Green Chemistry

Cite this: *Green Chem.*, 2012, **14**, 509

www.rsc.org/greenchem

PAPER

Conversion of carbohydrates and lignocellulosic biomass into 5-hydroxymethylfurfural using $AlCl_3 \cdot 6H_2O$ catalyst in a biphasic solvent system

Yu Yang,[a,b] Chang-wei Hu*[a] and Mahdi M. Abu-Omar*[b]

Received 7th August 2011, Accepted 1st November 2011
DOI: 10.1039/c1gc15972k

$AlCl_3 \cdot 6H_2O$ in a biphasic medium of water/tetrahydrofuran (THF) is effective for the synthesis of 5-hydroxymethylfurfural (HMF) from glucose-based carbohydrates. For glucose, an HMF yield of 61% was achieved in 10 min at 160 °C under microwave heating. The reaction time profile revealed the intermediacy of fructose *en route* to HMF with a dehydration rate constant that is approximately 4 times that of glucose isomerization to fructose. Addition of NaCl did not increase HMF yields significantly but it diminished lactic acid formation. Disaccharides (maltose and cellobiose) and starch gave good yields of HMF. However, cellulose required a higher temperature (180 °C) and longer reaction time (30 min) to give a modest yield of 37%. Several lignocellulosic biomass variants (corn stover, pine wood, grass, and poplar) were investigated with the $AlCl_3 \cdot 6H_2O$ biphasic system. The yields of HMF were modest (20–35%) but high concurrent yields of furfural were observed (51–66%). The described $AlCl_3 \cdot 6H_2O$–NaCl–H_2O/THF biphasic medium has potential because it is economic, nontoxic, and it exhibits fast kinetics (10 min) under microwave heating.

1. Introduction

5-Hydroxymethylfurfural (HMF) can be obtained from carbohydrates and lignocellulosic biomass. It has been hailed as the central biorenewable chemical from which liquid fuel and other important chemicals can be produced. HMF can serve as a precursor for levulinic acid (LA), 2,5-furandicarboxylic acid, 2,5-diformylfuran, dimethylfuran, and dihydroxymethylfuran, to name a few.[1] Dumesic and coworkers have shown that HMF can be used for the production of liquid alkanes.[2] It has also been shown that dimethylfuran, produced from hydrogenation of HMF, can directly serve as a high heating value fuel.[3] Hence, the demand for HMF will continue to grow as supply of petroleum feedstock diminishes and the price of petroleum continues to rise. Excellent yields of HMF can be achieved from the dehydration of fructose. However, obtaining HMF from glucose is more difficult because it requires a bifunctional catalyst that would affect the isomerization of glucose to fructose and subsequent dehydration of fructose.

Glucose is the most abundant and cheapest hexose, and therefore, it is the preferred source for the production of HMF. Glucose conversion to HMF proceeds *via* isomerization of glucose to fructose, followed by dehydration of fructose in the presence of a biological catalyst/enzyme,[4] base,[5] or metal chloride.[6] Among these catalysts, metal chlorides are favored because they catalyze effectively isomerization and dehydration. Zhao *et al.* have shown that using $CrCl_2$ in ionic liquid leads to HMF yields of 67% at 100 °C.[6a] Hu and co-workers reported a catalytic conversion of glucose using $SnCl_4$, in which HMF was formed in 64% yield.[6b] These catalyst systems, however, have drawbacks, as Cr and Sn are toxic, while ionic liquids are expensive and their application on industrial scale remains prohibitive.

$AlCl_3 \cdot 6H_2O$ is abundant and cheap; it has also been shown to catalyze the isomerization of glucose to fructose in aqueous solution.[7] However, in aqueous solution the reaction leads to further degradation of HMF to LA and humins.[8] In order to remove HMF from the reactant sugar and acidic catalyst as it is being produced, water immiscible organic solvent can be added to continuously extract HMF from the aqueous phase.[9] Among different extracting solvents, tetrahydrofuran (THF) is attractive because of its high partitioning coefficient and low boiling point. Moreover, THF is an ideal solvent for further upgrading of HMF with dihydrogen because THF is a saturated hydrocarbon and it does not contain functional groups that would be hydrogenated. Inorganic salts have been used as additives to

