Mild Upgrading of Bio-crude Pyrolysis Oil. A Concept based on Bio-based Alcohols with Selective Water Adsorption.

R. Kumar Pazhavelikkakath Purushothaman, ‡,[a] T. Buntara, ‡,[a] Z. Zhang, [a] I.J. Vehoff,[a] C. Boyadjian,[a] L. Falco, [a,c] K. Seshan,[b] Natalia Gómez, [c] H.J. Heeres, [a] and I. Melián-Cabrera [c] *

Abstract: Bio-crude pyrolysis oil is obtained by a process called fast-pyrolysis, in which almost any organic-based feedstock is thermally processed at moderate temperatures, in the range of 400-600 °C, in the absence of oxygen at short residence times. After condensing the vapors in a cooling tray, a dark-brown bio-liquid is obtained. The quality of the so-obtained fast pyrolysis oil has some barriers for its direct use as transportation fuel. Low-caloric value, high viscosity and corrosion are the major obstacles for its implementation in conventional engines. There have been sustained efforts to improve the quality of the oil. In this communication we are reporting a concept on improving the acidic properties, by means of a combined catalyzed and adsorption approach. We found that fast pyrolysis oil can be upgraded through alcoholysis using bio-based alcohols, *n*-BuOH and tetrahydrofurfuryl alcohol, that are biomass derived bulk chemicals. The reaction is acid catalysed, whereas water is continuously separated from the condensate mixture by a molecular sieve adsorption. Under optimal conditions, the ultimate acidity and water content of the upgraded product are marginal.

Bio-crude pyrolysis oil (BcPO) is produced by fast pyrolysis technology, a process where a priori any kind of organic-based feedstock can be heated in the absence of oxygen at low residence times, forming a gaseous product that is afterwards rapidly cooled down [1-3], with yields up to 80 *wt.* % [4]. The liquid product is formed by a complex mixture of polar compounds that is relatively easy to produce with limited capital cost investments. Due to the high oxygen content, this liquid can, however, be mixed only to a limited extent with conventional diesel or gasoline. It contains a substantial amount of water and oxygen-containing compounds, which implies a low heating value as well, that is estimated at 40-50% of that for hydrocarbon fuels [1].

The BcPO is acidic and its storage stability is limited [5-7] due to the presence of acids and polymerisation reactions of reactive aldehydes with phenolics. Thus, the direct use as transportation fuel, or co-feeding in conventional oil refineries, has still several barriers to be tackled. Therefore, in order to extend the application prospects, upgrading of the BcPO is crucial. Particularly reducing the organic acids and reactive aldehyde levels is necessary, though this will compromise other properties, as postulated by Bridgwater [4].

Research on upgrading of BcPO is an emerging field, becoming as extensive as the pyrolysis process itself. A number of approaches have been suggested, including physical and chemical routes. In terms of physical upgrading methods, Diebold *et al.* [8] proposed improving the viscosity of BcPO using a physical method denoted as 'hot-vapour filtration', by filtering the oil using sintered metals or ceramic elements. The use of micro-emulsions has also been applied, whereby surfactants are used to blend pyrolysis oil with conventional oils/fuels. This method was introduced by CANMET Energy Technology Centre (Ontorio, Canada) [9,10], which improves its ignition properties. Addition of solvents (without reaction) such as alcohols reduces its viscosity and increase the stability [11]. A high pressure and thermal treatment [12] decreases the oxygen content of the oil phase and hence increase the energy content, from 14.1 to 28.4 MJ/kg.

Chemical upgrading has been investigated by means of the catalytic cracking over an acidic material [13-16], resulting in a limited yield to hydrocarbons, mostly aromatics. Catalytic hydrotreatment has been the dominant research area, which is a hydro-de-oxygenation (HDO) process at high pressure and temperature using conventional hydro-processing catalysts, based on Ni–Mo or Co–Mo supported on alumina, to crack large molecules and reduce polar compounds. This HDO process was pioneered by Elliot and Baker (Pacific Northwest lab, USA) [17] and Delmon (Louvain) [18]. The process results in a higher-grade oil that can be co-processed in oil refineries. Alternatively, Ru-based catalysts have been reported as very efficient [19-21], with increased energy content ranging 25 to 35 MJ/kg [21].

