# Green Chemistry

## **RSC**Publishing

### COMMUNICATION

#### Cite this: DOI: 10.1039/c2gc36536g

Received 28th September 2012, Accepted 26th October 2012 DOI: 10.1039/c2gc36536g

www.rsc.org/greenchem

## Production and upgrading of 5-hydroxymethylfurfural using heterogeneous catalysts and biomass-derived solvents†

Jean Marcel R. Gallo, David Martin Alonso, Max A. Mellmer and James A. Dumesic\*

High yields of HMF from glucose can be achieved using biomassderived solvents and a combination of solid Lewis and Brønsted catalysts in a salt-free reaction system. The HMF produced in this system can be oxidized to FDCA or hydrogenated to DMF, both being highvalue chemicals.

The conversion of renewable biomass resources into chemicals and fuels traditionally obtained from petroleum is strategically important to improve the sustainability of the chemical industry. Lignocellulosic biomass is the non-edible portion of biomass, and extensive research has been carried out in its conversion into platform molecules. The platform molecule 5-hydroxymethylfurfural (HMF), produced from the Brønsted acid catalyzed dehydration of C<sub>6</sub> sugars (hexoses), is considered to be one of the top value-added chemicals.<sup>1</sup> Mechanistic studies have shown that HMF is formed from the dehydration of the hexoses in the furanose form (5-member ring).<sup>2-4</sup> Although glucose is the most abundant and least expensive hexose, it presents low amounts of furanose isomer in solution (1% in water<sup>5</sup>), and its dehydration into HMF thus takes place with low selectivity.<sup>6</sup> In contrast, fructose, which presents 21.5% of the furanose form in aqueous solution,<sup>5</sup> can be dehydrated to HMF in higher yields using monophasic or biphasic solvent systems and using homogeneous and heterogeneous Brønsted acids.7-13 Dumesic and co-workers14,15 employed a biphasic system consisting of an aqueous layer saturated with NaCl and containing fructose and HCl or H<sub>2</sub>SO<sub>4</sub> as catalysts, in combination with an extracting organic layer to protect HMF from degradation reactions. Several alcohols, ketones, and ethers were used as extracting organic layers, and yields for HMF as high as 70% were observed.<sup>14,15</sup> In monophasic solvent systems using dimethyl sulfoxide or ionic liquids as solvents, HMF can be obtained with yields

E-mail: dumesic@engr.wisc.edu; Fax: +1-608-262-5434; Tel: +1-608-262-109

†Electronic supplementary information (ESI) available: Experimental Section, Fig. S1, Fig. S2 and Table S1. See DOI: 10.1039/c2gc36536g



Fig. 1 Conversion of glucose to HMF by a combined isomerization/dehydration reaction pathway.

higher than 90%;<sup>7,11,16</sup> however, the separation and purification of HMF from these solvents are complicated.

While glucose can be obtained from cellulose by hydrolysis with yields of 98–100%, isomerization of glucose to fructose is economically limited to 42%,<sup>17</sup> requiring additional and expensive separation steps. As a consequence, the final market price of fructose is significantly higher than that of glucose. In order to obtain HMF in high yields from glucose, recent studies have aimed to use one-pot isomerization reactions to produce fructose by using a Lewis acid or Lewis base, followed by Brønsted acid-catalyzed dehydration of fructose to HMF (Fig. 1).