---

[a] *Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan, 610064, P. R. China. E-mail: gchem@scu.edu.cn*
[b] *Department of Chemistry and the Center for Direct Catalytic Conversion of Biomass to Biofuels (C3Bio), Purdue University, 560 Oval Drive, West Lafayette, Indiana, 47907, U. S. A. E-mail: mabuomar@purdue.edu*

increase the partitioning coefficient between THF and water.[3,10] NaCl is among the most effective and cheapest salts and has been shown by Román-Leshkov and Dumesic to significantly improve partitioning of HMF into the organic phase.[10] In this report, we describe a one-pot synthesis of HMF from carbohydrate and lignocellulosic biomass using $AlCl_3\cdot 6H_2O$ as a catalyst in an H_2O/THF biphasic medium. The effect of NaCl was also investigated.

2. Experimental

Glucose, maltose, cellobiose, starch, cellulose, $AlCl_3\cdot 6H_2O$, NaCl, HCl (37 wt%), THF, HMF, LA, and lactic acid were all analytical grade, purchased from Sigma-Aldrich, and used as received. Corn stover was obtained from Purdue University, Department of Agriculture. Dr Keith Johnson (Purdue University) supplied the switch grass, Mr. Jerry Warner (Defence LifeSciences, LLC) provided the pine wood, and the USDA Forest Product Lab (CAFI Consortium) supplied the poplar. The approximate composition of lignocellulosic biomass was based on published values.[11] For example, corn stover is 27% (by weight) pentose (xylose and arabinose), 35% hexose (glucose), 11% lignin, and 27% other (ash, protein, *etc.*).[11a]

All reactions were performed under microwave heating in the Discover TM System (CEM Corporation) using a 10 mL batch reaction vessel. Reaction solutions were mixed using a magnetic stir bar. The reactor temperature was measured by a fiber optic sensor. In a typical experiment for the transformation of glucose in single phase, a 10 mL reaction tube was charged with glucose (0.25 mmol), $AlCl_3\cdot 6H_2O$ (0.1 mmol), NaCl (0.35 g) and Millipore water (1 mL); the reaction was heated to 160 °C for 10 min. In a typical experiment for the transformation of glucose and other carbohydrates in biphasic system, a 10 mL reaction tube was charged with glucose or other carbohydrates (0.25 mmol based on monosaccharide units), $AlCl_3\cdot 6H_2O$ (0.1 mmol), NaCl (0.35 g), Millipore water (1 mL) and THF (3 mL); the reaction was heated to 160 °C for 10 min. In a typical experiment for the transformation of biomass in biphasic system, a 10 mL reaction tube was charged with biomass (0.05 g), $AlCl_3\cdot 6H_2O$ (0.1 mmol), NaCl (0.35 g), Millipore water (1 mL) and THF (3 mL); the reaction was heated to 180 °C for 30 min. The reaction was stopped by nitrogen flow cooling. Samples were filtered with a 0.2 mm syringe filter prior to analysis.

The aqueous phase was analyzed by HPLC using a Waters 1525 pump, an aminex column HPX-87 column (Agilent), and Waters 2412 Refractive Index detector. H_2SO_4 (5 mM) was used as the mobile phase at a flow rate of 0.6 mL min^{-1}, and the column temperature was maintained at 338 K. The concentrations of HMF, LA and lactic acid in the organic phase were determined by gas chromatography (Agilent 6890) equipped with DB-5 column and flame ionization detector (FID). All concentrations of carbohydrates in the aqueous phase and organic products in the aqueous phase and organic phase were determined by comparison to standards calibration curves. Conversion of glucose and yield of products are defined as follows:

Glucose conversion = moles of glucose reacted/moles of starting glucose

Fructose yield = moles of fructose produced/moles of starting glucose

HMF yield = moles of HMF produced/moles of starting glucose

HMF recovery = moles of HMF recovered/moles of starting HMF

LA yield = moles of LA produced/moles of starting glucose or HMF

Lactic acid yield = moles of lactic acid produced/2*moles of starting glucose

For other carbohydrates and lignocellulosic biomass feedstock, product yields are defined as follows:

HMF yield = moles of HMF produced/moles of starting hexoses

Furfural yield = moles of furfural produced/moles of starting pentoses

The pH value of the H_2O–$AlCl_3\cdot 6H_2O$ (3.03) and H_2O–$AlCl_3\cdot 6H_2O$–NaCl (2.22) solutions (at 25 °C) was measured on an Accumet AB15/15+ pH meter (± 0.01 pH units) calibrated with standard buffer solutions.