Removing oxygen as H_2O has also been carried out by reacting the oil chemically with alcohols through esterification and acetalization. Such a process would lower the acid content and enhance the stability; it is generally accepted that the carbonyl groups are related to the limited storage stability, which promotes further cross-linking reactions. Initially, three groups have investigated this route. VTT (Finland) reported in 2004 that the addition of alcohols in the presence of a liquid catalyst improved the oil properties [22], which was in agreement with the pioneering work of Radlein *et al.* [23]. In the latter, one-pot reactive

---

[a] Dr. R. Kumar Pazhavelikkakath Purushothaman, Dr. T. Buntara, Dr. Z. Zhang, I.J. Vehoff, Dr. C. Boyadjian, Prof. Dr. Ir. H.J. Heeres,
Chemical Reaction Engineering, ENTEG, University of Groningen,
Nijenborgh 4, 9747 AG Groningen, The Netherlands.

[b] Prof. Dr. Ir. K. Seshan, Catalytic Processes and Materials,
University of Twente, 7500 AE Enschede, The Netherlands.

[c] Dr. L. Falco, Dr. N. Gómez, Dr. I. Melián-Cabrera, European
Bioenergy Research Institute (EBRI), School of Engineering and
Applied Science, Aston University, Aston Triangle, Birmingham B4
7ET, United Kingdom.
E-MAIL: i.melian-cabrera@aston.ac.uk

‡ **Equal contribution.**

Supporting information for this article is given via a link at the end of the document.

WILEY-VCH

adsorption using molecular sieves was applied to remove water from the reaction. Vuthaluru's group investigated the odour control *via* esterification of pyrolysis oil with ethanol using sulphuric acid as a catalyst [24].

This direction drew considerable attention in the last decade for further development. In particular, the main technological driver has been using low-cost alcohols such as MeOH [25-30], EtOH [28,31-36] or *n*-BuOH [28,37-39] that would have a reduced impact on the final production cost of the upgraded BO; the real effect of the upgrading route, on the final costs, has been critically appraised by Zacher *et al.* [40]. The catalyst has played an important role too. As demonstrated by Moens *et al*. [28] the esterification reaction did not proceed further than 18% conversion without strong acid addition, at the applied reaction conditions. Most of the reported studies opted for commercially available resins, such as Amberlyst-70 [27,38], Amberlyst-15 [28,38,39], Nafion SAC-13 [28,37], Nafion NR50 [38], Dowex 50WX2 [38], 732 resin [26], NKC-9 resin [26], tailor-prepared mesopropus silica-based SO_3H-SBA-15 [25] and functionalized ionic liquid $C_6(mim)_2$-HSO_4 [35]. Homogeneous catalysts, such as *p*-toluene-sulfonic acid [28] and H_2SO_4 [28,39], have been claimed as well, though this would require an additional neutralization step. In particular, *p*-toluene-sulfonic [28] did not lead to high residual acidity; and this was explained by a possible decomposition or reaction with the bio-oil matrix.

In the alcoholysis condensation reactions, water is produced as by-product, either *via* esterification or acetalization, and both reactions are equilibrium limited (one must bear in mind that other water producing condensation reactions, catalysed by strong acids, might take place). Therefore, as far as the equilibria is concerned, water removal is an important driving force. This will 1) shift the equilibrium to the product side, thereby having a higher conversion of carboxlic acids and aldehydes, and 2) accelerate the rate of the reactions [41,42]. Both will ultimately improve relevant properties, such as acidity and stability, while others are compromised such as viscosity, because the water removal will make the final product more viscous. Therefore, for this particular alcoholysis route, it is important to have an excess of alcohol to maintain the viscosity in the lower side, at the expense of a higher production cost of the upgraded BcPO due to the alcohol excess.

Removal of water has been considered by several groups. Reactive distillation in EtOH combined with H_2O_2 oxidation provoked phase separation resulting in a 5 *wt.*% of H_2O in the heavy phase [33]. Reaction with EtOH over functionalized ionic liquid $C_6(mim)_2$-HSO_4 displayed phase separation [35], with a final water content of *ca.* 8 *wt.*% in the organic layer. A vacuum rectification method using *n*-BuOH led to a moderate pH increase while water was reduced to 5-9 *wt.*% [37]. Hydration of 1-octene to remove water was also proposed, resulting in a phase separation and 7 *wt.*% H_2O in the organic layer. Ultimately, azeotropic water removal [28] using cyclohexane was effective to shift the equilibrium and decrease the total acid number (TAN).

From a fundamental standpoint, these approaches provide evidence that the acidity and calorific value of the BcPO can be optimized *via* alcoholysis. In this work, we are reporting novel results about the alcoholysis of BcPO with the general goal of an experimental screening using bio-based alcohols which makes the process completely green, and a process with an effective water removal decoupled from the reaction vessel. Prior to the final optimal concept, we will be describing results using various reactor models to conduct the alcoholysis in a water-free environment.

