] In these studies, methyl oleate was employed most often as the substrate. Ruthenium alkylidenes, most prominently [(PCy$_3$)$_2$Cl$_2$Ru=CHPh] (**1**, Grubbs first-generation catalyst) and [(PCy$_3$)(η-*C*-C$_3$H$_4$N$_2$Mes$_2$)Cl$_2$Ru=CHPh] (**2**, Grubbs second-generation catalyst) have been utilized as catalyst precursors. However, alkylidene complexes of other metals are also precursors to very active catalysts for metathesis reactions of fatty acid derivatives; for example, molybdenum imido alkylidenes can display similar catalyst productivities.[27] Solid-supported defined alkylidene species have also been found to be active.[30]

A general issue to be considered is that plant oils always contain a mixture of fatty acids of different chain lengths, and in particular in addition to the monounsaturated component, the multiply unsaturated and saturated analogues are also present (see Table 1). Note that compositions can vary with the geographical source and with the type of breed. For example, high oleic sunflower oil can contain up to 90% oleic acid and high eruic rape seed oil up to 50% erucic acid. A separation is possible but tedious, and usually the fatty acid composition of the starting material for chemical conversions on a larger scale will reflect the composition of the natural feedstock. This differs not only from many academic studies on the metathesis reactions of fatty acids, but also from most homogeneously catalyzed industrial processes which employ chemically uniform reagents generated from petrochemical feedstocks. Metathesis of mixtures of fatty acid (esters) with variable numbers of double bonds will result in numerous compounds, which may be more or less difficult to separate.

Table 1: Typical compositions of common plant oils.[a][31,32]

Plant oil	Double bonds[b]	Palmitic[c] (16:0) [%]	Stearic[c] (18:0) [%]	Oleic[c] (18:1) [%]	Linoleic[c] (18:2) [%]	Linolenic[c] (18:3) [%]
palm oil	1.7	43	4	41	10	–
olive	2.8	14	3	72	10	0.6
rapeseed	3.8	4	2	56	26	10
soybean	4.6	11	4	23	53	8
sunflower	4.7	5	3	37	54	1
HO-sunflower[d]	3.0	2.5	1.5	93	2.5	–

[a] Wt% of a given fatty acid with respect to total fatty acid content. Compositions can vary from region to region. [b] Average number of double bonds per triglyceride. [c] Numbers of carbon atoms and double bonds given in brackets. [d] HO = high oleic.

Plant oil feedstocks can contain impurities such as water and peroxides which may deactivate the metathesis catalysts. This can be particularly relevant for industrial processes

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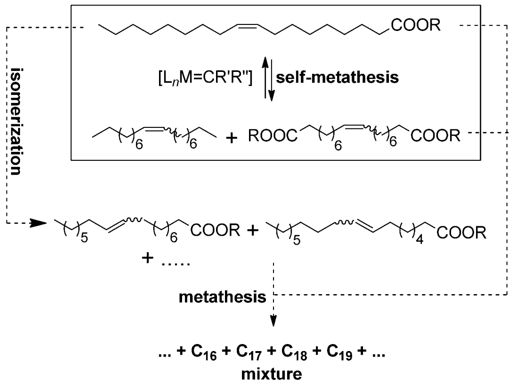
requiring high catalyst productivities (see Section 3). However, removal of impurities to low levels by, for example, distillation or filtration over inorganic absorbents[33] imposes additional cost.

2.1. Self-Metathesis

Self-metathesis of oleic acid esters yields linear monounsaturated hydrocarbons and α,ω-diesters (Scheme 1). They can be converted to the corresponding saturated waxes and long-chain diesters by hydrogenation. High catalyst productivities of several 10^5 turnovers have been reported with isolated ruthenium alkylidenes as catalyst precursors (e.g. **2**) in the self-metathesis of methyl oleate.[34] Complete self-metathesis yields a statistical 1:1:2 mixture of the two products and the starting material (isomerized to a *cis*/*trans* mixture), unless a product can be removed selectively from the equilibrium. Complete conversion thus would require separation of the reaction mixture (by e.g. vacuum distillation or crystallization) and recycling of the starting material.