3. Results and discussion

Glucose conversion in pure water in the presence of $AlCl_3\cdot 6H_2O$ affords a low HMF yield despite the high conversion of glucose (Table 1). The total combination of HMF, LA, and lactic acid accounts for only half of the starting glucose. The main reason for this poor selectivity is that HMF in the presence of an acidic catalyst is not stable in water due to formation of insoluble humins from the reaction of HMF with glucose.[12] This is supported by the poor recovery of HMF when used as the staring material under the same conditions (10 min microwave heating at 160 °C), last column of entry 1 in Table 1. The use of THF in a biphasic system with water increased HMF yield significantly to 52% (entry 2, Table 1). Meanwhile, only trace amounts of LA

Table 1 Glucose conversion with $AlCl_3\cdot 6H_2O$ in different media[a]

Entry	Solvent	Catalyst	Conv. (%)	Fructose yield (%)	HMF yield (%)	Lactic acid yield (%)	LA yield (%)	HMF recovery[c] (LA yield[d]) (%)
1	Single phase (H_2O)	$AlCl_3\cdot 6H_2O$	98	3	22	17	10	52 (22)
2	Biphasic (H_2O/THF)	$AlCl_3\cdot 6H_2O$	99	3	52	13	Trace	94 (1)
3	Single phase (H_2O–NaCl)	$AlCl_3\cdot 6H_2O$	98	0	17	—	29	19 (58)
4	Biphasic (H_2O–NaCl/THF)	$AlCl_3\cdot 6H_2O$	99	0	61	—	1	97 (2)
5	Biphasic (H_2O–NaCl/THF)	HCl[b]	30	0	12	—	2	—

[a] *Reaction conditions*: glucose = 0.25 mmol, $AlCl_3\cdot 6H_2O$ = 0.1 mmol, NaCl = 0.35g, H_2O = 1 mL, THF = 3 mL, reaction temperature = 160 °C, reaction time = 10 min. [b] pH = 1 in HCl (0.1 mmol) [c] *Reaction conditions*: HMF = 0.25 mmol, $AlCl_3\cdot 6H_2O$ = 0.1 mmol, NaCl = 0.35 g, H_2O = 1 mL, THF = 3 mL, reaction temperature = 160 °C, reaction time = 10 min. [d] Based on moles of starting HMF.

was formed, which also supports the notion that THF inhibited the rehydration of HMF to LA. Furthermore, in this H_2O/THF biphasic medium, the HMF recovery was high (94%) when HMF was employed as the reactant. The introduction of THF also decreased the yield of lactic acid. All of these improvements could be attributed to the continuous separation of HMF as it is being produced from the aqueous phase to the organic (THF) phase.

To increase the partitioning coefficient further, NaCl was used as an additive to the aqueous phase. The effect of NaCl additive on the conversion of glucose in water was tested first (entry 3, Table 1). In this instance, the yield of HMF decreased and the yield of LA increased (29%), nearly three times the yield obtained without NaCl additive. It is also worth noting that in the presence of NaCl, HMF recovery was only 19% with high LA yield of 58%. In summary, in single phase aqueous medium NaCl improved the rehydration of HMF to LA. This improvement might very well be attributed to the decrease in pH upon introduction of NaCl (pH = 2.22 *versus* pH = 3.03). A similar phenomenon was observed in an aqueous solution of $B(OH)_3$. Addition of NaCl resulted in an increase of acidity.[13] The rate of HMF hydration to LA is known to be acid dependent.[14] Of course, an increase in acidity also facilitates dehydration of fructose to HMF.[14] A notable feature of the NaCl additive is the absence of lactic acid from the product mixture (entries 1 *versus* 3). Although HMF was more stable without NaCl in the single phase aqueous system, the effect of NaCl in the biphasic medium H_2O/THF was worth investigating because of the noted reduction in lactic acid formation. Even though addition of NaCl to the biphasic reaction system gave modest improvement in HMF yield (61 *versus* 52%), it had marked influence on selectivity by reducing lactic acid to a trace amount (entries 2 and 4). In any event, the yield of HMF with and without NaCl using $AlCl_3{\cdot}6H_2O$ is superior to employing a strong protic acid such as HCl (entry 5). Although the acidity of the aqueous phase is stronger when HCl is used (pH = 1 *versus* pH = 2.22), the conversion of glucose is only 30% and the HMF yield only 12%.

