

Towards a Bio-Based Industry: Benign Catalytic Esterifications of Succinic Acid in the Presence of Water

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Abstract: The biorefinery of the future will need to integrate bioconversion and appropriate low environmental impact chemical technologies (Green Chemistry) so as to produce a wide range of products from biomass in an economically effective and environmentally acceptable manner. The challenge for chemists is to develop chemistry that works with fermentation-derived dilute, aqueous mixtures of oxygenated chemicals (platform molecules) rather than the petroleum-derived non-aqueous, non-oxygenated

feedstocks we have been working with for 50+ years and to avoid energy intensive and wasteful concentration and purification steps. Here we show that a new family of tuneable mesoporous carbonaceous catalysts derived from starch can be used to accomplish efficient chemistry in aqueous solution. Our new aqueous catalytic chemistry

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relies on the ability to adjust the surface properties including the hydrophobicity–hydrophilicity balance of mesoporous Starbons by carbonisation at different temperatures (250–750 °C). Simple treatment of these materials with sulfuric acid then provides a series of porous solid acids that can function under a range of conditions including dilute aqueous solution. The reactions of succinic acid (platform molecule) in aqueous alcohol demonstrate the outstanding activities of these new catalysts.

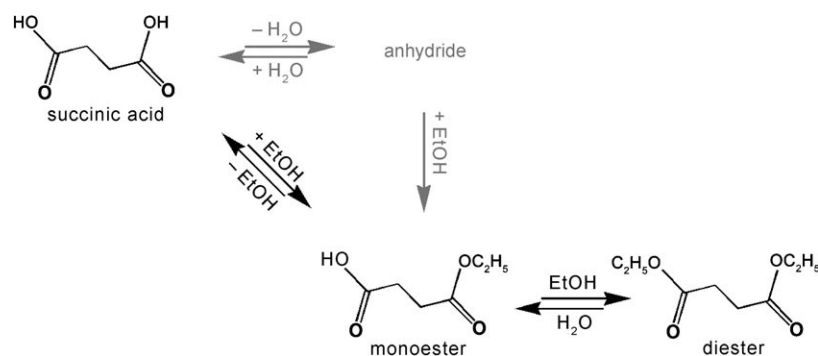
Introduction

The biorefinery concept is based on the selective conversion of biomass to value-added products. Biomass is a fully renewable resource that will increasingly be used for the production of heat and power, chemicals, materials and other products with substantial environmental, economic and security benefits.^[1,2] The biorefinery of the future is likely to integrate both bioconversion and appropriate chemical technologies. It is, however, essential that for truly sustainable production, the technologies that are used have a low environmental impact. In the case of chemical technologies and chemical production, this means the use of green chemistry methods, such as heterogeneous catalysis,^[3] and the application of green chemistry principles.^[4,5] The main problem is that chemical catalytic technologies have been developed for the transformation of hydrophobic molecules in hydrophobic environments whereas fermentation processes produce hydrophilic platform molecules in aqueous media.

Here we report the application of tuneable carbonaceous materials prepared from carbonisation of expanded starch (Starbon),^[6] after sulphonation, as acid catalysts for chemistry in dilute aqueous environments. Changes in preparation temperature (250–750 °C) provide the possibility to produce a wide range of carbonaceous materials with an unique continuous trend in surface chemistries from more starch-like (hydrophilic) to more graphitic-like (hydrophobic) together with a highly stable mesoporous region. The feasibility and simplicity of achieving an optimum catalytic activity by tuning the hydrophilicity/hydrophobicity surface properties of these mesoporous carbons provides us with outstanding potential for optimizing reactions such as the esterification of organic acids in water. In this study, we have tested the activity of our new solid acids in the esterification of succinic acid in aqueous ethanol (Scheme 1).

Succinic acid is one of the top (bio)platform molecules and is available from the bioconversion of glucose at concentrations as high as approximately 6 wt %.^[7] Esterification reactions are one of the most useful transformations for organic acids,^[8] especially for a dicarboxylic acid as the diester can be used as an intermediate in the manufacture of polymers, fine chemicals, perfumes, plasticizers and solvents.^[8–11] Many acid catalysts have been reported in these reactions,^[12] although only a few authors have dealt with the esterifica-

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Scheme 1. Esterification of succinic acid in aqueous ethanol.