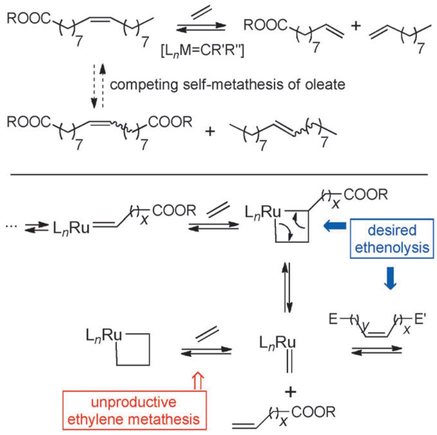
Scheme 1. Self-metathesis of a fatty acid ester and isomerization as a possible side reaction.

Isomerization resulting in double-bond migration can occur as a side reaction during metathesis,[35] catalyzed by decomposition products of the metal alkylidene catalyst.[36] This is illustrated here for the case of self-metathesis, but it also can occur in other metathesis reactions. Cross-metathesis of the double-bond isomers formed by isomerization of the starting material as well as of the primary products of metathesis would result in a range of monounsaturated hydrocarbons, α,ω-diesters, and monoesters with different chain lengths (Scheme 1). A complete separation is likely not practicable.

Subjecting triglycerides (i.e. R = trifunctional) to self-metathesis results in polymeric, cross-linked structures. Self-metathesized and hydrogenated plant oils find applications as components of cosmetics and candle waxes.[37]

2.2. Ethenolysis

Ethenolysis splits the fatty acids at their internal double bonds to terminal olefinically unsaturated compounds (Scheme 2, top). For example, methyl oleate is converted into 1-decene and methyl dec-9-enoate. This is an attractive reaction, as terminal olefins are often valuable intermediates. Even when the longer-chain products of self-metathesis (Scheme 1) are the desired products, an ethenolysis step followed by self-metathesis of the resulting terminal olefins with liberation of ethylene could be advantageous since the intermediates (e.g. C_{10} for oleate) may be easier to separate owing to their lower molecular weights and boiling points.[38] This may be relevant particularly for longer-chain-length substrates.



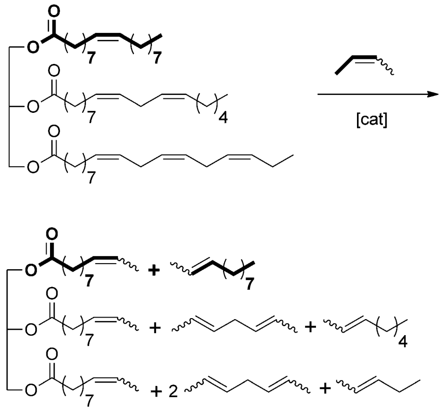
Scheme 2. Ethenolysis of a fatty acid ester (top). Simplified scheme of unproductive ethylene metathesis (bottom). E, E′ = alk(en)yl, ester.

In ethenolysis, the choice of reaction conditions can comprise a trade-off between selectivity and catalyst productivity in terms of substrate turnover. High ethylene concentrations enhance selectivity for ethenolysis over competing self-metathesis, but also promote unproductive ethylene metathesis (Scheme 2, bottom). Unsubstituted metal alkylidenes, $[L_nRu{=}CH_2]$, which occur particularly in metathesis reactions with ethylene, have a higher propensity for irreversible deactivation reactions[23,39–42] than their substituted analogues, $[L_nRu{=}CHR]$. This appears to be one key limiting factor of ethenolysis. Besides deactivation reactions involving intrinsic components of the catalytic cycle, traces of water or other polar molecules such as alcohols, peroxides, and free radicals introduced along with the substrate may also contribute to alkylidene decomposition.

High selectivities exceeding 95 % have been reported for the ethenolysis of methyl oleate catalyzed by ruthenium complexes with N-heterocyclic carbene ligands, as well as by molybdenum alkylidenes. In general, productivities corresponding to several 10^3 turnovers have been reported (higher values have been observed at low conversions).[23–27] This is currently still below the estimate of TON = 5×10^4 given by different companies as a requirement for a commercially viable, larger scale process.[23,24]

2.3. Alkenolysis

By comparison, cross-metathesis with internal olefins, like self-metathesis (Section 2.1), can be performed with very high turnovers. For the cross-metathesis of methyl oleate with 2-butene, productivities of up TON = 5×10^5 have been reported.[33,43] Careful purification of the oleate substrate by distillation as well as the utilization of pure butadiene-free 2-butene was required for this catalyst performance. The symmetric nature of 2-butene limits the number of possible products in this reaction (provided substantial isomerization does not occur). Nevertheless, owing to the multiply unsaturated fatty acids in technical plant oils, a range of products can form in the metathesis of plant oils in general. This is illustrated in Scheme 3 for the butenolysis of triglycerides of C_{18} fatty acids. The utilization of an internal olefin as the reagent for alkenolysis avoids the formation of sensitive methylidene ruthenium intermediates. The ethylidene ruthenium intermediates that occur have been shown to be highly active in metathesis.[44]