Although the amount of glucose relative to $AlCl_3{\cdot}6H_2O$ is 2.5 : 1, the reaction proceeds at lower catalyst loadings (Table 2). As the catalyst amount is decreased to 0.025 mmol, glucose conversion and HMF yield are reduced over the reaction time of 10 min. A longer reaction time of 30 min with 0.025 mmol catalyst loading (10 mol%) is required to reach high conversion and HMF yield (entry 5, Table 2).

Given that the H_2O–NaCl/THF biphasic system with $AlCl_3{\cdot}6H_2O$ resulted in the best yield and selectivity for HMF, we obtained a time profile of the reaction (Fig. 1). In the initial stage of the reaction fructose formation is observed reaching a maximum at *ca.* 1 min. It declines to zero as the reaction reaches completion in 5 min. This behavior supports fructose as an intermediate for HMF production from glucose in this system. For a kinetic model of A → I → P (where A is reactant, I intermediate, and P product) with rate constants k_1 and k_2, the following two equations describe the ratio of the rate constants based on the maximum concentration of I and the time that maximum is reached: $[\mathrm{I}]_{\max} = [\mathrm{A}]_0(k_2/k_1)^{(k_2/(k_1-k_2))}$ and $t_{\max} = \ln(k_2/k_1)/k_2-k_1$. The amount of fructose built up relative to glucose is consistent with a rate of formation of fructose that is approximately 4 times slower than its subsequent dehydration to HMF. In other words, with A = glucose, I = fructose, and P = HMF, k_2/k_1 ~4. Longer reaction times (> 10 min) lead to further degradation of HMF to LA and insoluble humins.

Table 2 Glucose conversion with $AlCl_3{\cdot}6H_2O$ as the catalyst[a]

Entry	Catalyst $AlCl_3{\cdot}6H_2O$ (mmol)	Glucose conversion (%)	Fructose yield (%)	HMF yield (%)
1	0.15	100	0	60
2	0.10	99	0	61
3	0.050	88	10	54
4	0.025	70	15	39
5	0.025[b]	98	0	65

[a] *Reaction conditions*: glucose = 0.25 mmol, NaCl = 0.35 g, H_2O = 1.0 mL, THF = 3.0 mL, reaction temperature = 160 °C, reaction time = 10 min. [b] Reaction time = 30 min.

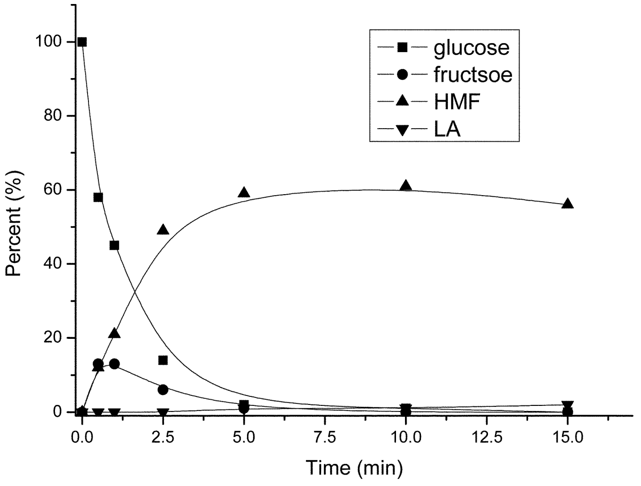

Fig. 1 Conversion of glucose as a function of time using $AlCl_3{\cdot}6H_2O$ in H_2O/THF biphasic medium. *Reaction conditions*: glucose = 0.25 mmol, $AlCl_3{\cdot}6H_2O$ = 0.1 mmol, NaCl = 0.35 g in H_2O/THF (1 : 3 mL) at 160 °C under microwave heating.