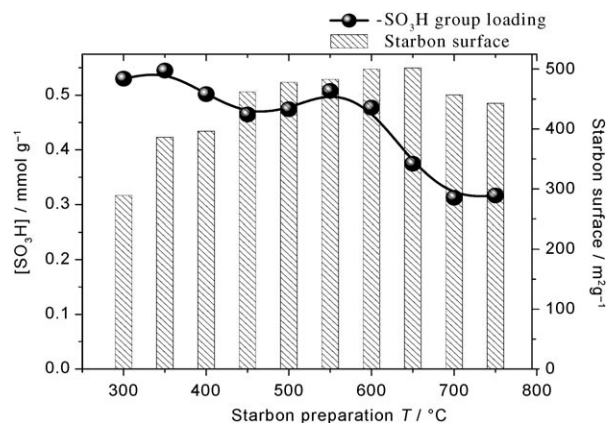
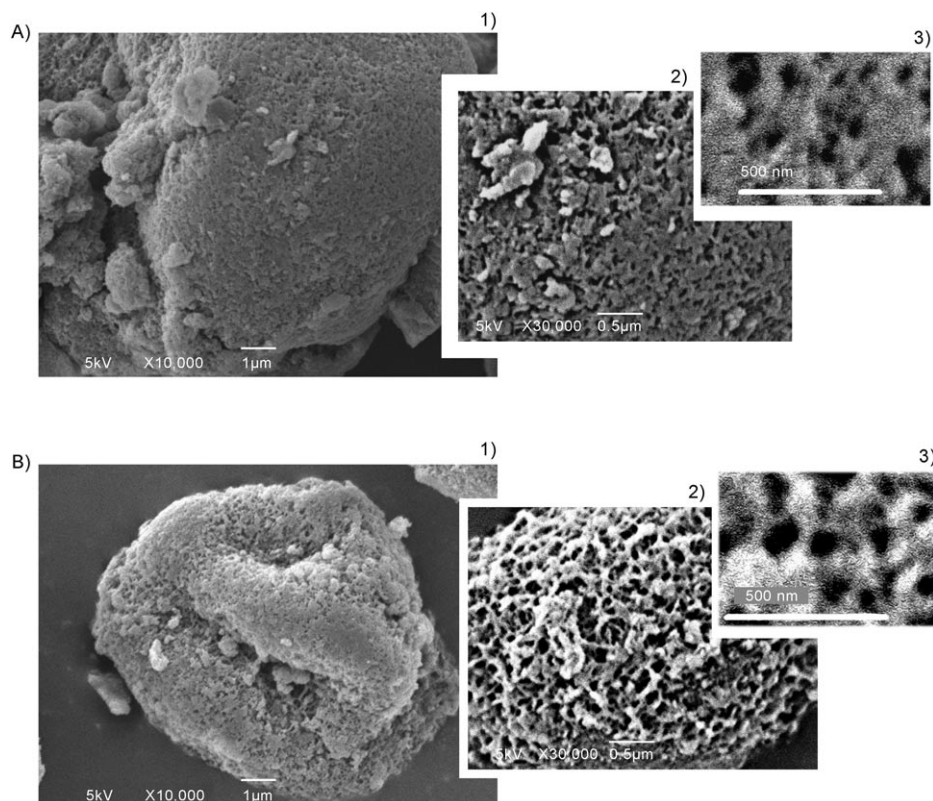
tion of either succinic acid^[13] or its cyclic anhydride.^[14] The esterification reaction has been reported as being very sensitive to water environments due to different equilibrium steps in which water is involved (Scheme 1).^[15] Water has been proved to affect the reaction activity, in homogeneous conditions,^[14b,16a] resulting in a decrease of the rate of esterification that has generally been attributed not only to reverse hydrolysis but also to a competitive protonation step involving the water and the alcohol (assuming the rate-determining step is the interaction between the protonated alcohol and the carboxylic acid).^[16] We can expect to increase the reaction rates in comparison with the homogeneous reactions by altering the local water concentration in the active centre of the solid acids through careful adjustment of the local surface properties.

Results and Discussion

Starbon acids surface properties: The sulfuric acid treatment did not significantly change the materials surface properties, as shown by N₂ adsorption measurements, SEM and DRIFT experiments (Figures 1, 2 and 3). Moreover, the acidity of Starbon acids (measured as SO₃H loading) was almost independent of the temperature of preparation of the parent materials, although a decrease in the SO₃H loading was found at high temperatures. This is consistent with the unchanged mesoporous environment. Elemental analysis of the solid acids confirms the %S (to ± 0.1) and the trend in reduction at higher temperatures (see the Experimental Section).