Zhao et al.11 first reported HMF yields of 68-70% from glucose in the ionic liquid 1-ethyl-3-methyl-imidazolium chloride using CrCl<sub>2</sub> as the Lewis acid catalyst. In subsequent studies with ionic liquids, HMF was produced from glucose with yields higher than 90%.18 However, ionic liquids are not yet suitable for large scale applications due to their high cost and deactivation by small amounts of water.7 Binder and Raines<sup>12</sup> reported that a system using dimethylacetamide (DMA), NaBr, and  $CrCl_2$  resulted in HMF yields of 81%, being as effective as ionic liquid systems. Other authors have explored biphasic systems. Huang et al.<sup>19</sup> reported a 63% HMF yield in a biphasic reactor system with a two-step process involving the isomerization of glucose to fructose in the presence of glucose isomerase and borate ions, followed by the HClcatalyzed dehydration of fructose to HMF. Dumesic and coworkers<sup>6</sup> reported 62% yield of HMF from glucose using a biphasic reactor consisting of AlCl<sub>3</sub>·6H<sub>2</sub>O and HCl as catalysts in water saturated with NaCl, in contact with sec-butylphenol. In all of these systems, the main goal was to maximize HMF yield, while the upgrading and purification of HMF and the

Department of Chemical and Biological Engineering, University of Wisconsin-Madison, 1415 Engineering Drive, Madison, WI 53706, USA.



Fig. 2 Pathways for the production of THF, GVL and other  $\gamma$ -lactones from biomass.  $^{(*)}2$ - and 3-pentenoic acid are also formed in the isomerization, however, the consecutive reaction takes place with the 4-pentenoic acid isomer.

sustainability of the process remained as secondary problems. For example, reutilization of homogeneous catalysts can be an issue, and these catalysts lead to corrosion problems that require expensive materials of construction. Moreover, the replacement of these homogeneous catalysts with heterogeneous catalysts is not possible in the presence of salts, due to exchange of protons on the catalyst with cations in solution, leading to deactivation of the heterogeneous catalyst. Furthermore, the sustainability of biomass conversion process would be improved by the use of biomass-derived solvents, alleviating the need to purchase and transport petroleum-derived solvents to the biomass conversion site. These solvents must operate in presence of solid catalysts at reaction conditions favorable for glucose or fructose dehydration, and they must be compatible with upgrading processes, which typically involve oxidation, hydrogenation, or hydrogenolysis reactions.

Herein, we present an integrated process using solid acid catalysts and biomass-derived solvents, y-lactones and tetrahydrofuran (THF), for the conversion of glucose to HMF, followed by the subsequent upgrading of HMF by hydrogenation or oxidation. As depicted in Fig. 2,  $\gamma$ -valerolactone (GVL) can be obtained from hydrogenation of levulinic acid, a platform molecule derived from monosaccharide dehydration. In addition, GVL is an important platform molecule used for the production of chemicals and fuels.<sup>20,21</sup> Other  $\gamma$ -lactones with higher molecular weights can be obtained from GVL, as described elsewhere,<sup>22,23</sup> or by ring closing of unsaturated acids.<sup>24</sup> Thus, in addition to using GVL, we have studied  $\gamma$ -hexalactone (GHL), y-octalactone (GOL), and y-undecalactone (GUL). Similar to GVL, THF can be derived from biomass from the decarbonylation and hydrogenation of furfural, a product of xylose dehydration.<sup>25,26</sup>

To begin our studies of  $\gamma$ -lactones and THF as biomassderived solvents for conversion of hexoses to HMF, we

**Table 1** Conversion of glucose or fructose to HMF in a biphasic system with  $\gamma$ -lactones, THF, and SBP as the extracting organic layer<sup>a</sup>

Feed	Organic layer	Time/ min	Conv./ %	Selec./ %	% HMF in org. layer	% HCl in org. layer
Fructose	GVI	20	9/	84	Q/I	30
Glucose	GVL	20 40	20	70	04	30
Clucose	CIT	40	00	65	02	30
Glucose	GUL	40	00	05	92	20
Glucose	GOL	40	89	65	92	10
Glucose	GUL	40	92	54	83	0
Glucose <sup>b</sup>	THF	_	80	71	93	30
Glucose <sup>b</sup>	SBP	40	91	68	97	0

<sup>*a*</sup> Reaction conditions: 1.5 g of NaCl-saturated aqueous feed (5 wt% glucose, or fructose, 5.0 mmol  $L^{-1}$  AlCl<sub>3</sub>, and 3.17 mmol  $L^{-1}$  HCl); 3.0 g of organic solvent; temperature 170 °C. <sup>*b*</sup> Results from ref. 6.

