DOI: 10.1002/cssc.201100608

Conversion of Hemicellulose to Furfural and Levulinic Acid using Biphasic Reactors with Alkylphenol Solvents

Elif I. Gürbüz, Stephanie G. Wettstein, and James A. Dumesic*[a]

Diminishing fossil fuel resources and the increasing impact of global climate change have driven research towards the utilization of lignocellulosic biomass resources as renewable feedstocks for the production of energy, fuels, and chemicals. The conversion of lignocellulosic biomass into fuels and chemicals requires effective utilization of the C_5 and C_6 sugars present in hemicellulose and cellulose, respectively, by either processing these fractions together or separating and processing them separately. While simultaneous processing, such as in gasification or pyrolysis, offers the potential for simplicity of operation, the fractionation of hemicellulose and cellulose allows the processing of each fraction to be tailored to take advantage of the different chemical and physical properties of these fractions, and provides increased flexibility of operation. For example, chemical processing methods can be employed to convert C_5 sugars into fuels/chemicals in hemicellulose, while employing recent advances in biological conversions allows to convert the C_6 sugars in cellulose into fuels and/or chemicals.[1,2] One can also take advantage of the physical properties of cellulose for pulp and paper applications.

Herein, we show that the hemicellulose fraction of lignocellulosic biomass can be converted into furfural and levulinic acid by using biphasic reactors with alkylphenol solvents that selectively partition furanic compounds from acidic aqueous solutions. These furfural and levulinic acid products are valu≪->able compounds for a variety of chemical applications,[3,4] and they serve as precursors for the synthesis of liquid transportation fuels.[5–7]

The conversion of cellulose to chemicals and liquid fuels has been demonstrated through the formation of several platform molecules, such as glucose, 5-hydroxymethylfurfural, and levulinic acid (LA), utilizing chemical routes;[6–9] however, fewer studies address the conversion of hemicellulose into chemicals and fuels.[10,11] Previous studies for the production of furfural (FuAL) from C_5 sugars (i.e., xylose) suffer from the low concentrations of FuAL in the product stream due to low xylose concentrations (1–2 wt%) obtained from hemicellulose deconstruction.[10,11] In addition, even though the production of LA from furfuryl alcohol (FuOH) has been reported with good yields over ion-exchange resin catalysts (e.g., Amberlyst),[12,13] the regeneration of these catalysts following deactivation by deposition of solid humins during reaction is problematic. In addition, while zeolite catalysts (i.e., ZSM-5) can be used to replace resin catalysts and can be regenerated with a calcination treatment following deactivation,[13] employing these catalysts results in significantly lower LA yields, especially when increased LA concentrations are desired in the product stream.

Considering the aforementioned challenges for processing hemicellulose, we present a new biorefining strategy for converting the hemicellulose portion of lignocellulosic biomass to FuAL and LA by utilizing biphasic systems that consist of an extractive organic layer and an aqueous layer that contains a mineral acid. These biphasic systems achieve high concentrations of FuAL and LA, enabling the recovery of both products at the top of distillation columns, and eliminating issues related to deactivation and regeneration of solid acid catalysts. Three organic solvents, 2-*sec*-butylphenol (SBP), 4-*n*-hexylphenol (NHP) and 4-propyl guaiacol (PG), are demonstrated to be effective extracting agents for the production of FuAL and LA in these biphasic systems. Information on the toxicity and availability of these alkylphenol solvents is given in the Supporting Information. The use of these solvents is particularly advantageous because they (i) have high partition coefficients for extraction of FuAL, FuOH, and LA; (ii) do not extract significant amounts of mineral acids from aqueous solutions; (iii) have higher boiling points than the final product; and (iv) could potentially be synthesized directly from biomass (i.e., lignin), such that these solvents would not have to be transported to the site of the biomass conversion steps.