Textural properties of Starbon acids were found to follow

a similar trend to those originally reported for Starbon materials,^[6] both surface area and microporous volume increasing with increasing temperature of preparation (Figure 1). SEM micrographs show that the Starbon materials have a homogeneous spherical morphology with macro-mesoporosity in the materials that can be seen at higher magnifications (Fig-

Figure 1. Effect of the temperature of preparation on the surface area (S_{BET}, m² g⁻¹) and SO₃H loading (mmol g⁻¹) of Starbon acids.Figure 2. SEM micrographs of A) Starbon-500 and B) Starbon-500-SO₃H at different magnifications.

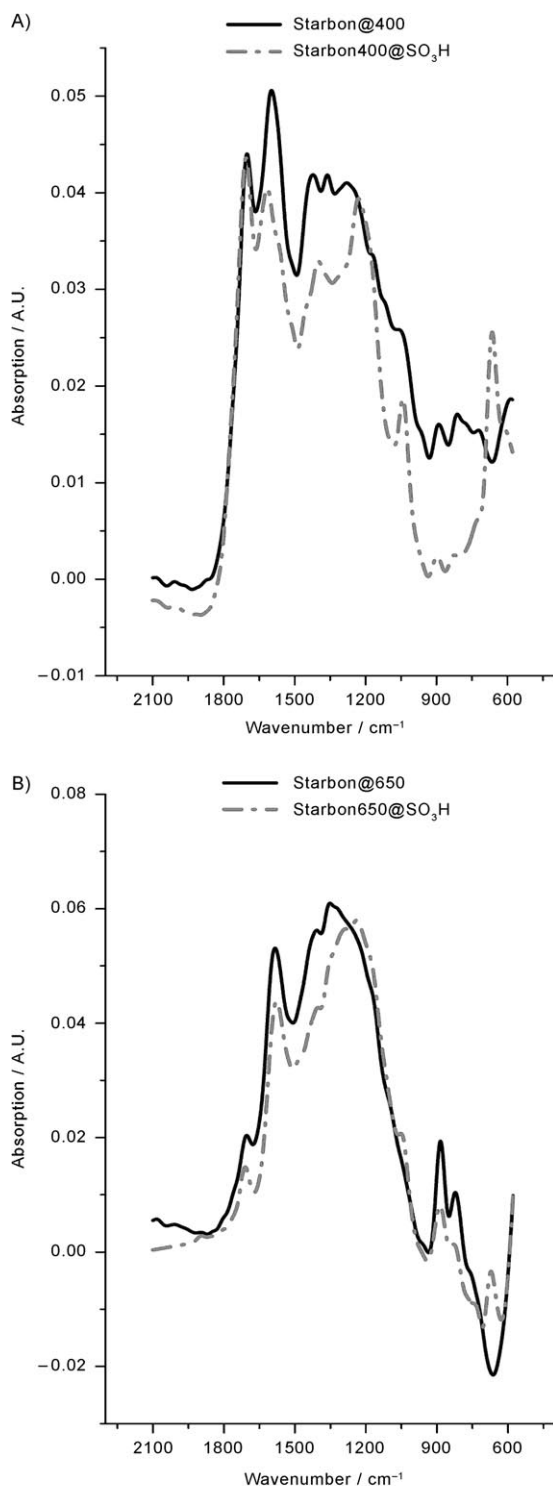


Figure 3. DRIFT spectra of Starbon materials prepared at different temperatures A) 400 °C and B) 650 °C before (continuous line) and after sulfonation (discontinuous line).

ure 2A3 and B3). Nitrogen adsorption measurements confirmed that Starbon acids were mostly mesoporous with an average pore diameter of approximately 8–12 nm. DRIFT

experiments were in good agreement with the textural and acid properties of the materials. There were no significant changes in the peaks due to the main functionalities (C=O, C=C, etc.) present in Starbon materials but new peaks do appear in the 1200–600 cm⁻¹ region consistent with sulfonic acid/sulfonate species. Kinetic experiments using Starbon acids in the esterification of succinic acid in aqueous ethanol demonstrate their high activity. Reactions typically reach close to quantitative conversion of the acid to the diester in five hours, as shown in Figure 4. A useful 35% conversion to monoester (< 2 h) was also obtained.