employed biphasic systems similar to those reported previously where THF and *sec*-butylphenol were used as the organic layers.<sup>6</sup> In biphasic reactors, monosaccharide dehydration takes place in the aqueous layer, followed by the extraction of HMF by the organic layer, where it is protected from the catalysts, minimizing side reactions. The aqueous layer has to be saturated with NaCl to diminish the solubility of both the organic solvent and HMF, improving the efficiency of the organic extracting layer. Aluminium chloride is used as isomerization catalyst, while dehydration is catalyzed by HCl.

As seen in the results presented in Table 1, the selectivity for conversion of glucose to HMF using the  $\gamma$ -lactones in a biphasic system (with the exception of GUL) are comparable with systems using THF and SBP as the extracting solvent. However, as observed previously with THF,  $\gamma$ -lactones extract part of the HCl from the aqueous layer, which not only affects HMF separation or upgrading, but also increases process cost, because the aqueous layer has to be re-acidified and the organic layer has to be neutralized. For example, the molar ratio of HMF formed to HCl lost is approximately 200 when using THF and GVL as the extracting solvents. The use of SBP appears to be the most promising solvent for these biphasic systems, due to high HMF selectivity and negligible extraction of HCl; however, the high toxicity of this solvent could limit its application.

Of the solvents listed in Table 1, THF, GVL, and GHL can form a monophasic mixture with water. THF and GVL are completely miscible in water, while GHL can dissolve 7–10 wt% of water. The use of monophasic solvent systems alleviates potential mixing problems that may be encountered when scaling up biphasic systems. Accordingly, we next studied the production of HMF from glucose in a solvent system consisting of GVL, GHL, or THF with 10 wt% water using AlCl<sub>3</sub> and HCl as catalysts. As shown in Table 2, the results obtained in these monophasic systems are similar to those shown in Table 1.

A potential advantage of using the above monophasic systems is that the addition of salt is not necessary (as it is to achieve a biphasic system with these solvents), allowing the homogeneous catalysts used for glucose isomerization and

Table 2 Conversion of glucose to HMF in a monophasic system with THF or  $\gamma\text{-lactones}$  and 10 wt% water  $^a$ 

Feed	Organic	Time/	Conversion/	Selectivity/
	solvent	min	%	%
Glucose	GVL	20	89	66
Glucose	GHL	20	90	65
Glucose	THF	20	90	56

<sup>*a*</sup> Reaction conditions: 1.5 g of organic solvent:water (9:1); feed (2 wt% glucose, 5.0 mmol  $L^{-1}$  AlCl<sub>3</sub>, and 3.17 mmol  $L^{-1}$  HCl); temperature 170 °C.

fructose dehydration to be replaced by solid acid catalysts. Accordingly, conversion of glucose to HMF would need two kinds of catalysts: a solid Lewis acid or Lewis base to substitute aluminium chloride and a solid Brønsted acid to substitute HCl.

Recent studies have shown that hydrotalcites<sup>27</sup> and tin containing zeolites and silicas<sup>28</sup> are active for glucose isomerization to fructose. Using a combination of Sn- $\beta$  and HCl in a biphasic system, Nikolla *et al.*<sup>29</sup> obtained HMF yields of 57% at 79% conversion of glucose. No tin leaching was observed.<sup>29</sup> Takagaki *et al.*<sup>27</sup> reported HMF yields of 42% at 73% conversion in a two-step process by combining the solid Brønsted acid catalyst, Amberlyst-70 (Amb-70), and a solid base catalyst, hydrotalcite, in *N*,*N*-dimethylformamide. The bifunctional catalyst Sulfated ZrO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub> led to 47.9% yield at total conversion in DMSO.<sup>30</sup>

To establish the most appropriate isomerization catalyst for glucose isomerization, a leaching test was performed for Sn- $\beta$  (Si:Sn = 400), Sn-SBA-15 (Si:Sn = 40) and hydrotalcite. For this test, 0.1 g of catalyst was stirred in a mixture GVL-H<sub>2</sub>O (9:1) for 30 min at 130 °C. The catalyst was removed by filtering (while the solution was still hot), and glucose was added to the solvent to make a 2 wt% sugar solution. The mixture was stirred for 30 min at 130 °C. Conversion of glucose was only observed in the solution contacted with hydrotalcite, indicating leaching.