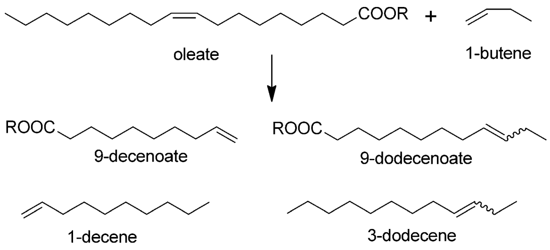


Scheme 3. Butenolysis of a model unsaturated triglyceride made up of oleic, linoleic, and linolenic acid.

Alkenolysis with terminal olefins can also be performed with relatively high productivities. For butenolysis with 1-butene TONs of roughly 10^5 have been reported.[33] A broader range of products is formed by comparison to alkenolysis with 2-butene. These products include the valuable 1-olefins and internal as well as terminal unsaturated esters (Scheme 4).

3. Large-Scale Industrial Scenario

In the utilization of the olefin metathesis of plant oils on a large scale, the formation of a spectrum of desirable products as well as catalyst performance are obvious crucial issues. Based on the considerations mentioned in Section 2, alkenolysis with a 1-olefin can in a sense represent a compromise between these issues. On a technical scale, short-chain olefins like propylene and 1-butene are attractive because of their low cost. As an aside, storage and transportation of these compounds to sites outside a pipeline network are less problematic than for ethylene.



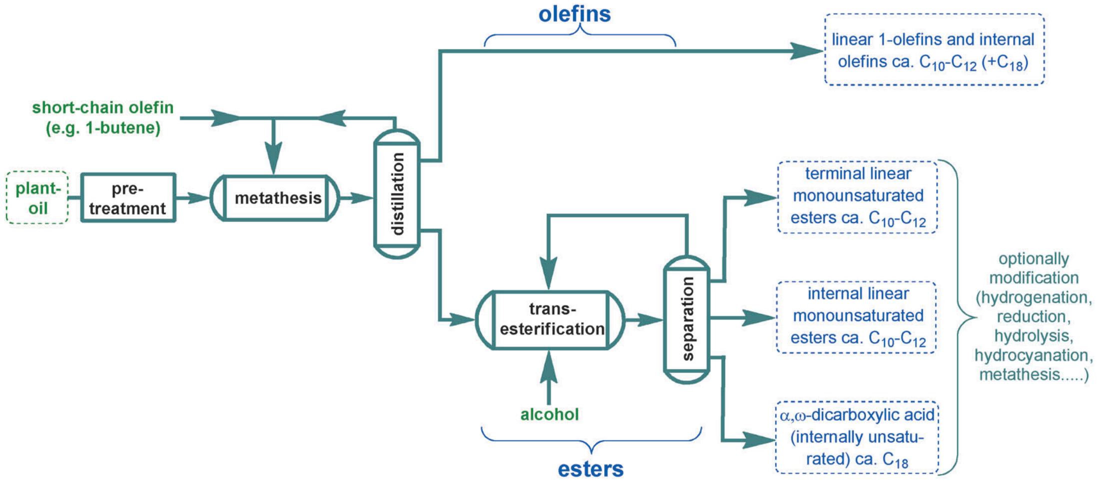
Scheme 4. Main products of the cross-metathesis of 1-butene with an oleate.

Regarding the plant oil substrate, a high content of monounsaturated fatty acid is desirable if the additional shorter-chain compounds that are formed from metathesis of multiple unsaturated fatty acids are not the primarily desired products. Amongst the available plant oil sources, palm oil (Figure 1) stands out with an annual yield of four tons of oil per hectare; this exceeds the yield of sunflower, rape seed, and soybean significantly.[45]

Figure 1. Palm tree plantation.