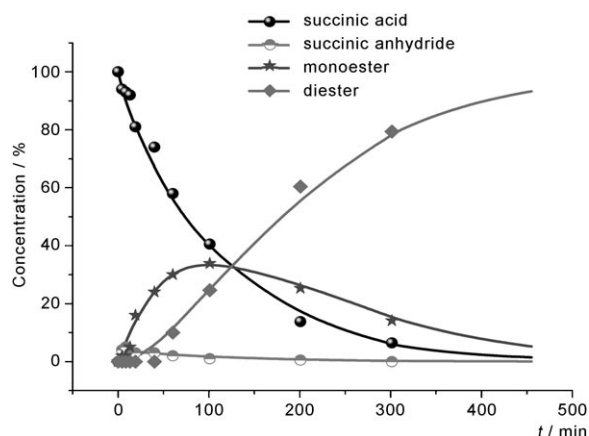


Figure 4. Kinetic profiles (concentration versus time) of Starbon-400-SO₃H in the esterification of succinic acid in aqueous ethanol.

For comparison, the activity of some other established solid acid catalysts (zeolites, sulphated zirconias and clays) in the esterification reaction were screened. In general, all of the reactions using known solid acids were very slow, taking 24+ hours at 80 °C to obtain reasonable conversions of concentrations of approximately 6 wt % succinic acid (Table 1). Zeolite-beta was the most promising catalyst for diester formation, whereas sulfated zirconia and montmoril-

Table 1. Catalytic activity comparison of different materials in the esterification of succinic acid in aqueous ethanol.

Cat.	k_{conv} [s ⁻¹]	Conditions for maximum product yield [mol %]		
		Products	Yield _{max} [mol %]	T_{max} [min]
H ₂ SO ₄	14.2×10^{-5}	monoester diester	20 90	90 1440
ZrO ₂ -SO ₃ H	4.2×10^{-5}	monoester Diester	50 45	1380 1380
β-25	5.5×10^{-5}	monoester diester	35 70 ^[a]	840 1440 ^[a]
DARCO-SO ₃ H	6.5×10^{-5}	monoester diester	52 90	600 1150
Starbon-400-SO ₃ H	32×10^{-5}	monoester diester	35 90	100 410

[a] Reaction not completed.

Ionite KSF (not shown) gave the highest observed selectivities to the monoester.

Commercial porous carbons, such as Darco, which were sulphonated, had activities slightly higher than those of the non-carbon solid acids we tested (Table 1). Activated carbons have been reported to adsorb large quantities of succinic acid at different temperatures^[17] changing the initial acid/water ratio in the active centres on the catalyst surface.

Figure 5 summarises the catalytic activity of the sulphonated Starbons in the esterification reaction as a function of the preparation temperature and the surface properties. At 400 °C, we have shown that the Starbon has an unusual blend of starch and carbon-like surface characteristics including hydroxyl, aldehyde, and aromatic functions.^[6] The type of acid sites ($-\text{SO}_3\text{H}$ from reaction with aromatic or $\text{C}=\text{C}$ groups and $-\text{OSO}_3\text{H}$ from reactions with hydroxyl groups) will also vary with the preparation temperature for the Starbon. Significantly, the activity of these materials peaked at approximately 400 °C with sharply reduced activities below or above this preparation temperature (Figure 5A). The rates of reaction for Starbon-400 acid were found to be at least five times greater than any of the other solid acid catalysts. The highly active sulphonated Starbon catalyst was easily recovered from the aqueous reaction mixture whereupon the reaction rates returned to the background values.

