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# Useful Products from Complex Starting Materials: Common Chemicals from Biomass Feedstocks

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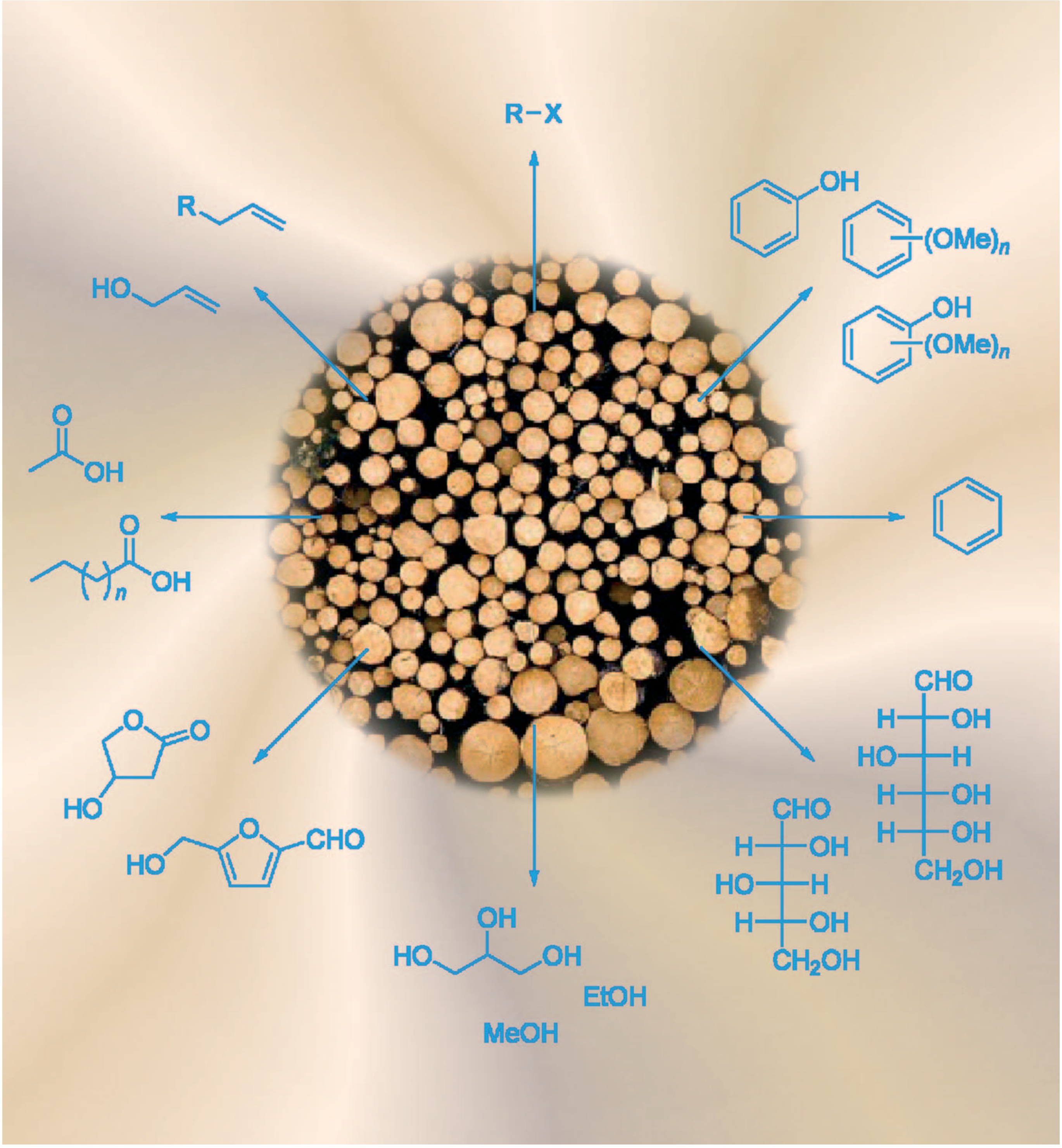


**Abstract:** A rapidly expanding area of inquiry is the use of plant biomass for the industrial production of organic compounds for which there is high demand. This interest is fuelled largely by the anticipated decline in the supply of petroleum, and the inevitable concomitant rise in cost. Over the past 30 years, significant progress has been made toward the large-scale conversion of plant biomass to common chemicals such as methanol, ethanol, glycerol, substituted furans, and carboxylic acids. However, examination of the list of top production organic chemicals reveals numerous opportunities for future development, including simple halocarbons, alkenes and arenes. Progress toward efficient and economical production of these challenging targets from biomass has recently been reported, and future success is likely to continue through academic and industrial collaboration.

**Keywords:** biotechnology • green chemistry • industrial chemistry • sustainable chemistry

## Introduction

A large fraction of organic chemistry research focuses on the synthesis of complex molecules that have desired physical, chemical, or biological properties.[1] These developments generally build complexity from comparatively simple starting materials. Most of the industrial and fine organic chemicals that are the starting materials for these studies have petroleum as their original source.[2] Because the rate at which we consume petroleum is vastly larger than the rates of petroleum discovery and/or creation, this is a sustainability issue of serious concern.[2,3]

While building complexity through synthesis has been the mainstay of organic chemistry, only recently have the reverse processes received considerable attention (Figure 1); that is, how do we take relatively complex natural materials, and generate useful chemicals from them? Given the limited supply and nonrenewability of petroleum, an important goal is the discovery of efficient methods for generating useful organic compounds from alternative resources that are abundant, inexpensive, and renewable.[4]

The most obvious alternative resource to petroleum is plant-derived material, also called plant biomass. The common sources of plant biomass include roots, tubers, stems, sap, foliage, seeds, fruits, and nuts.[4,5] Biomass from these sources is composed essentially of carbohydrates (75 %), lignin (20 %), as well as oils and proteins (5 %).[6] Currently, biomass feedstocks can provide a variety of intermediate chemicals, from which many other primary chemicals can subsequently be generated (Figure 2).[7–11] However, in general, petroleum (and the methods used to generate intermediate chemicals from it) is still cost-effective and remains the principal resource used by the chemical industry. This is due, in part, to the enormous past investment/optimization in petroleum-based methods. Nevertheless, as the world's petroleum supply decreases and petroleum costs rise, biomass-derived processes will eventually become economically competitive. In addition, continued research on the conversion of plant biomass into intermediate and primary chemicals is likely to lead to new processes and chemicals that are cheaper and more efficient than those currently known.[7,12]

Chemicals that represent ideal targets for production from alternative feedstocks include many of those that are

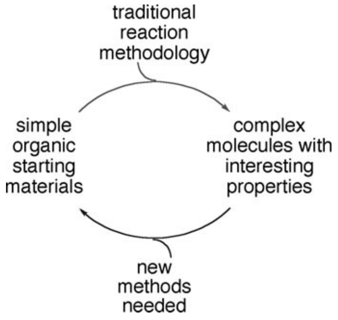
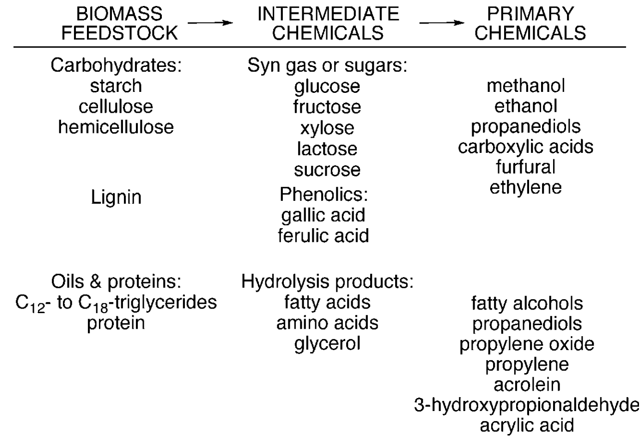