A possible industrial process[46] involves metathesis of purified plant oil with 1-butene (Schemes 4 and 5). In this step, a high excess of 1-butene would favor cross-metathesis of the plant oil over its self-metathesis, but would also result in undesirable excessive self-metathesis of the 1-butene. Thus, reaction conditions will likely be such that a relevant portion of the plant oil feedstock is converted to self-metathesis products. In a subsequent separation step, the hydrocarbons (olefins) are separated from esters. This separation can be facilitated when the metathesis is carried out on the triglycerides, since the ester-containing compounds in the reaction mixture are then much higher boiling than the hydrocarbons. In this scheme, transesterification to monoesters is carried out only subsequent to the aforementioned separation (Scheme 5). Note that the saturated fatty acid components of the plant oil (Table 1) would be transesterified with the ester stream to give the monoesters, most commonly the fatty acid methyl esters (FAME), and isolated in the subsequent separation step (this fraction, and also the glycerol formed by transesterification, is omitted in Scheme 5 for clarity). Note also that the self-metathesis of triglycerides, a relevant side reaction of butenolysis, will result in oligomeric and polymeric esters (see Section 2.1), which may complicate the handling of the product mixture owing to their high viscosity.

The 1-olefins obtained from oleate by these routes consist primarily of 1-decene. This chain length is suitable, for



Scheme 5. Scheme of an alkenolysis process that converts plant-oil triglycerides to medium- and long-chain linear olefins and esters (product chain length for C_{18} feedstock with oleate as a major component. Products from saturated fatty acid components in the feedstock are not shown).

example, for oligomerization to produce lubricants.[47,48] Internal olefins, mainly 3-dodecene, are formed in roughly similar amounts. An example of an existing industrial utilization of linear internal olefins in this range of carbon atoms (though with different positions of the double bond) is the conversion of petrochemistry-based C_{11} to C_{14} olefins by the Shell Higher Olefin Process[49] into linear alkyl benzene sulfonate (LABS) surfactants. The higher-molecular-weight olefin fraction originating from self-metathesis (with C_{18} as a main component) upon hydrogenation yields linear non-petroleum-derived waxes. Hydrogenation of the entire olefin stream yields n-alkanes (ca. C_8 to C_{18}) suitable, for example, as components of diesel or jet fuels.[46]

Transesterification of the triglyceride product fraction of metathesis yields an ω-unsaturated monoester; thus oleate provides dec-9-enoate. Such compounds are antimicrobially active.[50,51] Esters with internal double bonds, primarily dodec-9-enoate, are formed in approximately similar amounts. These esters may be utilized in antimicrobial surface coatings[51] and as intermediates, for example, for the production of lubricants[47c] and detergents. The double bond can be hydrogenated to yield saturated linear esters, and alternatively converted into other functional groups. For example, carbonylation, hydrocyanation, and cross-metathesis with polar-substituted olefins can provide linear α,ω-difunctional C_{11} to C_{14} esters with a second carboxylate and nitrile function, respectively, which can be converted further to an amine.[52] Linear ω-amino carboxylic acids in this chain-length range are AB monomers for nylons.

The self-metathesis products in the ester stream are α,ω-functionalized linear diesters; for example, oleate feedstock provides esters of 1,18-octadecane dicarboxylic acid (after hydrogenation). Note that the preparation of such compounds by ω-oxidation of saturated fatty acids, particularly of stearic acid to yield 1,18-octadecane dicarboxylic acid, has also been developed.[53] Metathesis thus is an alternative to this biotechnological route. Such long-chain α,ω-difunctional compounds are of interest as (co)monomers for polycondensates, like polyesters, polyamides, and polyurethanes. For example, owing to the crystallinity imparted by the long methylene sequences, long-chain aliphatic polyesters can have melting points high enough for thermoplastic processing.[54] In polyamides, the increased hydrophobicity relative to that of existing nylons results in decreased water uptake.

The presence of substantial amounts of multiply unsaturated fatty acids (Table 1) in the feedstock will result in numerous further products. Metathesis of linoleate with 1-butene affords various C_5 to C_{12} singly and doubly unsaturated hydrocarbons. Accompanying cross-metathesis of linoleate with oleate will yield further hydrocarbons and esters with chain lengths other than that of the C_{18} compounds discussed in the preceeding paragraphs.