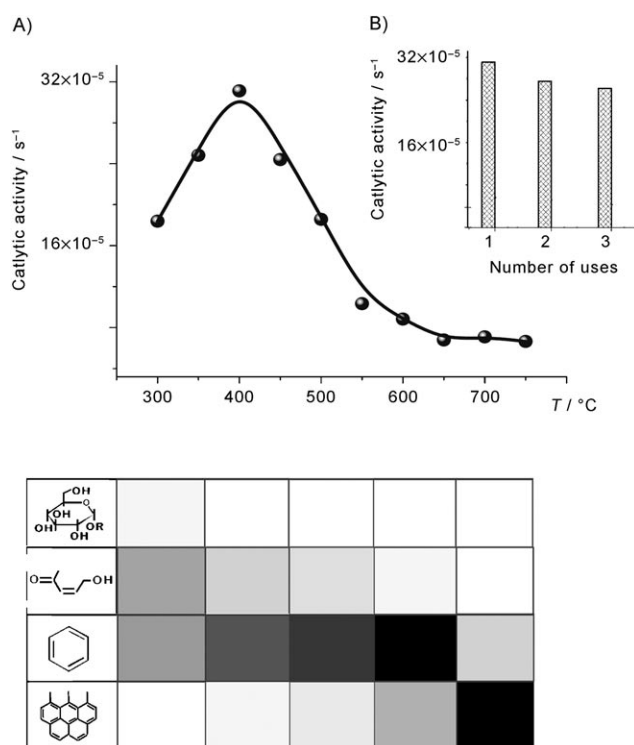


Figure 5. A) Catalytic activity (rate constant, s^{-1}) of Starbon materials, prepared at different temperatures, with different surface functionalities in the esterification of succinic acid in aqueous ethanol. The grid on the bottom of the figure represents distribution of functional groups on Starbons prepared at the different temperatures: gray scale to indicate relative amounts of different groups (black represents highest). B) Starbon-400- SO_3H reusability in the esterification reaction.

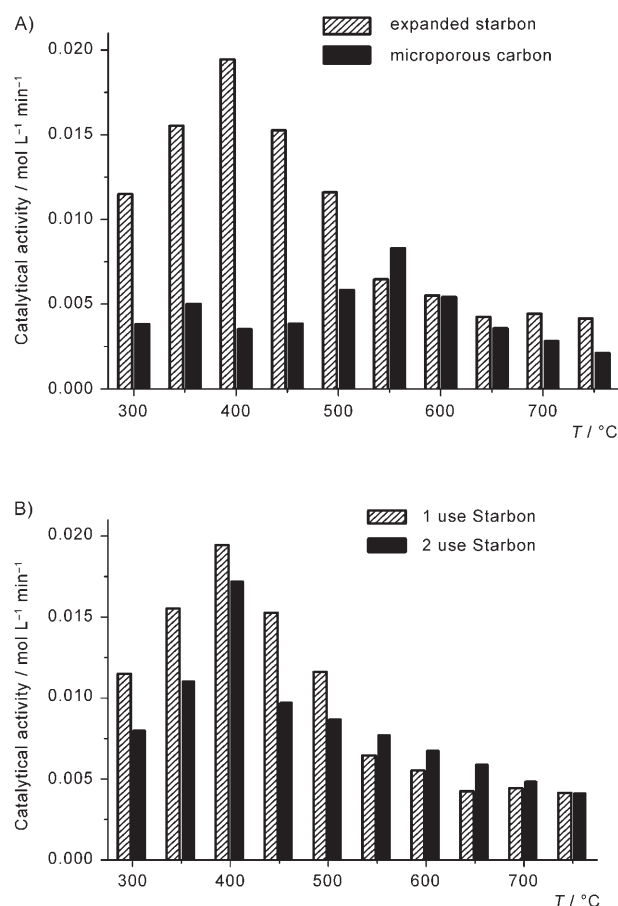


Figure 6. A) Catalytic activity (initial rate of succinic acid esterification) comparison between mesoporous expanded Starbon and microporous carbonaceous materials prepared from non-expanded starch. B) Starbon acids recyclability (1st and 2nd use) in the succinic acid esterification reaction.

The recovered Starbon acid could be added to fresh substrate solutions giving almost identical behaviour to that observed in the original reaction (Table 1, Figures 5B and 6B). Thus the catalyst is stable as well as active under aqueous conditions, which are most extraordinary characteristics.

The initial expansion process to generate the mesoporous expanded starch that was then carbonised can be proven to be critical to the catalysts high activity and reusability. We prepared similar microporous non-expanded materials from direct carbonisation at different temperatures of starch granules. The carbonaceous solids were subsequently functionalised with sulphonated groups in a similar way to that of the Starbons. These non-expanded materials, essentially microporous in nature, are reminiscent of the solid acids recently reported for biodiesel production.^[18] Sulphonated non-expanded carbons exhibited a catalytic activity that was at least five times lower than the optimized 400 °C sulphonated Starbons. Most interestingly, a maximum in activity was found at approximately 550 °C, which was shifted to 350 °C after the first use. Therefore, materials prepared at high temperature (>550 °C) with increased microporosity performed better in the first use but the catalytic activity was

dramatically reduced after reuse. This can be explained by the involvement of physisorbed H_2SO_4 in the catalytic performance (Figure 6).