Figure 1. Traditional reaction methodology is usually used to generate complex molecules that have useful physical, chemical, or biological properties. New methods are needed to generate useful organic starting materials from abundant, inexpensive, and renewable resources.



| BIOMASS FEEDSTOCK → | INTERMEDIATE CHEMICALS → | PRIMARY CHEMICALS |
|---|---|---|
| Carbohydrates: | Syn gas or sugars: | |
| starch | glucose | methanol |
| cellulose | fructose | ethanol |
| hemicellulose | xylose | propanediols |
| | lactose | carboxylic acids |
| | sucrose | furfural |
| Lignin | Phenolics: | ethylene |
| | gallic acid | |
| | ferulic acid | |
| Oils & proteins: | Hydrolysis products: | |
| $C_{12}$- to $C_{18}$-triglycerides | fatty acids | fatty alcohols |
| protein | amino acids | propanediols |
| | glycerol | propylene oxide |
| | | propylene |
| | | acrolein |
| | | 3-hydroxypropionaldehyde |
| | | acrylic acid |

Figure 2. Conversion of biomass feedstocks into intermediate chemicals and then primary chemicals. Note that only selected chemicals are included in this figure, rather than an exhaustive list, to focus on high-use chemicals.

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currently made from petroleum (although the use of alternative resources may reveal new targets as well).[12,13] For example, the top 50 industrial chemicals include many primary organic compounds such as alkanes and halocarbons (cyclohexane and 1,2-dichloroethane), alkenes (ethylene, propylene, isobutylene, styrene, and butadiene), ethers and epoxides (methyl *tert*-butyl ether, ethylene oxide, and propylene oxide), arenes (benzene, toluene, ethylbenzene, xylene (collectively called BTEX), and cumene), alcohols and phenols (methanol, ethanol, ethylene glycol, phenol, and bisphenol A), carbonyls (formaldehyde, butyraldehyde, acetone, acetic acid, adipic acid, and terephthalic acid), and several bifunctional organic molecules (vinyl chloride, acrylonitrile, and vinyl acetate).[14] Other primary chemicals that are good targets for alternative production include "high-use" fine chemicals. For the purposes of this review article, high-use fine organic chemicals are compounds that are found in countless synthetic procedures, usually in stoichiometric (or higher) ratios. Examples of these include simple halocarbons (MeX, EtX, *i*PrX, *t*BuX, and BnX; X = Cl, Br, I) and aldehydes (acetaldehyde, propionaldehyde, and benzaldehyde). The large volumes needed of these primary chemicals provide an opportunity for enormous impact through finding alternative sources for these materials. Thus, a significant challenge for the greening of the international chemical industry is the ability to produce these primary and high-use chemicals from plant biomass, an idea that is enunciated in the twelve principles of green chemistry.[15]

A few of the aforementioned high-use chemicals are available from plant biomass by using current technologies. For example, methanol, ethanol, glycerol, glycols, substituted furans, and numerous carboxylic acids can be generated from the fermented sugars derived from broken down cellulose or hemicellulose. Several recent review articles have focused on these targets.[3,12,13,16–24]

Despite the research conducted so far, many of the aforementioned high-use chemicals are not readily available from plant biomass. In particular, the production of halocarbons, alkenes, and arenes (either directly from biomass, or from the intermediate chemicals to which biomass provides ready access) represents a challenge for future academic and industrial development. This article presents these challenging targets, which have recently been accessed from plant biomass feedstocks or biomass-derived intermediate chemicals. The goal of this contribution is to provide a critically selected treatment of the material on this subject, and to discuss unsolved problems and possible developments.

## Halocarbons

Simple halocarbons are an intriguing class of chemicals to generate from biomass. Although other alkylating agents (e.g., dialkylcarbonates) are considered to be significantly more green than halocarbons,[25,26] they are not discussed herein because we are aware of no significant developments in their production from plant biomass. The importance of halocarbons stems from their use as reagents in many chemical transformations,[26] and their potential use in the large-scale generation of key products including gasoline,[27] olefins,[28] aromatics,[29] alcohols,[30] ethers,[30] and crop fumigants.[31] In addition, halocarbon production from biomass presents a particular challenge because of the large number of oxygen atoms and the relative scarcity of halogens found in biomass.

A growing body of research has recently expanded our mechanistic understanding of halogenation enzymes, such as the haloperoxidases, which catalyze the halogenation of thousands of natural products.[35] Focusing here on simpler halocarbons, it is known that numerous plants and microorganisms naturally produce low levels of halomethanes; several methylhalotransferases (MHTs) have been characterized.[32] The production of even di- and trihalomethanes by algae and fungi is under investigation.[33] However, efforts to co-opt these systems for the production of high-use chemicals, such as mono-, di-, and trihalomethanes, are in their infancy.

**Direct production from biomass**: Given this context, a fascinating development aimed at using natural halogenation systems for the large-scale production of halomethanes merits a detailed discussion. A system developed by Voigt and coworkers[34] uses engineered yeast (*S. cerevisiae*) to express an MHT gene from *B. maritime* known to produce high levels of MeCl, MeBr, and MeI.

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*Amanda-Lynn Marshall was born in 1988 in Georgia. She completed her undergraduate studies at Seattle University where she earned her B.S. in General Science with concentrations in Chemistry and Biology. She was recently awarded a Rotary Ambassadorial Scholarship, which will allow her the opportunity to study abroad and obtain her MPH. After her studies abroad she plans to attend medical school.*

The production of halomethanes in a single reactor was accomplished by using plant biomass and sodium halide as the reactor feedstocks in a coculture of engineered yeast and wild-type (wt) *A. fermentans* (a cellulolytic bacterium). The role of *A. fermentans* is to convert industrially important, nonfood crop biomass (e.g., unprocessed switchgrass, sugar cane bagasse, corn stover, or poplar) directly into acetate ion and ethanol (Figure 3). Although these products are suppressors of the *A. fermentans* mediated fermentation, they serve as the carbon source for *S. cerevisiae*, enabling the coculture to be mutually beneficial to both organisms. Just as the bacterium relies on the yeast in the coculture for removal of these fermentation suppressors from the medium, the yeast relies on the bacterium for its carbon source and energy. Added sodium halide (NaCl, NaBr, and NaI), and naturally produced *S*-adenosylmethionine (SAM; the common biological source of methyl group transfer equivalents) serve as the source of the halide and methyl group, respectively (Scheme 1).[35] In the optimized coculture, promising levels of iodomethane are produced ($\approx 150\,mg\,L^{-1}\,h^{-1}$).

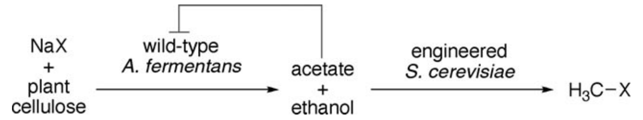
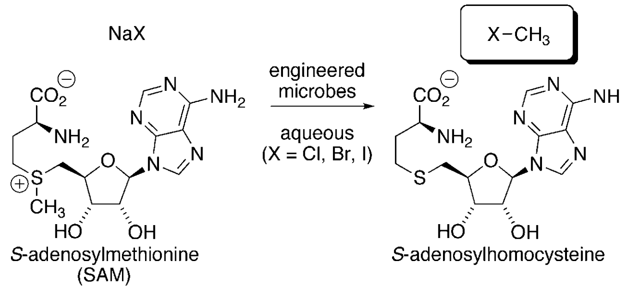


Figure 3. Production of halomethanes (X=Cl, Br, I) in a coculture of wt-*A. fermentans* and engineered *S. cerevisiae*. The bacteria produce the carbon source for the yeast, and the yeast detoxify the culture medium while producing $H_3CX$. The halogen source is exogenous sodium halide.