For the first step of this biorefining strategy (Figure 1), solid biomass (i.e., corn stover) is subjected to mild pretreatment in a dilute-acid, aqueous solution to solubilize the hemicellulose as xylose. After filtering the solution from the solid cellulose and lignin, an organic solvent (i.e., SBP) is added to the aqueous solution, and these liquids are heated in a biphasic reactor to achieve dehydration of xylose to FuAL, which is a valuable chemical intermediate.[3] FuAL can be distilled from SBP and sold as a chemical or, as depicted in Figure 1, converted to LA by first hydrogenating FuAL to FuOH over a metal-based catalyst (e.g., copper)[14,15] and then reacting the FuOH with water in a biphasic reactor to form LA. Similar to FuAL, the LA product can be distilled from the organic solvent and sold as a chemical.

Xylose dehydration to FuAL has been demonstrated with high yields (ca. 90%) in several previous studies using mineral acids and salts in biphasic systems with organic solvents, such as methyl isobutyl ketone (MIBK), 2-butanol, and tetrahydrofuran (THF).[9,11,16] However, the low partition coefficients for extraction of FuAL in these systems (i.e., the ratio of the FuAL concentration in the organic solvent to the FuAL concentration in aqueous solution) required the use of large amounts of organic solvent relative to the aqueous xylose solution, resulting

---

[a] E. I. Gürbüz, Dr. S. G. Wettstein, Prof. J. A. Dumesic
Chemical and Biological Engineering Department
University of Wisconsin
Madison, WI 53706 (USA)
Fax: (+1) 608-262-5434
E-mail: dumesic@engr.wisc.edu

Supporting Information for this article is available on the WWW under http://dx.doi.org/10.1002/cssc.201100608.

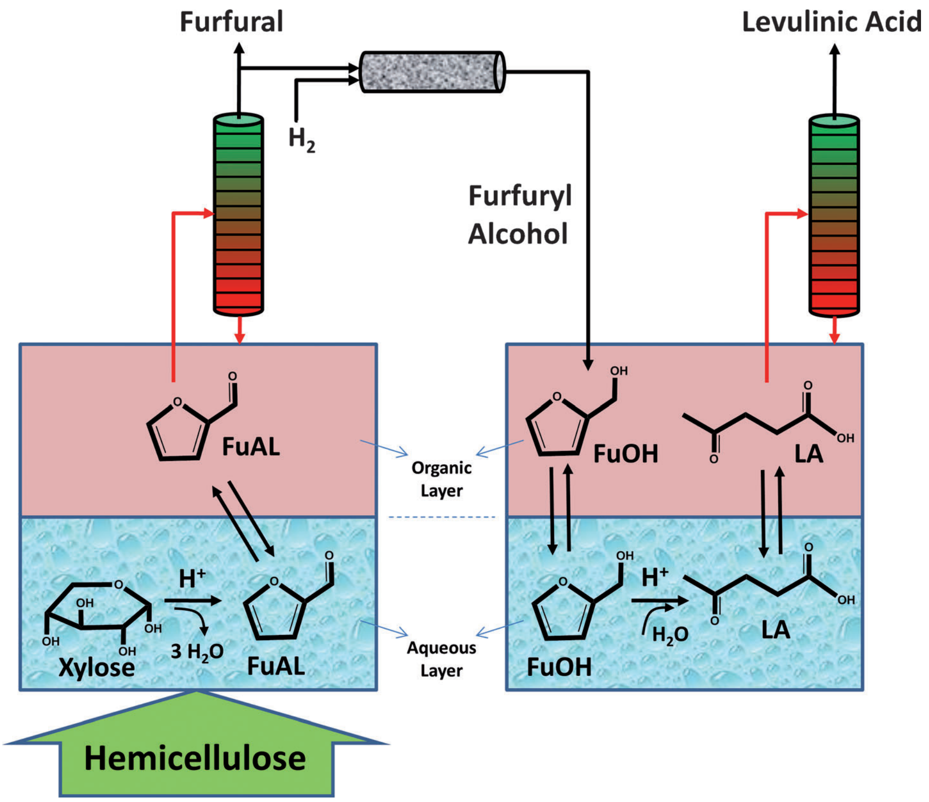

Figure 1. Schematic representation of the conversion of hemicellulose to furfural (FuAL) through the biphasic dehydration of xylose to furfural using an organic solvent, followed by the production of levulinic acid (LA) by reduction of furfural to furfuryl alcohol (FuOH) over a metal catalyst and further reaction of furfuryl alcohol with water in a biphasic reactor.

in low concentrations of FuAL in the organic phase compared to the starting concentration of xylose in the aqueous phase.