The solid Brønsted acid catalyst used for our studies in monophasic reactor systems was Amb-70, a sulfonic acid functionalized catalyst that was shown in a previous study to be more selective for HMF production from fructose than other solid acid catalysts, such as zeolites (mordenite, ZSM-5, Z-Y, USY, and Z- $\beta$ ), cubic and amorphous zirconium phosphate, titanium oxide, niobium oxide, and phosphated niobic acid.<sup>10,31</sup> The same study also showed low deactivation of Amb-70 in the dehydration of fructose at 130 °C in a flow reactor system using THF : H<sub>2</sub>O (4:1) as solvent.<sup>10,31</sup>

Because water is produced during glucose conversion to HMF and the presence of water increases the solubility of glucose, we studied the effect of water concentration for the conversion of glucose to HMF using GVL as the solvent and Amb-70 and Sn-SBA-15 as catalysts. Although water is known to promote side reactions in the dehydration of sugars,<sup>14</sup> it can be seen in the results from Fig. S1<sup>†</sup> that water can be beneficial in low concentration. At similar conversion (~70%), the system

Table 3	Conversion	of gluc	ose o	r fructose	to	HMF	in	а	monophasic	system
using γ-la	actones, THF	or THF :	NTHF	with wate	er ir	n a rat	io (	9 :	1) <sup>a</sup>	

Feed	Solvent	Lewis acid	Time/ min	Conv./ %	Selec./ %
Fructose <sup>b</sup>	GVL	_	9	89	80
Glucose <sup>c</sup>	GVL	_	30	92	32
Glucose <sup>d</sup>	GVL	Sn-β	20	92	64
Glucose <sup>e</sup>	GVL	Sn-SBA-15	15	90	51
Fructose <sup>b</sup>	GHL	_	10	91	81
Glucose <sup>c</sup>	GHL	_	30	85	30
Glucose <sup>d</sup>	GHL	Sn-β	20	93	59
Glucose <sup>e</sup>	GHL	Sn-SBA-15	15	90	50
Fructose <sup>b</sup>	THF	_	10	91	85
Glucose <sup>c</sup>	THF	_	50	90	25
Glucose <sup>d</sup>	THF	Sn-β	30	90	70
Glucose <sup>e</sup>	THF	Sn-SBA-15	20	90	40
Glucose <sup>c</sup>	MTHF : THF <sup>f</sup>	_	60	85	26
Glucose <sup>d</sup>	MTHF : THF <sup>f</sup>	Sn-β	40	91	66

<sup>*a*</sup> Reaction conditions: 1.5 g of feed (2 wt% glucose or fructose, organic : water weight ratio (9 : 1)); temperature 130 °C. <sup>*b*</sup> Catalysts: 0.05 g Amb-70. <sup>*c*</sup> Catalysts: 0.1 g Amb-70. <sup>*d*</sup> Catalysts: 0.05 g of Sn-β and 0.05 g Amb-70. <sup>*c*</sup> Catalysts: 0.05 g of Sn-SBA-15 and 0.05 g Amb-70. <sup>*f*</sup> THF : MTHF weight ratio (1 : 1).

with mass ratio GVL:  $\text{H}_2\text{O}(9:1)$  showed higher HMF selectivity than those with a GVL:  $\text{H}_2\text{O}$  ratio of 4:1 or pure GVL.