Scheme 1. Conversion of NaX salts (X=Cl, Br, I) and SAM (a common cosubstrate for methyl group transfer reactions) into halomethanes. The reaction is catalyzed by methylhalotransferases expressed in engineered *S. cerevisiae*.

Comparing this level of production to the annual U.S. production of iodomethane (<500000 lbs in 2006),[36] and assuming a continuous fermentation (24 h/day, 7 days/week) a coculture volume of nearly 173000 L would be needed to meet this level of production. Clearly, to make this an industrially viable process, future optimization needs to be aimed at increasing the efficiency of the system. However, this may well be worth the investment in research and development. A noteworthy advantage of this system is that it uses NaI as the halogen source, rather than $I_2$, which is used in all current industrial syntheses of iodomethane and is significantly more hazardous.[37]

Looking forward, we expect that this strategy, which takes advantage of known biocatalytic mechanisms and the power of transgenic organisms, can be appropriately modified for the generation of a range of interesting chemicals. To create this remarkable halomethane-generating system, Voigt and co-workers[34] used a synthetic metagenomic approach to generate a library of MHT genes from plants, fungi, bacteria, and unidentified organisms found in the NCBI[1] sequence database. The library of genes was then screened in *E. coli* to assess the rates of halomethane production. Finally, yeast were engineered to express the most efficient of the MHT genes and subsequently used to produce halomethanes.

In theory, this approach could be used for the production of other important high-use chemicals, such as ethylene, for which the SAM-dependent biosynthetic pathway and numerous signaling networks are well understood in several plant species.[38] Ethylene represents a particularly attractive target because it has the highest worldwide production of all organic chemicals.

## Alkenes

The production of alkenes from plant biomass represents an enormously important goal, mostly due to the mammoth scale on which polyolefins (e.g., polyethylene, polypropylene, polystyrene) are produced. Ethylene and propylene are the world's two highest production organic chemicals, and styrene is eighth on the list.[14] The combined U.S. production of these three olefins in 2002 was over 100 billion pounds.[14] In addition, six of the top eighteen organic chemicals are prepared industrially from ethylene.[14,39]

Production of ethylene by the dehydration of dimethyl ether through the methanol to olefin (MTO) process,[19] or from bioethanol using one of a wide variety of catalysts including alumina, activated clays, zeolites, and mordenite is well documented.[3,40] On the other hand, the production of propylene from biomass is substantially more challenging. Because the production of both ethylene and propylene have been previously discussed at length elsewhere, we mention them only briefly herein.[3,41]

In addition to ethylene, propylene, and styrene, numerous other alkenes are also important, or hold the potential to become high-use chemicals based on applications currently being investigated. Among these olefins are allyl alcohol, 2,5-dihydrofuran, long-chain α-olefins, and long-chain α,ω-bifunctional alkenes. Recent developments in the production of these higher alkenes from plant biomass are discussed below.

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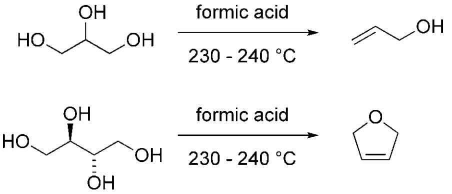
[1] National Center for Biotechnology Homepage; http://www.ncbi.nlm.nih.gov/ [accessed on April 2, 2010].

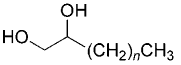
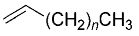
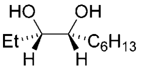
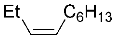
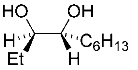
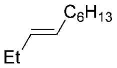
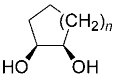
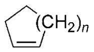
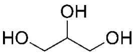
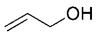
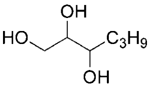
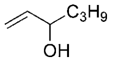
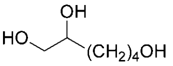
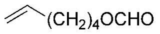
**Higher alkene production from biomass-derived intermediates**: An exciting development in the use of biomass-derived intermediate chemicals for the production of useful higher alkenes recently came from collaborative work done at University of California, Berkeley, in the Ellman and Bergman labs.[42] This work describes the direct didehydroxylation of 1,2-diols at 230–240 °C in high yields using only formic acid. The didehydroxylation reaction represents an important step in the discovery of methods to reduce the complexity of biomass-derived intermediate chemicals (e.g., glycerol and erythritol) to generate useful primary chemicals. Notably the reagent, formic acid, is an industrial chemical that has also shown promise for production from biomass,[43] making these reactions good candidates for completely biomass-derived processes.

The archetypal reaction in this paper is the conversion of glycerol to allyl alcohol (Scheme 2). Glycerol is a biomass-derived intermediate chemical; it is the primary byproduct in triglyceride transesterification, an important step in biodiesel production. Also demonstrated is the conversion of erythritol (*meso*-1,2,3,4-tetrahydroxybutane) to 2,5-dihydrofuran (Scheme 2). This, too, is important since polyols such as erythritol can be generated from the largest class of plant biomass—carbohydrates. The scope of these reactions was investigated by using petroleum-derived polyols, and the substrates investigated demonstrate the ability to generate α-olefins, *cis*- or *trans*-internal olefins, cycloalkenes, allylic alcohols, and α,ω-alkene formates (Table 1). Importantly no alkene isomerization (*cis*↔*trans,* or terminal↔internal) was observed under the reaction conditions.

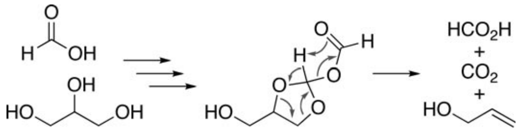


Scheme 2. The formic acid mediated didehydroxylation of glycerol and the cyclodehydration–didehydroxylation of erythritol.

Table 1. Scope of didehydroxylation reaction[a] demonstrates the ability to generate α-olefins, *cis* and *trans* alkenes, cycloalkenes, allylic alcohols, and α,ω-alkene formates.

| Entry | Substrate | Product | Yield [%][b] |
|---|---|---|---|
| 1 |  |  | $n=5$; 91<br>$n=7$; 93 |
| 2 |  |  | 74 |
| 3 |  |  | 83 |
| 4 |  |  | $n=1$; 86<br>$n=2$; 78<br>$n=4$; 96 |
| 5 |  |  | 80 |
| 6 |  |  | 56 |
| 7 |  |  | 84 |

[a] Formic acid, 230–240 °C. [b] Isolated yield.

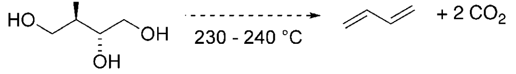


Scheme 3. Proposed *ortho*-ester-type intermediate in the formic acid mediated reaction to form allyl alcohol from glycerol.

Evidence suggests that the reaction proceeds through an *ortho*-ester-type intermediate, which undergoes thermal decarboxylation and proton transfer to generate the product olefin (Scheme 3). Evidence for this proposal comes from deuterium labeling experiments and demonstration that the reaction proceeds with complete stereospecificity. This mechanism requires that the two hydroxyl groups removed from glycerol in the reaction form $CO_2$ with the carbon atom of formic acid, a testable hypothesis by means of isotopic labeling studies (e.g., $^{17}O$ and/or $^{13}C$). This also suggests that formic acid is the only carboxylic acid that can mediate this reaction, because deprotonation of the *ortho*-ester proton (which corresponds to the formyl proton in formic acid) is required by this mechanism. Using an appropriate alternative carboxylic acid may even allow for isolation or direct detection of the proposed *ortho*-ester-type reaction intermediate. Mechanistic studies like those already performed and those suggested herein will assist in the development of improved systems for the conversion of other plant-derived polyols to value-added chemicals.