This problem is exacerbated by the low concentrations of xylose (e.g., 1–2 wt%) typically obtained in aqueous solutions from dilute acid treatment of real biomass feedstocks (e.g., corn stover). Thus, it is important to identify new methods to produce higher concentrations of FuAL in the organic phase of biphasic reactor systems to improve the efficiency of downstream processing options, such as distillation or further upgrading reactions.

We have recently identified a new extracting solvent, SBP, for the effective extraction of LA from acidic aqueous solutions.[17] We now show for the first time that SBP is also effective for extracting FuAL from acid aqueous solutions, with an exceptionally high partition coefficient of ca. 50 in the absence of salt in the aqueous phase and increasing to >90 when the aqueous phase is saturated with NaCl (these values were measured for a mass ratio of organic to aqueous layer equal to 2). This high partition coefficient of FuAL in the water–SBP system allows for high yields of FuAL in the organic phase, even when small amounts of the SBP solvent are used in the biphasic reactor (i.e., when the mass ratio of the aqueous solution to SBP is increased). Therefore, higher concentrations of FuAL can be obtained in a single stage compared to the starting xylose concentration. As shown in Table 1, entry 1, a 1.5 wt% xylose feed in an aqueous solution containing 0.1 M HCl and saturated with NaCl results in high yields of FuAL (78%), with 90% of FuAL partitioning to SBP, when a small amount of SBP is employed (xylose solution/SBP mass ratio of 6.67). The final organic phase contains 4.1 wt% FuAL in SBP. Another advantage of using SBP as the organic solvent is that it extracts only negligible amounts of Cl^- ions (13 ppm, detected via ion chromatography in Galbraith Laboratories) residing in the aqueous phase originating both from HCl and NaCl. In addition, no chlorinated organic compounds were detected within our detection limits.

To produce an aqueous solution of xylose from the hemicellulose fraction of a real biomass feedstock, corn stover was treated for 5 h at 363 K in an aqueous solution containing 0.1 M HCl and saturated with NaCl (see Supporting Information). This corn stover feed (1.1 wt% xylose) resulted in a maximum yield of ca. 70% for production of FuAL (Table 1, entry 2), with again ca. 90% of FuAL partitioning into SBP, using our bi-

Table 1. Results of xylose dehydration experiments carried out at 443 K in a biphasic reactor system (10 mL glass reactors), using SBP as the extracting solvent in a 6.67:1 aqueous/organic mass ratio, with aqueous solutions containing 0.1 M or 0.25 M HCl and saturated with NaCl. For all experiments, approximately 90% of total furfural is partitioned into the SBP phase.

Entry	Xylose [wt%]	HCl conc. [M]	*t* [min]	Xylose conv. [%] (±2)	Furfural select. [%] (±2)	Furfural yield [%] (±2)	Final furfural in SBP [wt%] (±0.5)
1	1.5	0.1	20	98	80	78	4.1
2	1.1 (from corn stover)	0.1	30	95	74	70	3.2
		0.25	15	92	82	75	3.2
3	5	0.1	15	92	77	71	11.6
4	2.1 (2 cycles from corn stover)	0.25	15	95	75	71	5.3

Table 2. Yields to levulinic acid starting from furfuryl alcohol solutions in 2-*sec*-butylphenol (SBP) in a biphasic reactor system with water or in a monophasic system with water at 398 K. All reactions were carried out in a batch reactor system. LA and SA correspond to levulinic acid and 1 M sulfuric acid, respectively. Furfuryl alcohol conversion is complete for all experiments.