Table 3 shows the results for conversion of fructose and glucose to HMF using Amb-70 or a combination of Amb-70 and Sn-based catalysts (Sn-ß or Sn-SBA-15) in GVL, GHL or THF containing 10 wt% water. These experiments were carried out using different catalysts and solvents at similar conversions (~90%). It can be seen that HMF was obtained from fructose using Amb-70 with selectivities between 80 and 85%. On the other hand, direct dehydration of glucose using Amb-70 led to selectivities lower than 35%, in agreement with early reports showing that direct dehydration of glucose with mineral acids leads to low selectivity to HMF.6,29 The combination of a Sn-based catalyst and Amb-70 leads to significant improvement in the selectivity to HMF from glucose. Systems using  $Sn-\beta$  show at least 9% higher selectivity than those using Sn-SBA-15. In this respect, Taarning and co-workers have shown that Sn-β displays higher Lewis acid strength than Sn-SBA-15 which gives it significantly higher catalytic activity.<sup>32</sup> Using Sn-β/Amb-70 for the conversion of glucose, selectivities of 64, 59 and 70% were obtained, respectively, using GVL, GHL and THF as the solvent.

Because methyltetrahydrofuran (MTHF) can be produced directly from biomass-derived furfural or GVL, we also explored the use of this solvent for conversion of glucose to HMF. MTHF is not miscible with water; therefore, to obtain a monophasic solvent system, MTHF was mixed with 50% THF. The solvent system consisting of THF : MTHF in a weight ratio of 1:1 and 10 wt% water produced a selectivity of 66% for HMF formation from glucose (Table 3), which is comparable to that obtained in GVL.

Fig. 3 shows the conversion of glucose to fructose and HMF as a function of time in the presence of Amb-70 and Sn- $\beta$  for



**Fig. 3** Glucose dehydration in (A) GVL, (B) GHL, (C) THF, and (D) THF: MTHF (1:1). Solvents contain 10 wt% water. Reaction conditions: 2 wt% glucose; 0.05 g Sn- $\beta$ ; 0.05 g Amb-70; temperature 130 °C.

GVL (Fig. 3A), GHL (Fig. 3B), THF (Fig. 3C), and THF: MTHF (Fig. 3D).

In glucose conversion (Fig. 3), the product observed initially is fructose, and formation of HMF begins at approximately 5 min of reaction time. Comparing the extent of fructose formation in the different solvents, it can be concluded that the effectiveness of glucose isomerization controls the HMF selectivity (Table 3), *i.e.*, THF > THF : MTHF = GVL > GHL. Diminishing the mass ratio Amb-70/Sn- $\beta$  in an attempt to increase the relative rate of glucose isomerization in GVL did not lead to any improvement in HMF selectivity (Fig. S2<sup>†</sup>). Thus, in addition to functioning as a catalyst for glucose isomerization, Sn- $\beta$  also appears to catalyze fructose degradation to unidentified products. After HMF has been formed, it can undergo further reaction to form equimolar amounts of levulinic (LA) and formic acid (FA) generated from HMF hydrolysis (HMF = LA + FA). The carbon balances in the reactions carried out using GVL, GHL, THF: MTHF (1:1) and THF were, respectively, 80, 65, 70 and 85%. Common degradation products, as solid humins and soluble polymers, formed by the crosspolymerization of glucose and HMF33 were not quantified. However, it was shown before that GVL, for example, can solubilize humins,<sup>34</sup> thereby facilitating the separation of the product and minimizing deposition of carbon on the solid catalyst surface.