We tested $AlCl_3{\cdot}6H_2O$ in biphasic H_2O/THF with NaCl additive for the conversion of disaccharides (maltose and cellobiose) and polysaccharides (starch and cellulose), Fig. 2. HMF yields

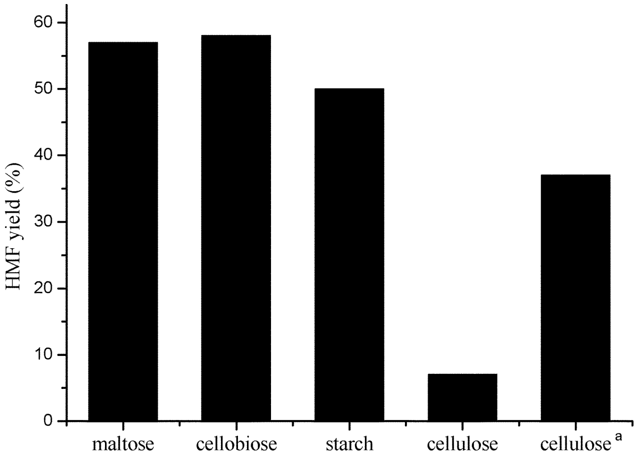

Fig. 2 HMF yields from various carbohydrates in biphasic H_2O–NaCl/THF system. *Reaction conditions*: carbohydrate = 0.25 mmol based on monosaccharide units, $AlCl_3{\cdot}6H_2O$ = 0.1 mmol, NaCl = 0.35 g, H_2O = 1 mL, THF = 3 mL, temperature = 160 °C, reaction time = 10 min. [a]Reaction temperature = 180 °C, reaction time = 30 min.

Table 3 Comparison of $AlCl_3 \cdot 6H_2O$ *versus* HCl as the catalyst for cellobiose and poplar conversion[a]

Entry	Starting material	Catalyst	Glucose yield (%)	HMF yield (%)	Xylose yield (%)	Furfural yield (%)
1	Cellobiose	$AlCl_3 \cdot 6H_2O$	1	58	na[b]	na
2	Cellobiose	HCl	62	10	na	na
3	Poplar[c]	$AlCl_3 \cdot 6H_2O$	0	26	0	51
4	Poplar[c]	HCl	18	21	0	29

[a] *Reaction conditions*: cellobiose = 0.25 mmol based on glucose units, $AlCl_3 \cdot 6H_2O$ or HCl = 0.10 mmol, NaCl = 0.35 g, H_2O = 1.0 mL, THF = 3.0 mL, reaction temperature = 160 °C, reaction time = 10 min. [b] na = not applicable. [c] *Reaction conditions*: poplar = 0.05 g, $AlCl_3 \cdot 6H_2O$ or HCl = 0.10 mmol, NaCl = 0.35 g, H_2O = 1.0 mL, THF = 3.0 mL, reaction temperature = 180 °C, reaction time = 30 min.

from disaccharides were slightly lower than those obtained from glucose. Therefore, our biphasic system under microwave heating is effective in hydrolyzing the glycosidic linkage of disaccharides.[15] Conversion of starch to HMF was also quite efficient and selective (50% yield of HMF). However, cellulose conversion was quite poor, affording 7% HMF yield under the same conditions. The majority of the cellulose remained unconverted as a solid suspension in the aqueous phase. We reasoned that this poor reactivity with cellulose is most likely due to ineffective depolymerization and decrystallization with $AlCl_3 \cdot 6H_2O$ at 160 °C.[16] Indeed a higher temperature was needed for cellulose conversion. When the reaction was run at 180 °C for 30 min, HMF yields increased to 37%. These results demonstrate that $AlCl_3 \cdot 6H_2O$ in biphasic H_2O–NaCl/THF system can be used for conversion of complex carbohydrates to HMF with reasonable yields.