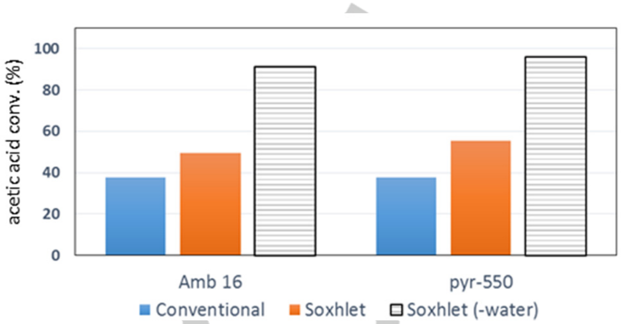

Figure 1. Acetic acid conversion (%) during the esterification with *n*-BuOH for two catalysts, Amberlyst-16 (Amb 16) and beta zeolite (pyr-550). Conditions: 110 °C, 1280 min, acetic acid (0.5 mol), *n*-butanol (0.5 mol), water (0.78 mol), catalyst (0.8 g) using a conventional configuration (🟦, see configuration in Fig S1a) and Soxhlet (🟧, Fig S1b). In one case, water was omitted, denoted Soxhlet (–water), ■. Full time dependency curves can be in the Supporting Information.

We started looking at the model reaction between acetic acid and *n*-BuOH, in the presence of H_2O to simulate the typical water concentration in BcPO; acetic acid was chosen as the model compound since the bio-oil contains ~10 *wt.*% acetic acid [43]. Commercial Amberlyst 16 and a tailor-made catalyst was employed: the latter is an as-synthesized beta zeolite (Si/Al=12.5) whose organic template was pyrolyzed 550 °C (beta-pyr550); the zeolite was in this way thermally treated to enhance its hydrophobicity (see experimental section in ESI). The steady state reaction conversion over the two catalysts using a conventional reaction system (see rector sketch in Figure S-1a) was almost identical (Fig. 1); with a final acetic acid conversion of 38% due to the equilibrium water inhibition. Notable changes were observed when the conventional set-up was modified having an *in-line* soxhlet (represented in Fig. S-1b). Such modification allows for the temporary hold-up of water, and light compounds in the separate soxhlet, facilitating the esterification reaction in the reaction vessel. This is concluded from the improved conversion over Beta-pyr550 and Amberlyst-16 with conversions up to 50-55 % (Fig. 1), compared to 38% for the conventional reactor, as presented above. Moreover, these results show that the Brønsted sites of Beta-pyr550 are resistant to H_2O, having a comparable strength to the SO_3^- groups in Amberlyst-16 under these reactions conditions.

A similar reaction concept was applied for upgrading the BcPO. The reaction conditions were identical while the catalyst type was varied using a wide range of commercial resins, H_2SO_4, sulfonated pyrolized glucose and beta-pyr550. An overview of the results is given in Table S-1. The performance was evaluated using a definition of an average pH (see definition in the Supporting Information section), to get a rough estimate for the extent of the esterification reactions. It was generally observed that the resins performed well; the best results were obtained with Dowex 50WX8 Na^+, Amberlyst 15 H^+ and Nafion NR50, yielding an average pH of 4. A similar value was found for Beta-pyr550.