One way this system could become even more interesting would be to use it to generate 1,3-butadiene. Butadiene is produced commercially from butanes. It has been proposed that it may be economically feasible to produce it instead from bioethanol by dehydration to acetaldehyde, aldol condensation, and dehydration in a process called the Lebedew process.[3,21,44] The hypothesized double didehydroxylation of erythritol has the potential to be a simple, inexpensive, and industrially useful alternative.

Butadiene could, in principle, come from erythritol through two sequential didehydroxylation reactions (Scheme 4). Ellman, Bergman, and co-workers[42] found that treatment of erythritol generated 2,5-dihydrofuran, not 1,3-butadiene; however, it may be possible to optimize the



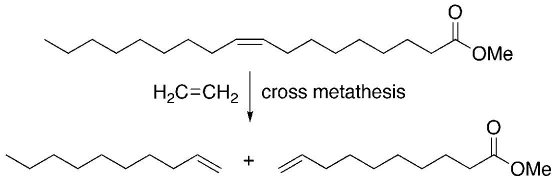
Scheme 4. Hypothetical method for the formation of 1,3-butadiene from erythritol by double didehydroxylation.

system to favor the production of 1,3-butadiene over 2,5-dihydrofuran. Accomplishing this would provide a new route, from a biomass-derived intermediate chemical, to a high-production olefin that has been difficult to generate without resorting to the use of a petrochemical feedstock.

Another possible extension of this work is the use of other polyols that are derived from plant biomass (e.g., the intermediate chemicals listed in Figure 2) as substrates for this didehydroxylation reaction. In addition to glycerol and erythritol, other abundant plant-derived polyols could serve as substrates for the generation of useful primary chemicals through didehydroxylation reactions.

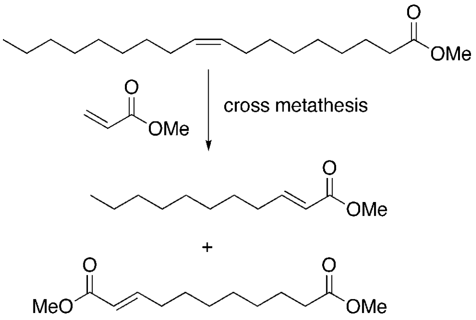
A second avenue of research for the production of higher α-olefins entails the treatment of unsaturated fatty acid esters with ethylene and a Grubbs/Schrock/Hoveyda-type alkene metathesis catalyst. This cross-metathesis reaction (ethenolysis) also generates an equivalent of an α,ω-alkene fatty acid ester, which is a useful substrate for numerous polymer-based applications.[45] This approach has been an area of active research for over 30 years,[45,46] and several recent reviews are available that detail the cross-metathesis of oleochemicals and the polymers they are used to create.[16,47] However, two recent developments warrant further discussion here.

A recent contribution from the Hoveyda and Schrock labs details the ethenolysis of methyl oleate (methyl *cis*-9-octadecenoate; Scheme 5).[48] This report demonstrates the conversion of methyl oleate to 1-decene and methyl 9-decenoate in yields up to 95 %, conversions up to 96 %, and with a selectivity of >99 % (Scheme 5). Most impressively, these results were obtained by using relatively low ethylene pressures (4–10 atm) at room temperature, in overnight runs. These reactions have turnover numbers (TON) up to 4750, which is an improvement over most of the previous results; however, TON > 50 000 are needed to make this an economically viable industrial process.[45] The other product of this metathesis reaction is methyl 9-decenoate, an α,ω-alkene ester, which is a starting material in the synthesis of diacids, diesters, and in the production of new microbiocidal coatings.[49]



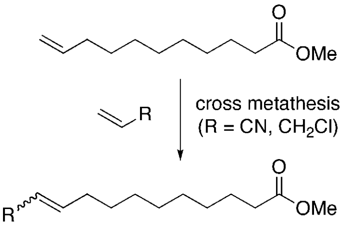
Scheme 5. Cross-metathesis of methyl oleate (methyl *cis*-9-octadecenoate) with ethylene gives decene and methyl 9-decenoate, an α,ω-alkene formate ester. This reaction occurs under exceptionally mild reaction conditions: 4–10 atm ethylene at room temperature overnight.

Further recent development in this area involves the use of cross-metathesis partners other than ethylene to install alternative reactive functional groups on the terminus of the fatty acid ester chain. The work by the groups of Meier[47] and Dixneuf[53] is particularly noteworthy in this regard. Meier and co-workers[50] described the synthesis of a panel of α,ω-bifunctional molecules using methyl acrylate as the cross-metathesis partner in reactions of unsaturated fatty acid derivatives. This transformation is challenging because methyl acrylate is not tolerated by all metathesis catalysts.[47c] These reactions provide α,ω-diesters, which can be used in the synthesis of condensation polymers, such as polyesters and polyamides. The α,β-unsaturated fatty acid esters that are also produced are valuable starting materials for making detergents (Scheme 6).[50] These reactions proceed at conversions up to 97 %, to give 92 % cross-metathesis products, at 50 °C overnight, when using catalyst loadings of only 0.2 %. Using other fatty acid esters (methyl erucate, methyl petroselinate, and methyl ricinoleate), they have demonstrated a method to make these products in various chain lengths, and to retain the stereochemistry of an optically active, unprotected, secondary alcohol on the fatty acid ester chain, in the case of methyl ricinoleate.[50,51]



Scheme 6. Cross-metathesis of methyl oleate (methyl *cis*-9-octadecenoate) with methyl acrylate gives (*E*)-methyl undecenoate and (*E*)-dimethyl undec-2-enedioate.

In addition, the Meier and Dixneuf research groups have expanded the utility of this strategy by performing similar reactions using allyl chloride,[52] acrylonitrile,[53a] or fumaronitrile[53a] as the cross-metathesis partner. These reactions provide α,ω-chloroallyl esters and α,ω-nitrile esters, respectively, enabling a greater variety of orthogonal reactions on each end of the unsymmetrical products (Scheme 7). Because the reaction selectivities are not perfect (some self-metathesis occurs), improving this aspect of these systems represents important remaining work.[54] This issue, as well

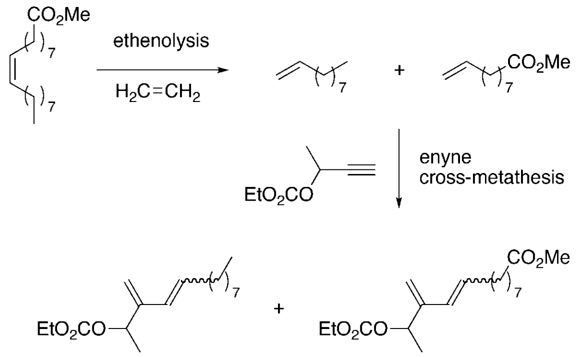


Scheme 7. Cross-methathesis of methyl undec-10-enoate with acrylonitrile or allyl chloride to provide α,ω-bifunctional products.

as achieving higher TON, percent yield, and percent conversion may be achieved through screening new and existing catalysts.