Conclusion

The outstanding Starbon acid performance in aqueous esterification is believed to be a consequence of an ideal combination of properties including hydrophobicity encouraging partitioning of the organic acid into the pores and production of the more hydrophobic esters, mesoporosity enhancing molecular diffusion rates, surface functionality allowing the formation of (two different types of) acid sites and surface energy providing strong site activity. We can foresee our approach being successfully extended to many of the “top” bioplatfrom molecules, together with other chemistries including the production of other small molecules (amides, imides, acylated and alkylated products) providing enormous potential applications in the Biorefinery chemical production units of the future.

Experimental Section

Starbon synthesis: The method comprises three key stages: Firstly, corn starch was gelatinised by heating in water for 48 h and subsequently cooled to 5°C for 1–2 d to yield a porous gel block. In the second stage, the water in the block was exchanged with a solvent of lower surface tension, such as ethanol, and oven dried to yield a predominantly mesoporous starch. In the final stage, the mesoporous starch was doped with a catalytic amount of an organic acid (for example, 0.1 mmol of *p*-toluene-sulfonic acid per 1 g of starch) and heated under vacuum at a temperature of 180°C for 6 h. Samples were heated to various temperatures (up to 750°C) in 3.5 mL alumina sample caps in a NETZSCH STA analyser.

Starbon sulphonation: As-synthesized materials were suspended in H_2SO_4 of 99.999% purity (10 mL acid/g material, 4 h at 80°C). After sulphonation, samples were subsequently washed with distilled water until the washings were neutral, boiled in toluene (4 h) and water (3 h, 80°C) and finally oven dried (100°C) overnight before being tested in the catalytic reaction. Elemental analysis gave a sulfur content of 1.9 (Starbon-400- SO_3H), 1.4 (Starbon-650- SO_3H) and 1.3% (Starbon-750- SO_3H).

Characterisation: Starbons nitrogen adsorption measurements were carried out at 77 K by using an ASAP 2010 volumetric adsorption analyser from Micromeritics. Before measurement, the samples were under vacuum (3–4 h at the temperature equal to temperature of sample preparation).

Thermogravimetric analysis coupled with IR (TGIR) was used to determine the loading of SO_3H groups and was performed by using a Netzsch STA 409 (at scan rates of 10°C min⁻¹, with typically 20 mg sample under flowing N_2 at 100 mL min⁻¹), coupled with a Brüker EQUINOX-55 instrument equipped with a liquid N_2 cooled MCT detector.

Scanning electron Micrographs (SEM) were recorded in a JEOL JSM-6490 LV. Samples were Au/Pd coated on a high resolution sputter SC7640 at a sputtering rate of 1500 V per minute, up to 7 nm thickness.

Diffuse reflectance IR Fourier transform (DRIFT) spectra were recorded on a Brüker EQUINOX-55 instrument equipped with a liquid N_2 cooled MCT detector. Resolution was 2 cm⁻¹ and 1024 scans were averaged to obtain the spectra in the 4000–600 cm⁻¹ range. Spectra were recorded by using KBr as a reference. The samples for DRIFTS studies were prepared by mechanically grinding all reactants to a fine powder (sample/KBr 1:1000 ratio).

Catalytic test: A typical catalytic test was performed as follows: Succinic acid (1 mmol, SA, 0.124 mg, 6 wt% in solution), EtOH (30 mmol, 2.4 mL) and water (50 mmol, 0.9 mL) were added to a round-bottomed flask with sulphonated Starbon (0.1 g), increasing the temperature to 80°C. Samples were withdrawn periodically from the reaction mixture and the mixture was left reacting (5 h). Products were analysed by GC analysis by using an Agilent 6890N GC model equipped with a 7683B series autosampler. Response factors of the reaction products (succinic anhydride, monoethyl succinate and diethyl succinate) were determined with respect to succinic acid from GC analysis by using known compounds in calibration mixtures of specified compositions.