Entry	Furfuryl alcohol [wt %]	Organic solvent	Org./aq. [mL mL^{-1}]	Catalyst	t [h]	Yield to LA [%]	LA in org. [%]
1	1	–	–	ZSM-5	1	15 ± 1	–
2	1	–	–	SA	1	32 ± 1	–
3	1	SBP	1	SA	1	68 ± 4	67 ± 5
4	1	SBP	1	SA	3	72 ± 4	67 ± 5
5	1	SBP	2	SA	1	66 ± 4	81 ± 5
6	10	SBP	1	SA	1	31 ± 2	66 ± 2

phasic reactor system. The small decrease in yield compared to the simulated feed could be due to inhibiting effects of byproducts produced in the hemicellulose deconstruction step; however, the overall yield from this biomass derived feed can be increased to ca. 75 % by increasing the HCl concentration to 0.25 M (entry 2). It should be noted that increasing the HCl concentration for the corn stover deconstruction step results in the same xylose yields by decreasing the reaction time to 2 h. It is shown in entry 3 with a simulated 5 wt % xylose feed that the overall furfural yield (ca. 71 %) and the partitioning into SBP are not altered when the xylose concentration is increased. Thus, the xylose concentration in the aqueous phase can be increased by adding corn stover to the HCl solution in progressive stages. With two cycles of corn stover deconstruction, the concentration of xylose is doubled (2.1 wt %), reaching similar overall yields. Using this feed for biphasic dehydration (entry 4), a maximum FuAL yield of ca. 71 % is obtained with ca. 90 % of FuAL partitioning into SBP, resulting in 5.3 wt % FuAL in SBP. Finally, scaling up the biphasic reaction from a 10 mL glass reactor to a 450 mL Parr reactor leads to a similar overall yield to FuAL (66 %).

As shown in Figure 1, the FuAL can now be distilled out of SBP (see the Supporting Information for distillation calculations) and sold as a chemical, or it can be hydrogenated with nearly quantitative yields over a metal catalyst (e.g., copper) in the vapor phase to form FuOH, an important chemical in the polymer industry.[14,15] Importantly, as explored below, this FuOH intermediate can be used in another biphasic reactor system to produce LA, another attractive platform molecule from which fine chemicals (e.g., δ-aminolevulinic acid, diphenolic acid) and fuel additives (e.g., levulinate esters, MTHF) can be produced.[18]

The conversion of FuOH in alcohol solvents to produce levulinate esters has been reported in the literature with high yields;[13] however, when LA is the desired product, the conversion of FuOH to LA in aqueous acidic solutions is plagued by polymerization reactions that lead to low selectivities at even modest concentrations (e.g., 1 wt %) when compared to production of levulinate esters. For example, we have achieved an ethyl levulinate yield of 85 % starting with 1 wt % FuOH in ethanol using Amberlyst-15 as the acid catalyst, as opposed to a lower yield of 55 % for production of LA in water at 398 K with equal amount of catalyst and reaction time (see the Supporting Information). The same trend is also seen for ZSM-5. We achieved 64 % yield to ethyl levulinate in alcohol compared to 15 % yield to LA (Table 2, entry 1) in water at the same reaction conditions. This behavior is observed because the rates of undesirable reactions in acidic aqueous solutions increase more rapidly with reactant concentration than the rates of desirable reactions, such that the selectivity for desirable reactions becomes lower at higher reactant concentrations.

The strategy employed in this paper is to utilize biphasic reactors to achieve a low concentration of reactive species in acidic aqueous solutions to increase LA yields by minimizing undesirable polymerization reactions, and yet to achieve a high concentration of the final product to facilitate product separation and purification. To apply this concept, a biphasic reactor with SBP was employed to form LA, as seen in Figure 1, in a manner analogous to the case of xylose dehydration to FuAL. In the case of FuOH conversion to LA, the organic extracting solvent partitions the reactant out of the reactive aqueous phase (thereby maintaining a low concentration in the aqueous solution), whereas in the case of xylose dehydration to FuAL, the product is partitioned out of the reactive aqueous phase.