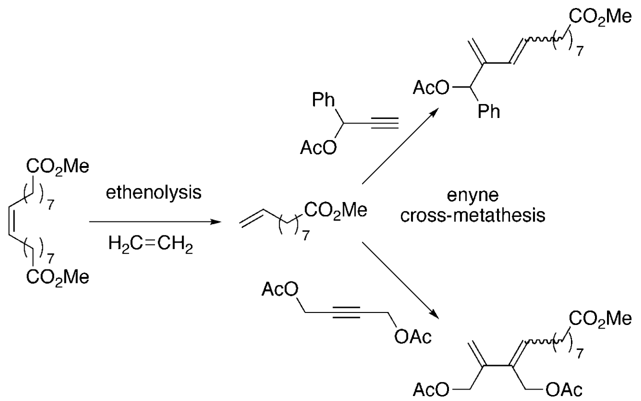
Although these bifunctional products are not currently on the list of high-use organic chemicals, this metathesis research is included herein for its ability to generate molecules with the potential to become high-use chemicals of the future. For example, research by Meier and co-workers has demonstrated numerous uses of these products, including the synthesis of block copolymers,[55] branched polymers,[56] polyamides,[57] and as probes for the study of the temperature dependence of alkene isomerization during acyclic diene metathesis (ADMET) polymerization reactions.[58]

Conjugated 1,3-dienes represent another useful class of chemicals that has recently been accessed by using oleochemicals as starting materials in cross-metathesis reactions. Bruneau and co-workers recently published the first example of enyne cross-metathesis of plant-derived fatty esters, such as methyl oleate, with either internal or terminal alkynes.[59] In a unique one-pot method, ethenolysis of methyl oleate gave a 1:1 mixture of 1-decene and methyl 9-decenoate (as in Scheme 5), which was then treated with alkyne to generate the desired 1,3-dienes (Scheme 8). The ethenolysis step occurs in 90 % conversion to give 1.7 equivalents of the olefin intermediates (1-decene and methyl 9-decenoate). Because the ethenolysis reaction produces two olefins, two 1,3-diene products were subsequently formed in the enyne metathesis with added alkyne.



Scheme 8. One-pot ethenolysis of methyl oleate generates decene and methyl 8-decenoate intermediates that undergo enyne cross-metathesis with added propargyl carbonate to generate 1,3-dienes.

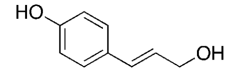
Although these one-pot reactions are highly efficient, the product mixture was obtained with small amounts of unreacted methyl oleate, the intermediates of ethenolysis, and some self-metathesis products. To simplify the isolation of the 1,3-dienes, the authors investigated performing this one-pot enthenolysis–enyne metathesis sequence using a symmetrical olefin obtained from the self-metathesis of methyl oleate. Accordingly, the ethenolysis of dimethyl octadec-9-enedioate, followed by treatment with alkyne and an enyne cross-metathesis catalyst, results in high yield of the desired 1,3-dienes (Scheme 9). Although the particular 1,3-dienes that are produced in these reactions are not currently high-use chemicals, this approach could prove to be useful for the synthesis of other 1,3-dienes. To become industrially useful, future work will need to focus on the formation of high-use 1,3-dienes.



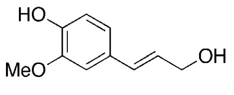
Scheme 9. One-pot ethenolysis/enyne cross-metathesis of a symmetrical olefin that is derived from the self-metathesis of methyl oleate.

## Aromatics

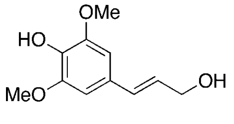
The production of arenes from plant biomass has long been a focus of both basic and applied research. Among the most obvious renewable sources for arene production is lignin, which is a complex polymer that is an integral part of the secondary cell wall of plants. As such, it is one of the most common organic polymers on earth. Three of its principle monomers are *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol.[60] Because of the high abundance of these lignin monomers, as well as related arenes, such a ferulic acid, plant biomass represents a clear choice for arene production.



*p*-coumaryl alcohol



coniferyl alcohol



sinapyl alcohol

A variety of approaches for the production of arenes are under active investigation by using plant-derived resources, including carbohydrates, lignin, and plant oils. An important historical example of the production of aromatic compounds from biomass appeared in 1979.[61] That study used ZSM-5-type zeolite catalysts and tested a panel of biomass components (corn oil, castor oil, jojoba oil, dipentene, *Hevea braziliensis* latex, and methanol) to generate mixtures of organic products that included aromatics. More recently, vigorous research has made impressive headway toward the twin goals of making pure chemicals and transportation fuels. Numerous technologies[16,62] are used for the conversion of biomass to aromatics, including liquefaction[61,63,64] (generation of water-insoluble bio-oil at high pressure (50–200 atm) and low temperature (250–450 °C)), gasification (generation of syngas (a mixture of CO, $H_2$, $CO_2$, and $N_2$) from solid or liquid carbonaceous material),[61,67] pyrolysis (generation of bio-oils at 1–5 atm and 375–525 °C),[61,63,65,66,76] chemical processing,[67–69] biological processing,[70–72] and treatment with supercritical solvents.[73]

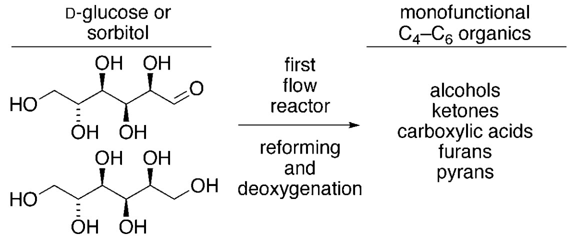
From the standpoint of this review article, the most important aromatic target is benzene, followed by toluene, ethylbenzene, and xylenes (BTEX).[66] The importance of benzene stems from two facts. First, it has manifold uses in industrial synthesis; a wide variety of industrially important compounds are readily available from benzene, including styrene, ethylbenzene, phenol, and cyclohexane.[74,75] Second, benzene is considerably more difficult to generate from biomass than cymenes,[16] furans,[16,72,75–78] or any number of oxygenated benzene derivatives (e.g., substituted anisoles, phenols, and benzoic acids).[62,75] Taken together, the usefulness of benzene and the challenges associated with its production from biomass, make it an important topic for further discussion.

Catalytic fast pyrolysis is actively being investigated for the production of aromatics from biomass-derived intermediate chemicals. The first step of this process involves the thermal decomposition of biomass to smaller oxygenated compounds, which then react with the catalyst to generate CO, $CO_2$, water, coke, and volatile aromatics. Since this field of research has been reviewed recently in several very clear and complete articles,[16,61,79–81] we limit our discussion herein to a few very recent contributions that exemplify the promise of these technologies.

Huber and co-workers at the University of Massachusetts at Amherst recently reported the production of gasoline-range aromatics (mostly BTEX, indanes, and naphthalenes) from the catalytic fast pyrolysis of solid biomass feedstocks.[82] Their article details impressive reaction conditions: a single reactor that uses short residence times (<2 min) and intermediate temperatures (400–600 °C). Huber and co-workers showed that aromatic production can be preferred (over the production of other organics, coke, CO, and $CO_2$) by selecting a proper catalyst, by using high heating rates, and by using a high ratio of catalyst/intermediate chemical feed. Catalysts tested included silicate, β-zeolite, silica-alumina, and Y-zeolite, in addition to ZSM-5, which gave the highest percentage of aromatic products (ca. 30 %). By using a variety of different chemical feeds (glucose, cellulose, cellobiose, and xylitol), the following approximate yields were generated for the aromatic fraction of products generated: 10 % benzene, 20 % toluene, 40 % naphthalene, 15 % ethylbenzene and xylenes, with the remainder being mostly indanes and substituted benzenes containing three additional carbon atoms (such as mesitylene or ethylmethylbenzene). Significant improvements in this rapidly growing area are likely to result from the development of improved catalysts.