It has also been noted that the product mixture from metathesis may be used as a fuel without further separation. A subsequent series of catalytic hydrogenations, ultimately at high temperature, saturates all double bonds and also (partially) converts esters to alkanes. In this way, the metathesis product of soybean oil with 1-butene yielded a product mixture consisting of predominantly C_9 to C_{18} alkanes, which is suggested to be applicable as jet fuel.[55]

Concerning the possible realization on an industrial scale, the construction of a plant for the conversion of plant oil by metathesis with 1-butene has been announced by Elevance (a joint venture of the catalyst company Materia and Cargill).[56,57] The initial capacity was given as 185 000 metric tons annually. The plant, which employs palm oil as a substrate, is reportedly under construction near Surabaya, Indonesia, and is to be part of a biorefinery operated by Wilmar International, a global processor of palm, palm kernel, and coconut oil. A production run on a 500 ton scale has recently been carried out at a different facility according to Elevance, presumably using the same technology.[58]

4. Conclusions and Assessment

Existing applications of plant oils as a feedstock for the production of chemicals rely on their utility as a starting material for the generation of medium- and long-chain di- or monofunctional hydrocarbons. That the substrate is renewable has not been decisive per se. Today there is an increasing and broad demand by customers of the chemical industry for products based on renewable resources. This may promote the introduction of novel processes and products—provided that their performance and cost do not compromise existing technologies. The latter restriction may be altered temporarily by political regulation, as exemplified by the requirement of a certain portion of renewables in transportation fuels in many countries. Increased cost also may not be prohibitive for some "lifestyle" niche products. Larger-scale processes, such as the technology discussed here, however, will have to be cost-competitive on the long term in order to succeed. It has been claimed that the capital as well as the operating costs of the conversion of plant oils by metathesis are lower than comparable petrochemical operations.[57]

Regarding the generation of the feedstock, the per acre yields of oil plants are not particularly high in comparison to the yields of other industrially utilizable plants. However, the high-energy, functionalized hydrocarbon feedstocks provide a convenient entry into the synthesis of certain chemicals. Since plant oils are not very low-cost feedstocks, novel approaches for their further conversion and upgrading will require efficient processes. The olefin metathesis reactions reviewed here nicely illustrate this.

The "food versus fuel" discussion may await any novel renewables-based process. Taking polymeric materials as a final product as an example, a novel class of materials prepared from renewable resources realistically would account for at most a small share of the overall production of polymeric materials. This is because a given material must possess a rather specific property profile and meet many requirements for a particular application. Even the commodity polymer polyethylene is actually differentiated into many different grades. Current worldwide biodiesel production from fatty acids amounts to roughly 20 million tons per year, though this accounts for only 1 % of total transportation fuels consumed. By comparison, bringing 100000 tons of a new polymer or other novel chemical onto the market successfully is a challenging and costly task. These arguments obviously apply to a lesser extent to the utilization of known monomers generated from alternative sources, for example, ethylene from sugarcane and 1-olefins from plant oils. From a different perspective, the replacement of 10% of the current annual polymer production of 260 million tons by renewable-resource-based new polymers is rather visionary. This again shows that, rationally considered, competition with food production is of rather limited concern with regard to the production of chemicals, particularly for specialty and performance chemicals.

The metathesis of technical-grade plant oils inevitably produces a number of hydrocarbon and ester products because of the presence of multiply unsaturated fatty acids. Since olefin metathesis reactions are often equilibrium reactions, without a strong kinetic preference for a particular product, product mixtures are formed especially when unsymmetric olefins, such as 1-butene, are employed as the reaction partner. This considered, it is a general advantage of metathesis that only linear products are formed. The term "biorefinery",[59] which is generally used rather freely, perhaps applies to this type of process scheme in the sense that, like in a petrochemical refinery, a feedstock is converted to a range of products. In contrast to the traditional petrochemical refining scheme, however, the products obtained do not correspond to basic chemicals like ethylene and propylene, which serve as starting materials for the synthesis of numerous intermediates. Instead the products correspond directly to intermediates in the current scheme of the chemical industry. For some of these products there is a clear need, as they are already utilized as intermediates today. Others can stimulate the development of new applications and markets. The development and profitability of these new applications will be critical to the success of novel processes, in addition to the process economics including the catalyst.

Given that laboratory and pilot-plant studies cannot foreclose all crucial aspects of a reaction on a large scale, future developments in this area will be exciting and further stake out the practical scope of olefin metathesis. Likewise, new avenues for the conversion of plant oils to chemicals may arise. The novel intermediates that become available can inspire the creativity of synthetic chemists to develop novel performance chemicals and polymer materials.

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