Our next step was to apply the $AlCl_3 \cdot 6H_2O$ biphasic system to raw biomass variants. HMF yields from corn stover, pine wood, grass and poplar were 19%, 35%, 23% and 26%, respectively (Fig. 3). These values from raw biomass are lower than those obtained from pure cellulose. Biomass is more complex than crystalline cellulose and it contains protein and ash,[11] which could affect the conversion of cellulose in the biomass to HMF. Interestingly, high furfural yields can be obtained from the raw biomass in our system (Fig. 3), ranging from 51–66% depending on the source of lignocellulosic biomass. Raines and Binder reported conversion of lignocellulosic biomass into furans using $CrCl_3$ and HCl as co-catalysts.[17] Moderate HMF yields can be obtained but with a low furfural yield (37% furfural yield was based on xylan analysis of 22.8% for untreated stover). Oktay used HCl for the conversion of straw biomass into furans.[18] Although the furfural yields were reasonable (46–72% based on different biomass samples), the HMF yields were very low (< 3%). We have also compared herein $AlCl_3 \cdot 6H_2O$ with HCl to ascertain that the role of $AlCl_3 \cdot 6H_2O$ goes beyond just generating a Brønsted acid (H_3O^+). The results for cellobiose and poplar are presented in Table 3. HCl is clearly less effective at converting cellobiose. Even though with poplar, HCl gave comparable HMF yield, it was less effective in converting the resulting glucose and in its yield of furfural. It should also be noted that HCl was used at an amount equal to $AlCl_3 \cdot 6H_2O$ (0.10 mmol), which results in a more acidic solution than that of $AlCl_3 \cdot 6H_2O$. In conclusion, compared to previous reports, our method provides moderate HMF yields along with quite high furfural yields from varying biomass sources in a one-pot reaction. Hence, the approach we describe herein with $AlCl_3 \cdot 6H_2O$ and biphasic medium should be valuable for the conversion biomass into biofuels and platform chemicals.

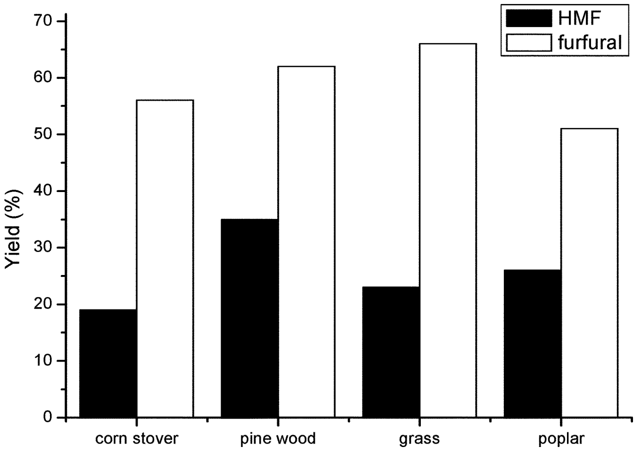

Fig. 3 Furfural and HMF yields from various lignocellulosic biomass in biphasic H_2O–NaCl/THF system using $AlCl_3 \cdot 6H_2O$ under microwave heating. *Reaction conditions*: Biomass = 0.05 g, $AlCl_3 \cdot 6H_2O$ = 0.1 mmol, NaCl = 0.35 g, H_2O = 1 mL, THF = 3 mL, temp = 180 °C, reaction time = 30 min. Yields of HMF from corn stover, pine wood, grass and poplar were based on a hexose content of 35%, 26%, 35% and 45% by weight and yields of furfural were based on a pentose content of 27%, 22%, 23 and 29% by weight, respectively.

4. Conclusions

The introduction of THF to the $AlCl_3 \cdot 6H_2O$ aqueous reaction system increases the yield and selectivity for HMF from glucose. The addition of NaCl increases the partitioning coefficient of HMF into a biphasic system and retards the route to lactic acid, enhancing the yield and selectivity for HMF. Satisfactory results were obtained with glucose-based disaccharides (maltose and cellobiose), polysaccharides (starch and cellulose), and raw biomass. While the yields of HMF from variant lignocellulosic biomass sources (corn stover, pine wood, poplar, and grass) were modest, 20–35% based on hexose content, the reaction produced high yields of furfural (51–66%) concurrently in one-pot reactions. The described aluminum system has excellent potential for application because it is cheap and nontoxic.