Another noteworthy recent contribution comes from University of Wisconsin, Madison, where Dumesic and co-workers used a catalytic approach to convert aqueous solutions of carbohydrates to mixtures of monofunctional organic compounds that were subsequently upgraded to alkanes, olefins, and small aromatic compounds.[83] Their aim was to generate specific classes of liquid fuels (e.g., jet fuel, diesel, gasoline); moreover, from the standpoint of the production of industrial chemicals, this work is also remarkable. Their system consists of several flow reactors operated in a cascade, where the effluent of one reactor is fed directly into the next reactor.

In the first reactor much of the carbohydrate feed is deoxygenated (by numerous C–O bond cleavage reactions) to obtain the desired monofunctional organic molecules as a mixture called bio-oil. The key to accomplishing this in a single reactor is to allow a fraction of the carbohydrate feed to be reformed, a term used for the collection of C–C bond cleavage reactions that ultimately lead to the production of a mixture of CO, $CO_2$, and $H_2$. This was accomplished over Pt–Re/C at temperatures as low as 500 K to generate in situ the $H_2$ that is required for the deoxygenation reactions. This work demonstrated the formation of a relatively simple mixture of alcohols, ketones, carboxylic acids, alkanes, furans, and pyrans that each contains four to six carbon atoms (Scheme 10). A comparison of this method to the production of bio-oil using pyrolysis (>770 K), a competing technology, shows it to have several advantages. First, biomass pyrolysis typically gives a more complex mixture of over 300 highly oxygenated compounds. Second, the bio-oil made from pyrolysis of biomass often contains a great deal of water (up to 50 wt %) that can be relatively acidic (pH ≈2.5), preventing its direct use as a transportation fuel. In contrast, this method generates a well-defined mixture of hydrophobic compounds.



Scheme 10. Catalytic conversion of glucose or sorbitol into a well-defined mixture of $C_4$–$C_6$ alcohols, ketones, carboxylic acids, and oxacycles.

These researchers also tested several subsequent catalytic processes designed to upgrade the bio-oil to transportation fuels. The most interesting process with respect to this review article entails the hydrogenation of the ketones

(433 K, 55 bar $H_2$, 5 wt % Ru/C), followed by heating to 673 K at atmospheric pressure over H-ZSM-5 catalyst. Analysis of the fate of the carbon atoms of the original sorbitol starting material shows that 25 % is converted to $C_3$–$C_4$ paraffins, 29 % is converted to $C_3$–$C_4$ olefins, and 38 % is converted to aromatics. The aromatic fraction is composed of 12 % benzene (5 % of the total), 37 % toluene (14 % of the total), 30 % substituted benzenes containing two additional carbon atoms (such as xylenes or ethylbenzene), and 22 % substituted benzenes containing three to six additional carbon atoms. Since most of the compounds obtained are high-use aromatics, this work represents an exciting development in the production of aromatics from biomass.

Looking forward from the state-of-the-art of arene production from biomass, there is clearly much progress to be made in terms of the yield and purity of the desired arenes (BTEX). In addition, a critical problem to be solved is the dehydroxylation and the demethoxylation of substrates typified by phenol and anisole. Advancing our ability to dehydroxylate and demethoxylate arenes could provide ready access to benzene from lignin-derived materials. Often the relative rates of hydrogenolysis of the hydroxyl–arene or the methoxy–arene bond are slower than arene hydrogenation;[84] this gives cyclohexanol, rather than the desired aromatic product. Thus a challenge of enormous potential impact is the development of direct methods to convert phenol or anisole to benzene.

## Summary and Outlook

A flurry of recent research activity has demonstrated that numerous high-use organic chemicals are available either directly from plant biomass or from intermediate chemicals that are readily obtained from plant biomass. In particular, we have highlighted the use of biochemical and thermochemical methods to convert plant biomass, a renewable resource, into high-use chemicals such as halocarbons, alkenes, and aromatics. These primary chemicals were highlighted in this article because they have historically been resistant to efficient production from plant-biomass-derived feedstocks. Recently molecules containing these functional groups have been generated from plant biomass, but the methods still require substantial additional research to generate processes that will be economically feasible for industrial production. We hope that this critical analysis of recent developments will aid in the development of new methods for the production of chemicals from plant biomass. Collaboration between academic and industrial research groups is seen as the most likely path toward success.

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[1] a) E. J. Corey, X.-M. Cheng, *The Logic of Chemical Synthesis*, Wiley, New York, **1995**, pp. 1–5; b) K. C. Nicolaou, E. J. Sorensen, *Classics in Total Synthesis*, VCH, Weinheim, **1996**, pp. 1–19.
[2] T. E. Graedel in *Handbook of Green Chemistry and Technology* (Eds.: J. Clark, D. Macquarrie), Blackwell Science, Oxford, **2002**, pp. 56–61.
[3] J. van Haveren, E. L. Scott, J. Sanders, *Biofuels Bioprod. Biorefin.* **2008**, *2*, 41–57.
[4] D. B. Turley in *Introduction to Chemicals from Biomass* (Eds.: J. H. Clark, F. E. I. Deswarte), Wiley, New York, **2008**, pp. 21–46.
[5] B. Kamm, *Angew. Chem.* **2007**, *119*, 5146–5149; *Angew. Chem. Int. Ed.* **2007**, *46*, 5056–5058.
[6] J. Thoen, J. L. Guillaume in *Methods and Reagents for Green Chemistry: An Introduction* (Eds.: P. Tundo, A. Perosa, F. Zecchini), Wiley, New York, **2007**, pp. 201–217.
[7] For the purpose of this article, "feedstock" is defined as the raw material going into a chemical process, "intermediate chemicals" are defined as the products generated directly from the feedstock in a chemical process, and "primary chemicals" are generated from the intermediate chemicals in subsequent chemical processes. Of course, some intermediate chemicals are useful in their own right as primary chemicals.
[8] D. L. Klass *Biomass for Renewable Energy, Fuels, and Chemicals*, Academic Press, San Diego, **1998**, pp. 495–546.
[9] R. A. Sheldon, I. Arends, U. Hanefeld *Green Chemistry and Catalysis*, Wiley-VCH, Weinheim, **2008**, pp. 329–388.
[10] a) D. Peters in *Advances in Biochemical Engineering/Biotechnology: White Biotechnology* (Ed.: T. Scheper), Springer, Berlin, **2007**, pp. 1–30; b) B. Kamm, M. Kamm in *Advances in Biochemical Engineering/Biotechnology: White Biotechnology* (Ed.: T. Scheper), Springer, Berlin, **2007**, pp. 175–204.
[11] J. J. Bozel, *Clean* **2008**, *36*, 641–647.
[12] C. H. Christensen, J. Rass-Hansen, C. C. Marsden, E. Taarning, K. Egeblad, *ChemSusChem* **2008**, *1*, 283–289.
[13] T. Werphy, G. Petersen, Top value added chemicals from biomass. http://www1.eere.energy.gov/biomass/pdfs/35523.pdf [Accessed on April 2, 2010].
[14] P. J. Chenier *Survey of Industrial Chemistry*, 3rd ed., Springer, New York, **2002**, pp. 17–18.
[15] a) P. T. Anastas, J. C. Warner *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, **1998**; b) M. Lancaster in *Handbook of Green Chemistry and Technology* (Eds.: J. Clark, D. Macquarrie), Blackwell Science, Oxford, **2002**, pp. 10–27.
[16] A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411–2502.
[17] A. Behr, J. Eilting, K. Irawadi, J. Leschinski, F. Lindner, *Green Chem.* **2008**, *10*, 13–30.
[18] K. A. Gray, L. Zhao, M. Emptage, *Curr. Opin. Chem. Biol.* **2006**, *10*, 141–146.
[19] G. A. Olah, A. Goeppert, G. K. S. Prakash, *J. Org. Chem.* **2009**, *74*, 487–498.
[20] B. J. Nikolau, M. A. D. N. Perera, L. Brachova, B. Shanks, *Plant J.* **2008**, *54*, 536–545.
[21] H. Danner, R. Braun, *Chem. Soc. Rev.* **1999**, *28*, 395–405.
[22] V. P. Kukhar, *Kem. Ind.* **2009**, *58*, 57–71.
[23] a) J. Barrault, F. Jerome, *Eur. J. Lipid Sci. Technol.* **2008**, *110*, 825–830; b) L. Prati, P. Spontoni, A. Gaiassi, *Top. Catal.* **2009**, *52*, 288–296; c) S. Sato, M. Akiyama, K. Inui, M. Yokota, *Chem. Lett.* **2009**, *38*, 560–561.
[24] C. E. Wyman, *Annu. Rev. Energy* **1999**, *24*, 189–226.
[25] P. Tundo, A. Perosa, *Chem. Rec.* **2002**, *2*, 13–23.
[26] M. Selva, A. Perosa, *Green Chem.* **2008**, *10*, 457–464, and references therein.
[27] C. M. White, L. J. Douglas, J. P. Hackett, R. R. Anderson, *Energy Fuels* **1992**, *6*, 76–82.