Because HMF is a platform chemical and not a final product, it is important to find methods to separate HMF from the reaction medium or to integrate the production of HMF with subsequent upgrading reactions, thereby decreasing the cost of the final product. GVL and GHL have high boiling points that are similar to HMF; therefore, the separation of HMF from these solvents by distillation would require the use of low pressures and could lead to degradation of HMF. In contrast, MTHF and THF have a low boiling point (80 and 66 °C,

respectively) and can be easily separated from HMF. In the reaction solvent consisting of THF: MTHF (1:1) or THF with 10% water, organic solvents can be evaporated to yield an aqueous solution of HMF, or alternatively, water can be removed using a drying agent such as magnesium sulfate or calcium chloride, followed by distillation to obtain pure HMF. Another route to separate HMF from GVL or GHL is to convert HMF to a lower boiling point compound. For example, the high value chemical 2,5-dimethylfuran (DMF)<sup>14</sup> has a boiling point significantly lower than GVL or GHL. Also, it is more stable than HMF, such that DMF can be removed by distillation. To achieve this separation route, we have shown that DMF can be produced with 46% yield by hydrogenolysis of HMF in the presence of lactones using a RuSn/C catalyst at 200 °C. Importantly, this catalyst produced DMF from HMF without conversion of the solvent (GVL or GHL), in accordance with previous literature.<sup>34</sup>

One of the most attractive compounds that can be produced from HMF is 2,5-furandicarboxylic acid (FDCA). FDCA can be produced by oxidation of HMF with molecular oxygen in an aqueous alkaline solution using supported gold, platinum or palladium catalysts.<sup>35–37</sup> FDCA is a monomer that can be used to produce polymers similar to polyethylene terephthalate (PET). PET has a growing market, with more than 49 million tons produced in 2009.38 For this reason, FDCA has been rated as a top twelve value added chemical by the U.S. Department of Energy.<sup>39</sup> For the production of FDCA, HMF has to be separated to avoid oxidation of the organic solvent. As mentioned above, HMF can be removed from THF and MTHF by distillation, and it can thus be used directly in the oxidation reaction. Removal of HMF from the less volatile y-lactones can be achieved by contacting these solutions containing HMF with water and cyclopentane (CP) in different proportions, as shown in Table S1.<sup>†</sup>

Contacting 1 part of a solution containing HMF in GHL with 1 part of water and 16 parts of CP, leads to an aqueous layer containing 80 wt% of the initial HMF and 5 wt% of the initial GHL. Contacting the resultant aqueous layer twice with 6 parts of CP decreases the GHL concentration to 0.35 wt% of the initial value, while retaining all of the HMF in the aqueous layer. The HMF : GHL molar ratio in the final aqueous layer is equal to 2.51. GVL is more soluble in water than GHL; therefore, extractions of HMF from GVL requires 4 consecutive extractions with 20 parts of CP to yield an aqueous solution with 80 wt% of the initial HMF amount and 0.5 wt% of the initial amount of GVL. The HMF : GVL molar ratio in the final aqueous layer is equal to 1.52. The boiling point of CP (50 °C) is much lower than GVL (207 °C) and GHL (219 °C), hence it can be separated easily from the lactone by distillation.

Aqueous solutions of HMF and  $\gamma$ -lactones (that could be produced by the method outlined above using CP) were used as feed solutions for studies of HMF oxidation under the reaction conditions proposed by Davis *et al.*,<sup>36</sup> *i.e.*, aqueous solution containing 0.1 mol L<sup>-1</sup> HMF, 2 mol L<sup>-1</sup> NaOH, 2000 kPA oxygen, 1 wt% Au/TiO<sub>2</sub> (HMF:Au = 100) at 22 °C. Using an aqueous solution of HMF with up to 0.5% of GVL or GHL,



**Fig. 4** Overall yields for DMF and FDCA production from glucose starting with THF, GVL or GHL as solvent.

yields of 80% for FDCA and 20% for 2-hydroxymethylfurancarboxylic acid (HFCA) were observed, in accordance with previous literature in the absence of lactones.<sup>36</sup> If the reaction is carried out in the presence of larger amounts of lactones (*i.e.* 5%), yields of 56% for FDCA and 44% for HFCA are observed, and 35% of the  $\gamma$ -lactone is converted to levulinic acid (from GVL) or 4-oxohexanoic acid (from GHL). Separation of FDCA was achieved by decreasing the pH of the reaction mixture to a value of one, leading to precipitation of FDCA, while HFCA and salt remained in solution. The precipitate was filtered and washed with ethanol.