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- [1] *Feedstocks for the Future* (Eds.: J. Bozell, M. Patel), ACS, New York, **2006**.
- [2] A. J. Ragauskas, C. K. Williams, B. H. Davison, G. Britovsek, J. Cairney, C. A. Eckert, W. J. Frederick, J. P. Hallet, D. J. Leak, C. L. Liotta, J. R. Mielenz, R. Murphy, R. Templer, T. Tschaplinski, *Science* **2006**, *311*, 484–489.
- [3] J. H. Clark, *Acc. Chem. Res.* **2002**, *35*, 791–797.
- [4] J. H. Clark, *Green Chem.* **2006**, *8*, 17–21.
- [5] P. Anastas, J. C. Warner, *Green Chemistry, Theory and Practice*, Oxford University Press, Oxford **1998**.
- [6] V. Budarin, J. H. Clark, J. J. E. Hardy, R. Luque, K. Milkowski, S. J. Tavener, A. J. Wilson, *Angew. Chem.* **2006**, *118*, 4894–4897; *Angew. Chem. Int. Ed.* **2006**, *45*, 3782–3786.
- [7] A. Koutinas, R. Wang and C. Webb, *Top Value chemicals from biomass* (Eds.: T. Werpy, G. Petersen): <http://www.eere.energy.gov/biomass/pdfs/35523.pdf>, unpublished results.
- [8] a) J. Otera, *Esterification*, Wiley-VCH, Weinheim, Germany, **2003**; b) J. Mulzer, *Comprehensive Organic Synthesis* (Eds.: B. M. Trost, L. Fleming), Pergamon Press, Oxford, **1991**.
- [9] Y. Liu, E. Ranucci, M. S. Lindblad, A. C. Albertsson, *J. Pol. Sci. Pol. Chem.* **2001**, *39*, 2508–2519.
- [10] D. Shekhawat, K. Nagarajan, J. E. Jackson, D. J. Miller, *Appl. Catal. A* **2002**, *223*, 261–273.
- [11] Diversified Natural Products, Inc. <http://www.dnpworld.com>
- [12] a) B. R. Jermy, A. Pandurangan, *Appl. Catal. A* **2005**, *288*, 25–33; b) B. Rabindram Jermy, A. Pandurangan, *J. Mol. Catal. A* **2005**, *237*, 146–154; c) F. Tataroglu Seyidov, Y. Mansoori, N. Goodarzi, *J. Mol. Catal. A* **2005**, *240*, 186–190; d) Y. Mansoori, F. Seyidov Tataroglu, M. Sadaghian, *Green Chem.* **2005**, *7*, 870–873; e) T. A. Peters, N. E. Benes, A. Holmen, J. T. F. Keurentjes, *Appl. Catal. A* **2006**, *297*, 182–188; f) J. Lilja, J. Wärnå, T. Salmi, L. J. Pettersson, J. Ahlqvist, H. Grénman, M. Rönnholm, D. Y. Murzin, *Chem. Eng. J.* **2005**, *115*, 1–12; g) J. Lilja, J. Aumo, T. Salmi, D. Y. Murzin, P. Mäki-Arvela, M. Sundell, K. Ekman, R. Peltonen, H. Vainio, *Appl. Catal. A* **2002**, *228*, 253–267; h) T. Okuhara, *Chem. Rev.* **2002**, *102*, 3641–3665.
- [13] C. R. Reddy, P. Iyengar, G. Nagendrappa, B. S. Jai Prakash, *Catal. Lett.* **2005**, *101*, 87–91.
- [14] a) H. J. Bart, J. Reidetschläger, K. Schatka, A. Lehmann, *Int. J. Chem. Kinet.* **1994**, *26*, 1013–1021; b) C. R. Reddy, P. Iyengar, G. Nagendrappa, B. S. Jai Prakash, *J. Mol. Catal. A* **2005**, *229*, 31–37.
- [15] T. Higuchi, L. Eberson, J. D. McRae, *J. Am. Chem. Soc.* **1967**, *89*, 3001–3004.
- [16] a) Y. Liu, E. Lotero, J. G. Goodwin, Jr., *J. Mol. Catal. A* **2006**, *245*, 132–140; b) R. Aafaqi, A. R. Mohamed, S. Bhatia, *J. Chem. Tech-*

- nol. Biotechnol.* **2004**, 79, 1127–1134; c) D. Kusdiana, S. Saka, *Biore-sour. Technol.* **2004**, 91, 289–295; d) H. Smith, *J. Am. Chem. Soc.* **1939**, 61, 254–260.
- [17] C. Y. C. Lee, E. O. Pedram, A. L. Hines, *J. Chem. Eng. Data* **1986**, 31, 133–136.
- [18] T. Toda, A. Takagaki, M. Okamura, J. N. Kondo, S. Hayashi, K. Domen, M. Hara, *Nature* **2005**, 438, 178–178.

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