[28] a) I. M. Lorkovic, M. L. Noy, W. A. Schenck, C. Belon, M. Weiss, S. L. Sun, J. H. Sherman, E. W. McFarland, G. D. Stucky, P. C. Ford, *Catal. Today* **2004**, *98*, 589–594; b) D. K. Murray, T. Howard, P. W. Goguen, T. R. Krawietz, J. F. Haw, *J. Am. Chem. Soc.* **1994**, *116*, 6354–6360.

[29] a) A. Breed, M. F. Doherty, S. Gadewar, P. Grosso, I. M. Lorkovic, E. W. McFarland, M. J. Weiss, *Catal. Today* **2005**, *106*, 301–304; b) I. Lorkovic, M. Noy, M. Weiss, J. Sherman, E. McFarland, G. D. Stucky, P. C. Ford, *Chem. Commun.* **2004**, 566–567.

[30] a) O. Dewaele, V. L. Geers, G. F. Froment, G. B. Martin, *Chem. Eng. Sci.* **1999**, *54*, 4385–4395; b) G. A. Olah, O. Farooq, V. V. Krishnamurthy, G. K. S. Prakash, K. Laali, *J. Am. Chem. Soc.* **1985**, *107*, 7541–7545.

[31] F. N. Martin, *Annu. Rev. Phytopathol.* **2003**, *41*, 325–350.

[32] a) A. M. Wuosmaa, L. P. Hager, *Science* **1990**, *249*, 160–162; b) R. C. Rhew, L. Østergaard, E. S. Saltzman, M. F. Yanofsky, *Curr. Biol.* **2003**, *13*, 1809–1813; c) N. Ohsawa, M. Tsujita, S. Morikawa, N. Itoh, *Biosci. Biotechnol. Biochem.* **2001**, *65*, 2397–2404.

[33] a) S. L. Manley, *Biogeochemistry* **2002**, *60*, 163–180; F. Weinberger, B. Coquempot, S. Forner, P. Morin, B. Kloareg, P. Potin, *J. Exp. Bot.* **2007**, *58*, 4365–4372; R. A. Marshall, J. T. G. Hamilton, M. J. Dring, D. B. Harper, *Chemosphere* **2003**, *52*, 471–475.

[34] Although there are more green methylating agents known, these halomethanes (MeCl, MeBr, MeI) remain important chemicals today. For example, see: T. S. Bayer, D. M. Widmaier, K. Temme, E. A. Mirsky, D. V. Santi, C. A. Voigt, *J. Am. Chem. Soc.* **2009**, *131*, 6508–6515.

[35] D. G. Fujimori, C. T. Walsh, *Curr. Opin. Chem. Biol.* **2007**, *11*, 553–560.

[36] Inventory update reporting (IUR). U.S. Environmental Protection Agency. http://cfpub.epa.gov/iursearch/2006_iur_natlcheminfo.cfm?id=881 [Accessed on April 2, 2010].

[37] Acute exposure guideline levels (AEGLs) for methyl iodide U.S. Environmental Protection Agency. http://www.epa.gov/oppt/aegl/pubs/methyl_iodide_proposed_nov_2009.v1.pdf [Accessed on April 2, 2010].

[38] For leading references, see: a) M. D. Kendrick, C. Chang, *Curr. Opin. Plant Biol.* **2008**, *11*, 479–485; b) B. Chow, P. McCourt, *Genes Dev.* **2006**, *20*, 1998–2008; c) N. Etheridge, B. P. Hall, G. E. Shaller, *Planta* **2006**, *223*, 387–391; d) Y. F. Chen, N. Etheridge, G. E. Schaller, *Ann. Bot.* **2005**, *95*, 901–915; e) C. Chang, A. B. Bleecker, *Plant Physiol.* **2004**, *136*, 2895–2899; f) L. Alexander, D. Grierson, *J. Exp. Bot.* **2002**, *53*, 2039–2055; g) K. L.-C. Wang, H. Li, J. R. Ecker, *Plant Cell* **2002**, S131–S151; h) A. B. Bleecker, H. Kende, *Annu. Rev. Cell Dev. Biol.* **2000**, *16*, 1–18; i) A. N. Stepanova, J. R. Ecker, *Curr. Opin. Plant Biol.* **2000**, *3*, 353–360.

[39] K. Weissermel, H. J. Arpe *Industrial Organic Chemistry*, 4th ed., Wiley-VCH, Weinheim, **2003**, pp. 59–90; K. Weissermel, H. J. Arpe *Industrial Organic Chemistry*, 4th ed., Wiley-VCH, Weinheim, **2003**, pp. 107–126; K. Weissermel, H. J. Arpe *Industrial Organic Chemistry*, 4th ed., Wiley-VCH, Weinheim, **2003**, pp. 145–192.

[40] a) E. Hunter, C. G. Paulin, R. B. Richards, GB587378, **1946**; b) I. Takahara, M. Saito, K. Murata, M. Inaba, JP2006116439, **2006**; c) L. Lijian, D. Jiaojiao, CN 1884232, **2006**; d) S. Arenamnart, W. Trakarnpruk, *Int. J. Appl. Sci. Eng.* **2006**, *4*, 21–32; e) I. Takahara, M. Saito, M. Inaba, K. Murata, *Catal. Lett.* **2005**, *105*, 249; f) M. Inaba, K. Murata, M. Saito, I. Takahara, *Green Chem.* **2007**, *9*, 638–646.

[41] A. Sardesai, S. Lee, *Energy Sources* **2005**, *27*, 489–500.

[42] E. Arceo, P. Marsden, R. G. Bergman, J. A. Ellman, *Chem. Commun.* **2009**, 3357–3359.

[43] J. L. Zheng, W. M. Yi, N. N. Wang, *Energy Convers. Manage.* **2008**, *49*, 1724–1730.

[44] *Industrial Organic Chemistry*, 4th ed. (Eds.: K. Weissermel, H. J. Arpe), Wiley-VCH, Weinheim, **2003**, p. 145; *Industrial Organic Chemistry*, 4th ed. (Eds.: K. Weissermel, H. J. Arpe), Wiley-VCH, Weinheim, **2003**, p. 268.