Due to a high partition coefficient (7.5) of FuOH in the SBP–water system, the FuOH reactant remains mostly in the organic phase, decreasing the FuOH concentration in the acidic aqueous medium and, thus, decreasing the rates of degradation reactions accordingly. When the reaction is carried out in a biphasic reactor, mineral acids can be used instead of solid acid catalysts, and these mineral acids can be recovered and recycled,[17,19] eliminating any issues of deactivation and regeneration of possible solid acid catalysts. It should be noted that another important function of the extracting solvent for production of LA is to extract the majority of LA to the organic layer to enable its separation from the mineral acid in the aqueous layer. It can be seen in Table 2 that up to ca. 72 % yield of LA can be obtained using a biphasic system containing aqueous 1 M H_2SO_4 solution and SBP (entry 3 and 4), while only 32 % yield of LA is obtained in a single aqueous phase medium with 1 M H_2SO_4 and 1 wt % FuOH feed (Table 2, entry 2). Approximately 67 % of LA can be retained in the SBP layer when the volume ratio of organic to aqueous layer is 1 (entry 3). However, by decreasing the amount of aqueous layer to obtain a ratio of 2 (entry 5), a higher amount of LA (ca. 81 %) can be recovered in the organic layer, while still reaching approximately 66 % total yield, compared to 68 %, shown in entry 3. (The LA that remains in the aqueous solution after phase separation of the solvents will be essentially inert when the aqueous phase is used in subsequent biphasic processing of furfuryl alcohol, and thus this LA can be recovered in the process.)

While use of the SBP solvent leads to a significant increase in the yield of LA compared to monophasic reaction in water, it can be seen in Table 2, entry 6 that increasing the concentration of FuOH from 1 to 10 wt% in SBP leads to a decrease in the LA yield (ca. 31%). An additional strategy to ensure that the concentrations of the reactant and the intermediates always remain low versus time is to employ semi-batch operation, similar to Lange et al.[13] (see Supporting Information), in which the FuOH solution in SBP is slowly fed to the reactor that includes a heated solution of 1 M H_2SO_4 solution. This semi-batch operation resulted in LA yields of around 65% starting with 10–20 wt% FuOH solutions (Table 3, entries 3–4), and more than 70% of the total LA is partitioned into the organic layer. In contrast to these high yields obtained using SBP and semi-batch operation, the yields of LA are still low (Table 3, entries 1 and 2) in a semi-batch mode with a single aqueous phase using ZSM-5, these yields being ca. 45% and ca. 35% starting with feeds containing 10 and 20 wt% FuOH concentrations, respectively. Thus, the high partition coefficient of FuOH in the SBP-water system allows for high yields of LA even at high feed concentrations that cannot be obtained in monophasic water systems. The solution of LA in SBP can then be processed further as presented in our earlier work to form GVL over a Ru–Sn catalyst.[17]

Since the boiling point of LA (519 K) is higher than that of SBP (500 K), LA cannot be removed from the SBP solvent at the top of a distillation column. For this reason, two possible alkylphenol solvents with higher boiling points were studied. One alkylphenol solvent is 4-*n*-hexyl phenol (NHP; boiling point 560 K), which as seen in Table 3 (entry 5), resulted in good yields of LA (ca. 70%) with a 10 wt% FuOH feed and 1:1 volume ratio of the organic solvent to the acidic aqueous solution, with a slightly lower partitioning of LA (60% being in NHP).

Another possible alkylphenol solvent for biphasic reactor operation is 4-propyl guaiacol (PG), which has a boiling point of 537 K. Importantly, this compound has been reported to be isolated from lignin degradation.[20] It can be seen in entry 6 that good overall yields of LA (ca. 69%) can be obtained with 2:1 organic to aqueous volume ratio, with ca. 60% being retained in PG. As shown in entries 7 and 8, higher concentrations of FuOH result in lower overall yields, however, the yields of LA in these biphasic reactor systems are still considerably higher than those obtained in monophasic aqueous phase systems with ZSM-5.