The overall yields we have achieved for production of DMF and FDCA on a glucose basis for each of the solvent systems considered in this paper are shown in Fig. 4. Starting with THF as solvent, an overall yield of 50% is obtained for FDCA, while 38 and 35% are the yields when the process uses GVL and GHL as the solvents, respectively. If the target product is DMF, then yields of 27 and 25% can be obtained in the systems using GVL and GHL as solvents, respectively.

### Conclusions

The highest yields we have achieved for production of HMF from glucose using a combination of Amb-70 and Sn- $\beta$  as solid acid catalysts are 59, 55, 60 and 63% using GVL, GHL, THF : MTHF (1:1) and THF as solvents, respectively. These results are comparable or higher than values obtained in the literature using a combination of Lewis and Brønsted acids. In addition to achieving high yields, the systems reported in this communication replace the use of homogeneous catalysts and salts, leading to a more sustainable and economically viable process. Separation and purification of HMF can be achieved by distillation for the case of THF as the solvent. In contrast, GVL and GHL have boiling points that are similar to HMF, requiring the isolation of HMF by different methods. In this respect, we show that HMF can be converted to DMF with 46%

yield, and this low boiling point product can then be separated from the solvent by distillation. Alternatively, we show that HMF can be extracted to water assisted by cyclopentane. The oxidation of HMF to FDCA can then be carried out in the presence of small amounts of lactones, and yields of 80% were obtained. Thus, the catalytic systems proposed in this work not only replace the use of homogeneous catalysts and salts, but they also allow the integration of HMF production with processes for HMF upgrading to valuable products.

#### Acknowledgements

The authors thank Haldor Topsøe A/S, Denmark for the Sn- $\beta$ and Fabiola Lárraga and Nestor Hernandez Lozada for their help with the experiments. This work was supported by the U.S. Department of Energy; the Center Enabling New Technologies through Catalysis (CENTC); and the Defense Advanced Research Projects Agency (DARPA). The views, opinions, and/ or findings contained in this article are those of the author and should not be interpreted as representing the official views or policies, either expressed or implied, of the DARPA or the Department of Defense.

#### Notes and references

- 1 J. J. Bozell and G. R. Petersen, *Green Chem.*, 2010, 12, 539–554.
- 2 M. J. Antal Jr., W. S. L. Mok and G. N. Richards, *Carbohydr. Res.*, 1990, **199**, 91–109.
- 3 J. Guan, Q. A. Cao, X. C. Guo and X. D. Mu, *Comput. Theor. Chem.*, 2011, **963**, 453–462.
- 4 A. S. Amarasekara, L. D. Williams and C. C. Ebede, *Carbohydr. Res.*, 2008, **343**, 3021–3024.
- 5 J. F. Robyt, *Essentials of Carbohydrate Chemistry*, Springer Pub. Co., New York, 1998.
- 6 Y. J. Pagan-Torres, T. F. Wang, J. M. R. Gallo, B. H. Shanks and J. A. Dumesic, *ACS Catal.*, 2012, 2, 930–934.
- 7 C. Moreau, A. Finiels and L. Vanoye, J. Mol. Catal. A: Chem., 2006, 253, 165–169.
- 8 Y. Roman-Leshkov, J. N. Chheda and J. A. Dumesic, *Science*, 2006, **312**, 1933–1937.
- 9 J. N. Chheda, Y. Roman-Leshkov and J. A. Dumesic, *Green Chem.*, 2007, 9, 342–350.
- 10 A. J. Crisci, M. H. Tucker, M. Y. Lee, S. G. Jang, J. A. Dumesic and S. L. Scott, ACS Catal., 2011, 1, 719–728.
- 11 H. Zhao, J. E. Holladay, H. Brown and Z. C. Zhang, *Science*, 2007, **316**, 1597–1600.
- 12 J. B. Binder and R. T. Raines, *J. Am. Chem. Soc.*, 2009, **131**, 1979–1985.
- 13 G. Yong, Y. Zhang and J. Y. Ying, *Angew. Chem., Int. Ed.*, 2008, 47, 9345–9348.
- 14 Y. Roman-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature*, 2007, 447, 982–U985.