[45] K. A. Burdett, L. D. Harris, P. Margl, B. R. Maughon, T. Mokhtar-Zadeh, P. C. Suacier, E. P. Wasserman, *Organometallics* **2004**, *23*, 2027–2047.

[46] a) Y. Schrodi, T. Ung, A. Vargas, G. Mkrtumyan, C. W. Lee, T. M. Champagne, R. L. Pederson, S. H. Hong, *Clean Soil Air Water* **2008**, *36*, 669–673; b) X. Bei, D. P. Allen, R. L. Pederson, *Pharm. Technol.* **2008**, s18; c) D. R. Anderson, T. Ung, G. Mkrtumyan, G. Bertrand, R. H. Grubbs, Y. Schrodi, *Organometallics* **2008**, *27*, 563–566; d) G. S. Forman, A. E. McConnell, M. J. Hanton, A. M. Z. Slawin, R. P. Tooze, W. J. vanRensburg, W. H. Meyer, C. Dwyer, M. M. Kirk, D. W. Serfontein, *Organometallics* **2004**, *23*, 4824–4827.

[47] a) M. A. R. Meier, *Macromol. Chem. Phys.* **2009**, *210*, 1073–1079; b) A. Rybak, P. A. Fokou, M. A. R. Meier, *Eur. J. Lipid Sci. Technol.* **2008**, *110*, 797–804; c) M. A. R. Meier, *Lipid Technol.* **2008**, *20*, 84–87; d) M. A. R. Meier, J. O. Metzger, U. S. Schubert, *Green Chem.* **2007**, *9*, 1788–1802.

[48] S. C. Marinescu, R. R. Schrock, P. Muller, A. H. Hoveyda, *J. Am. Chem. Soc.* **2009**, *131*, 10840–10841.

[49] a) J. L. Zullo, J. C. Anderson, H. Kaido, R. L. Pederson, Y. Schrodi, W. H. Sperber, M. J. Tupy, E. H. Wagener, US 20070227400, **2007**; b) J. L. Zullo, J. C. Anderson, J. Carney, M. L. De Souza, W. H. Sperber, M. J. Tupy, E. H. Wagener, US 20080033026, **2008**.

[50] A. Rybak, M. A. R. Meier, *Green Chem.* **2007**, *9*, 1356–1361.

[51] T. T. T. Ho, T. Jacobs, M. A. R. Meier, *ChemSusChem* **2009**, *2*, 749–754.

[52] T. Jacobs, A. Rybak, M. A. R. Meier, *Appl. Catal. A* **2009**, *353*, 32–35.

[53] a) R. Malacea, C. Fischmeister, C. Bruneau, J.-L. Dubois, J.-L. Couturier, P. H. Dixneuf, *Green Chem.* **2009**, *11*, 152–155; b) C. Thurier, C. Fischmeister, C. Bruneau, H. Olivier-Bourbigou, P. H. Dixneuf, *ChemSusChem* **2008**, *1*, 118–122.

[54] A. Rybak, M. A. R. Meier, *Green Chem.* **2008**, *10*, 1099–1104.

[55] A. Rybak, M. A. R. Meier, *ChemSusChem* **2008**, *1*, 542–547.

[56] P. A. Fokou, M. A. R. Meier, *Macromol. Rapid Commun.* **2008**, *29*, 1620–1625.

[57] H. Mutlu, M. A. R. Meier, *Macromol. Chem. Phys.* **2009**, *210*, 1019–1025.

[58] P. A. Fokou, M. A. R. Meier, *J. Am. Chem. Soc.* **2009**, *131*, 1664–1665.

[59] V. Le Ravalec, C. Fischmeister, C. Bruneau, *Adv. Synth. Catal.* **2009**, *351*, 1115–1122.

[60] R. Vanholme, K. Morreel, J. Ralph, W. Boerjan, *Curr. Opin. Plant Biol.* **2008**, *11*, 278–285.

[61] P. B. Weisz, W. O. Haag, P. G. Rodewald, *Science* **1979**, *206*, 57–58.

[62] G. W. Huber, S. Iborra, A. Corma, *Chem. Rev.* **2006**, *106*, 4044–4098.

[63] Y. Yang, A. Gilbert, C. Xu, *AIChE J.* **2009**, *55*, 807–819.

[64] D. C. Elliott, *Energy Fuels* **2007**, *21*, 1792–1815.

[65] Z. Ji-lu, Y. Wie-ming, W. Na-na, *Energy Convers. Manage.* **2008**, *49*, 1724–1730.

[66] S. Hosokai, M. Sugawa, K. Norinaga, C. Z. Li, J. Hayashi, *Ind. Eng. Chem. Res.* **2008**, *47*, 5346–5352.

[67] J. C. Gentry, *Asia-Pac. J. Chem. Eng.* **2007**, *2*, 272–277.

[68] D. Kubicka, *Collect. Czech. Chem. Commun.* **2008**, *73*, 1015–1044.

[69] P. J. Dauenhauer, B. J. Dreyer, N. J. Degenstein, L. D. Schmidt, *Angew. Chem.* **2007**, *119*, 5968–5971; *Angew. Chem. Int. Ed.* **2007**, *46*, 5864–5867.

[70] L. R. Lynd, C. E. Wyman, T. U. Gerngross, *Biotechnol. Prog.* **1999**, *15*, 777–793.

[71] M. L. Rizk, J. C. Liao, *PLoS ONE* **2009**, *4*, e6903.

[72] C. E. Wyman, B. E. Dale, R. T. Elander, M. Holtzapple, M. R. Ladisch, Y. Y. Lee, *Bioresour. Technol.* **2005**, *96*, 1959–1966.

[73] S. Saka, *For. Stud. China* **2006**, *8*, 9–15.

[74] C. Perego, P. Ingallina, *Green Chem.* **2004**, *6*, 274–279.

[75] K. Weissermel, H. J. Arpe *Industrial Organic Chemistry*, 4th ed., Wiley-VCH, Weinheim, **2003**, pp. 337–386.

[76] Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, *Nature* **2007**, *447*, 982–986.

[77] J. Zhang, H. Toghiani, D. Mohan, C. U. Pittman, R. K. Toghiani, *Energy Fuels* **2007**, *21*, 2373–2385.

[78] Y. Su, H. M. Brown, X. Huang, X.-D. Zhou, J. E. Amonette, Z. C. Zhang, *Appl. Catal. A* **2009**, *361*, 117–122.

[79] T. R. Carlson, G. A. Tompsett, W. C. Conner, G. W. Huber, *Top. Catal.* **2009**, *52*, 241–252.
[80] J. N. Chheda, G. W. Huber, J. A. Dumesic, *Angew. Chem.* **2007**, *119*, 7298–7318; *Angew. Chem. Int. Ed.* **2007**, *46*, 7164–7183.
[81] G. W. Huber, A. Corma, *Angew. Chem.* **2007**, *119*, 7320–7338; *Angew. Chem. Int. Ed.* **2007**, *46*, 7184–7201.
[82] T. R. Carlson, T. P. Vispute, G. W. Huber, *ChemSusChem* **2008**, *1*, 397–400.
[83] E. L. Kunkes, D. A. Simonetti, R. M. West, J. C. Serrano-Ruiz, C. A. Gartner, J. A. Dumesic, *Science* **2008**, *322*, 417–421.
[84] C. Zhao, Y. Kou, A. A. Lemonidou, X. Li, J. A. Lercher, *Angew. Chem.* **2009**, *121*, 4047–4050; *Angew. Chem. Int. Ed.* **2009**, *48*, 3987–3990.

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