The biorefining strategy outlined here offers the production of FuAL and LA from the hemicellulose portion of lignocellulosic biomass utilizing biphasic systems with new solvent systems. In the case of xylose dehydration, the presence of an extractive organic solvent enables the continuous removal of the highly reactive product (FuAL) from the acidic aqueous medium to prevent further degradation. In the case of FuOH hydrolysis, the biphasic system avoids high concentrations of the highly reactive reactant and/or intermediates in the acidic aqueous medium to prevent oligomerization reactions of FuOH that result in the formation of solid humins. In both of these reaction systems, the organic solvent extracts the majority of the FuAl and LA products, enabling the separation of these valuable products from the mineral acid in the aqueous layer. Use of solvents such as SBP, NHP and PG allows for the production of FuAL and LA at higher concentrations compared to monophasic reactions in water, leading to more efficient separation of these products at the top of distillation columns. In addition, these three new solvents may possibly be produced from lignin, leading to new research directions for the creation of sustainable biorefineries that utilize effectively the hemicellulose, cellulose, and lignin fractions of lignocellulosic biomass.

Experimental Section

Dehydration of xylose and hydrolysis of FuOH were carried out in biphasic systems that consisted of an aqueous mineral acid solution (HCl and H_2SO_4, respectively) and an organic extracting solvent (SBP, NHP, and PG). The experiments with solutions of xylose and FuOH (1 wt%) were carried out in 10 mL glass reactors kept at constant temperature (443 K and 398 K, respectively) in a pre-heated oil bath using magnetic stirring. Semi-batch experiments for higher FuOH feed concentrations were carried out in a 50 mL Parr reactor by slowly feeding FuOH solutions to the preheated aqueous H_2SO_4 solutions. Upon completion of the reactions, the two phases were separated and analyzed to quantify FuAL, FuOH, LA, and xylose using GC (Shimadzu GC 2060, equipped with a DB-5 column (Restek) and an FID) and HPLC (Waters 2695 system with a Bio-Rad

Table 3. Yields to levulinic acid starting from furfuryl alcohol solutions in 2-*sec*-butylphenol (SBP), 4-*n*-hexylphenol (NHP), or 4-propyl guaiacol (PG) in a biphasic reactor system with water or in a monophasic system with water at 398 K. All reactions were carried out in a semi-batch reactor system. LA and SA correspond to levulinic acid and 1 M sulfuric acid, respectively. Furfuryl alcohol conversion is complete for all experiments.

Entry	Furfuryl alcohol [wt%]	Organic solvent	Org./aq. [mL mL^{-1}]	Catalyst	WHSV [h^{-1}]	Yield to LA [%]	LA in org. [%]	LA in soln. [wt%]
1	10 (20)[a]	–	–	ZSM-5	0.24	45 ± 1	–	5.7 ± 0.2
2	20 (40)[a]	–	–	ZSM-5	0.48	35 ± 1	–	10.0 ± 0.2
3	10 (20)[a]	SBP	1	SA	0.08	67 ± 2	72 ± 1	5.2 ± 0.2
4	20[b]	SBP	1	SA	0.16	65 ± 2	67 ± 1	10.2 ± 0.2
5	10[b]	NHP	1	SA	0.08	70 ± 2	60 ± 2	4.7 ± 0.2
6	10[b]	PG	2	SA	0.16	69 ± 3	58 ± 2	4.6 ± 0.4
7	20 (40)[a]	PG	2	SA	0.32	59 ± 3	61 ± 2	8.8 ± 0.6
8	30 (60)[a]	PG	2	SA	0.48	55 ± 3	60 ± 2	13.0 ± 0.6

[a] Experiments carried out by starting with solvent and catalyst and feeding a concentration of furfuryl alcohol (shown in parenthesis) to reach a final furfuryl alcohol concentration (value not in parenthesis). [b] Experiments carried out by starting with aqueous SA solutions and feeding the given concentration of furfuryl alcohol.

Aminex HPX-87H column and a UV detector) for organic and aqueous phase analyses, respectively. All the yields reported in Tables 1–3 are based on GC and HPLC analyses and are not isolated yields. Details of the experimental set-up and procedures are given in the Supporting Information.