- 15 Y. Román-Leshkov and J. Dumesic, *Top. Catal.*, 2009, **52**, 297–303.
- 16 K.-i. Shimizu, R. Uozumi and A. Satsuma, *Catal. Commun.*, 2009, **10**, 1849–1853.
- 17 Y. Zhang, K. Hidajat and A. K. Ray, *Biochem. Eng. J.*, 2004, **21**, 111–121.
- 18 M. E. Zakrzewska, E. Bogel-Lukasik and R. Bogel-Lukasik, *Chem. Rev.*, 2011, **111**, 397–417.
- 19 R. L. Huang, W. Qi, R. X. Su and Z. M. He, *Chem. Commun.*, 2010, 1115–1117.
- 20 D. M. Alonso, J. Q. Bond and J. A. Dumesic, *Green Chem.*, 2010, **12**, 1493–1513.
- 21 J. C. Serrano-Ruiz, R. Luque and A. Sepulveda-Escribano, *Chem. Soc. Rev.*, 2011, **40**, 5266–5281.
- 22 L. E. Manzer, Appl. Catal., A, 2004, 272, 249-256.
- 23 T. M. Ugurchieva, A. V. Lozanova, M. V. Zlokazov and V. V. Veselovsky, *Russ. Chem. Bull.*, 2008, **57**, 657–659.
- 24 Y. Zhou, L. K. Woo and R. J. Angelici, *Appl. Catal. A*, 2007, 333, 238–244.
- 25 O. W. Cass, Ind. Eng. Chem., 1948, 40, 216-219.
- 26 E. J. Garcia-Suarez, A. M. Balu, M. Tristany, A. B. Garcia, K. Philippot and R. Luque, *Green Chem.*, 2012, 14, 1434– 1439.
- 27 A. Takagaki, M. Ohara, S. Nishimura and K. Ebitani, *Chem. Commun.*, 2009, 6276–6278.

- 28 M. Moliner, Y. Roman-Leshkov and M. E. Davis, *Proc. Natl. Acad. Sci. U. S. A.*, 2010, **107**, 6164–6168.
- 29 E. Nikolla, Y. Roman-Leshkov, M. Moliner and M. E. Davis, *ACS Catal.*, 2011, **1**, 408–410.
- 30 H. P. Yan, Y. Yang, D. M. Tong, X. Xiang and C. W. Hu, *Catal. Commun.*, 2009, **10**, 1558–1563.
- 31 M. H. Tucker, PhD thesis, University of Wisconsin-Madison, 2011.
- 32 C. M. Osmundsen, M. S. Holm, S. Dahl and E. Taarning, *Proc. R. Soc. London, A*, 2012, **468**, 2000–2016.
- 33 H. M. Pilath, M. R. Nimlos, A. Mittal, M. E. Himmel and D. K. Johnson, *J. Agric. Food Chem.*, 2010, 58, 6131– 6140.
- 34 S. G. Wettstein, D. M. Alonso, Y. Chong and J. A. Dumesic, *Energy Environ. Sci.*, 2012, 5, 8199–8203.
- 35 B. N. Zope, S. E. Davis and R. J. Davis, *Top. Catal.*, 2012, 55, 24–32.
- 36 S. E. Davis, B. N. Zope and R. J. Davis, *Green Chem.*, 2012, 14, 143–147.
- 37 S. E. Davis, L. R. Houk, E. C. Tamargo, A. K. Datye and R. J. Davis, *Catal. Today*, 2011, **160**, 55–60.
- 38 In Eurasian Chemical Market International Magazine, 2011, 8, 56.
- 39 T. A. Werpy and G. Petersen, U.S. Department of Energy, 2004.