Acknowledgements

This work was financially supported by the National Basic Research Program of China (973 program, No. 2007CB210203), NNSFC 21072136, PCSIRT (No. IRT0846), the Center for Direct Catalytic Conversion of Biomass to Biofuels (C3Bio), an

Energy Frontier Research Center funded by the U. S. Department of Energy, Office of Science, and Office of Basic Energy Sciences under Award Number DE-SC0000997. C3Bio provided funding for laboratory space, instrumentation, and chemical supplies at Purdue University. We are also thankful for support from the China Scholarship Council (Grant 2010624099).

References

1 (*a*) A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411–2502; (*b*) A. A. Rosatella, S. P. Simeonov, R. F. M. Frade and C. A. M. Afonso, *Green Chem.*, 2011, **13**, 754–793.
2 G. Huber, J. Chheda, C. Barrett and J. Dumesic, *Science*, 2005, **308**, 1446–1450.
3 Y. Román-Leshkov, C. Barrett, Z. Liu and J. Dumesic, *Nature*, 2007, **447**, 982–985.
4 R. L. Huang, W. Qi, R. X. Su and Z. M. He, *Chem. Commun.*, 2010, **46**, 1115–1117.
5 (*a*) M. Watanabe, Y. Aizawa, T. Iida, R. Nishimura and H. Inomata, *Appl. Catal., A*, 2005, **295**, 150–156; (*b*) A. Takagaki, M. Ohara, S. Nishimura and K. Ebitani, *Chem. Commun.*, 2009, 6276–6268; (*c*) H. Yan, Y. Yang, D. Tong, X. Xiang and C. Hu, *Catal. Commun.*, 2009, **10**, 1558–1563.
6 (*a*) H. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, *Science*, 2007, **316**, 1597–1600; (*b*) S. Hu, Z. Zhang, J. Song, Y. Zhou and B. Han, *Green Chem.*, 2009, **11**, 1746–1749.
7 C. Rasrendra, I. G. B. N. Makertihartha, S. Adisasmito and H. Heeres, *Top. Catal.*, 2010, **53**, 1241–1247.
8 L. Peng, L. Lin, J. Zhang, J. Zhuang, B. Zhang and Y. Gong, *Molecules*, 2010, **15**, 5258–5272.
9 (*a*) Y. Román-Leshkov, J. Chheda and J. Dumesic, *Science*, 2006, **312**, 1933–1937; (*b*) J. Chheda, Y. Román-Leshkov and J. Dumesic, *Green Chem.*, 2007, **9**, 342–350.
10 Y. Román-Leshkov and J. A. Dumesic, *Top. Catal.*, 2009, **52**, 297–303.
11 (*a*) Y. L. Lu and N. S. Mosier, *Biotechnol. Prog.*, 2007, **23**, 116–123; (*b*) Y. L. Lu and N. S. Mosier, *Biotechnol. Bioeng.*, 2008, **101**, 1170–1181; (*c*) C. E. Wyman, B. E. Dale, R. T. Elander, M. Holtzapple, M. R. Ladisch, Y. Y. Lee, C. Mitchinson and J. N. Saddler, *Biotechnol. Prog.*, 2009, **25**, 333–339.
12 A. A. Rosatella, S. P. Simeonov, R. F. M. Frade and C. A. M. Afonso, *Green Chem.*, 2011, **13**, 754–793.
13 T. S. Hansen, J. Mielby and A. Riisager, *Green Chem.*, 2011, **13**, 109–114.
14 B. F. M. Kuster and H. M. G. Temmink, *Carbohydr. Res.*, 1977, **54**, 185–191.
15 A. Charmot and A. Katz, *J. Catal.*, 2010, **276**, 1–5.
16 J. Zhang, B. Zhang, L. Lin, S. Liu and P. Ouyang, *Biotechnol. Adv.*, 2010, **28**, 613–619.
17 J. B. Binder and R. T. Raines, *J. Am. Chem. Soc.*, 2009, **131**, 1979–1985.
18 O. Yemis and G. Mazza, *Bioresour. Technol.*, 2011, **102**, 7371–7378.