Acknowledgements

This work was supported in part by the US Department of Energy Office of Basic Energy Sciences, and by the DOE Great Lakes Bioenergy Research Center (http://www.greatlakesbioenergy.org), which is supported by the US Department of Energy, Office of Science, Office of Biological and Environmental Research, through Cooperative Agreement DE-FC02–07ER64494 between The Board of Regents of the University of Wisconsin System and the US Department of Energy. We thank Sercan Murat Sen for the help with ASPEN simulations.

Keywords: furfural · hemicelluloses · heterogeneous catalysis · levulinic acid · sustainable chemistry

[1] B. C. Saha, *J. Ind. Microbiol. Biotechnol.* **2003**, *30*, 279.
[2] J. Zaldivar, J. Nielsen, L. Olsson, *Appl. Microbiol. Biotechnol.* **2001**, *56*, 17.
[3] A. S. Mamman, J.-M. Lee, Y.-C. Kim, I. T. Hwang, N.-J. Park, Y. K. Hwang, J.-S. Chang, J.-S. Hwang, *Biofuels, Bioprod. Biorefin.* **2008**, *2*, 438.
[4] H. Mehdi, V. Fabos, R. Tuba, A. Bodor, L. T. Mika, I. T. Horvath, *Top. Catal.* **2008**, *48*, 49.
[5] G. W. Huber, J. N. Chheda, C. J. Barrett, J. A. Dumesic, *Science* **2005**, *308*, 1446.
[6] J.-P. Lange, R. Price, P. M. Ayoub, J. Louis, L. Petrus, L. Clarke, H. Gosselink, *Angew. Chem.* **2010**, *122*, 4581; *Angew. Chem. Int. Ed.* **2010**, *49*, 4479.
[7] J. Q. Bond, D. M. Alonso, D. Wang, R. M. West, J. A. Dumesic, *Science* **2010**, *327*, 1110.
[8] M. Mascal, E. B. Nikitin, *Angew. Chem.* **2008**, *120*, 8042; *Angew. Chem. Int. Ed.* **2008**, *47*, 7924.
[9] Y. Roman-Leshkov, J. N. Chheda, J. A. Dumesic, *Science* **2006**, *312*, 1933.
[10] J. N. Chheda, Y. Roman-Leshkov, J. A. Dumesic, *Green Chem.* **2007**, *9*, 342.
[11] R. Xing, A. V. Subrahmanyam, H. Olcay, W. Qi, W. G. P. van, H. Pendse, G. W. Huber, *Green Chem.* **2010**, *12*, 1933.
[12] W. D. Van De Graaf, J.-P. Lange, WO2007023173A1, **2007**.
[13] J.-P. Lange, W. D. van de Graaf, R. J. Haan, *ChemSusChem* **2009**, *2*, 437.
[14] B. M. Nagaraja, A. H. Padmasri, B. D. Raju, K. S. R. Rao, *J. Mol. Catal. A: Chem.* **2007**, *265*, 90.
[15] R. S. Rao, R. T. K. Baker, M. A. Vannice, *Catal. Lett.* **1999**, *60*, 51.
[16] R. M. West, Z. Y. Liu, M. Peter, J. A. Dumesic, *ChemSusChem* **2008**, *1*, 417.
[17] D. M. Alonso, S. G. Wettstein, J. Q. Bond, T. W. Root, J. A. Dumesic, *ChemSusChem* **2011**, *4*, 1078.
[18] J. J. Bozell, L. Moens, D. C. Elliott, Y. Wang, G. G. Neuenschwander, S. W. Fitzpatrick, R. J. Bilski, J. L. Jarnefeld, *Resour. Conserv. Recycl.* **2000**, *28*, 227.
[19] E. I. Gürbüz, D. M. Alonso, J. Q. Bond, J. A. Dumesic, *ChemSusChem* **2011**, *4*, 357.
[20] M. Phillips, *Science* **1931**, *73*, 568.

Received: September 29, 2011