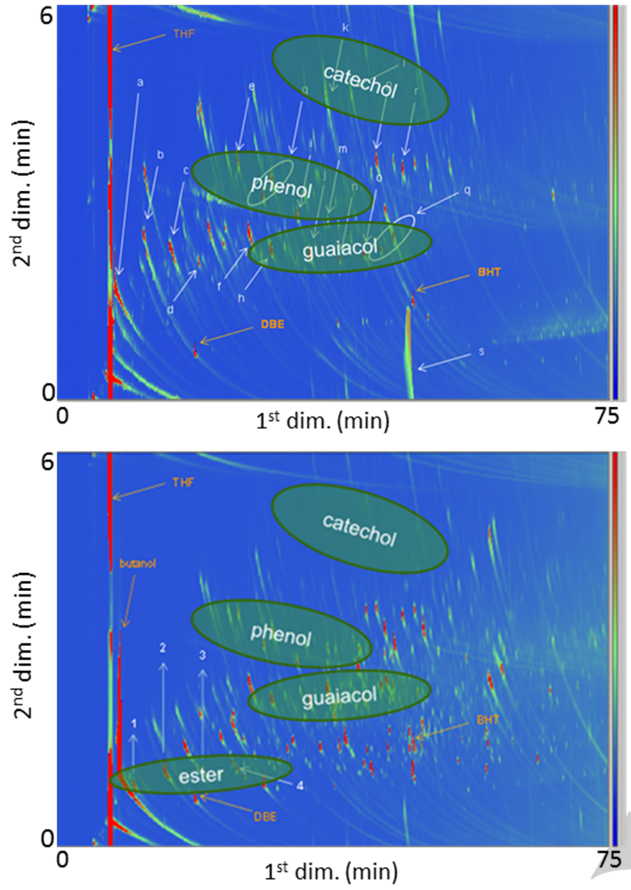

Figure 2. **Top**. 2D GC chromatogram of the raw BcPO diluted in THF. **a** = acetic acid; **b** = propanal; **c** = 2-furancarboxaldehyde; **d** = 5-methyl (c); **e** = phenol; **f** = 1,2-cyclopentanedione, 3-methyl-; **g** = 2- and 3-methyl-phenol; **h** = guaiacol; **i** = phenol, 2,4-dimethyl-; **j** = 4-methyl-guaiacol; **k** = 1,2-benzenediol; **l** = 3- or 4-methyl (k); **m** = HMF; **n** = 4-ethyl-guaiacol; **o** = eugenol (allyl-guaiacol); **p** = vanillin (formyl-guaiacol); **q** = isoeugenol (propenyl-guaiacol); **r** = apocynin (acetyl-guaiacol); **s** = levoglucosan. **Bottom**. 2D GC chromatogram for the upgraded BcPO (over Beta-pyr550, Pyrolysis oil/*n*-butanol = 0.5 (vol), cat. = 2 *wt.*%, time = 7 h), indicating the esters formation: **1** = formic acid, butyl ester; **2** = acetic acid, butyl ester; **3** = propanoic acid, butyl ester; **4** = butanoic acid, butyl ester.

The proof of esterification was investigated by two-dimensional GC analysis, shown in Figure 2 (bottom). The chromatogram detects four characteristic butyl esters; formic acid butyl ester; acetic acid, butyl ester; propanoic acid, butyl ester; and butanoic acid, butyl ester. These compounds were not detected in the raw BcPO (Fig. 2-Top). Therefore, the esterification between the various carboxylic acids present in the BcPO and *n*-BuOH occur. Despite the esterifications take place, experiments at longer reaction time (24 h) with *n*-BuOH/BcPO = 3 only increased further the average pH up to 4.7, which was not a significant improvement. This means that the water hold-up effect in the soxhlet was not as effective as we expected.

An additional test was carried out in the model reaction (Fig. 1) using the soxhlet without externally added water, simulating to have an effective water adsorbent in the Soxhlet chamber. The results reveals notable yileds with 91-96% conversion; a slightly better performance of the Beta-pyr550 was found. This result indicates that the water content present in the bio-oil (*ca.* 8.2 *wt.*%) can have an adverse effect on the catalytic performance. Moreover, esterification leads to additional water. So water removal is vital to improve the activity of acid catalysts.

Table 1. TAN and water content of the final upgraded BcPO with selective water removal.[a]

Entry	Catalyst	Time, h [c]	TAN, mg KOH/g	H_2O, wt.%
1 [b]	-	-	25	8.2
2	Amberlyst 16	24	6	2.6
3	Beta-pyr550	24 (90)	10	4.3
4 [c]	Beta-pyr550	48 (75)[d]	2	0.1

[**a**] Conditions: BcPO/THFA=1:3, T≈178 °C (reflux equilibrium temperature), molecular sieve 3Å, catalyst: 1.3 *wt.*%; [**b**] starting unreacted mixture BcPO/THFA= 1:3; [**c**] Value in parenthesis is the mass ratio given as recovered upgraded oil to the water-free starting BcPO, as percentage; [**d**] The molecular sieve was replaced after 24h reaction time.

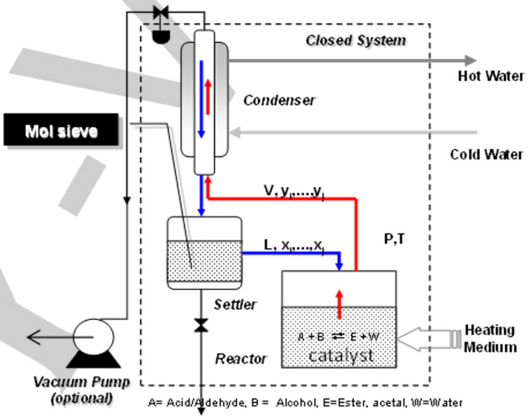

Figure 3. Batch reactive distillation set-up showing the reaction and water separation (zeolite adsorption) in separated compartmens. Nomenclature: ***L***, liquid phase; ***V***, vapour phase; ***x*** molar fraction in the liquid phase, ***y*** molar fraction in the gas phase; ***P***, pressure; ***T***, temperature.

Based on the promise seen in the above results using model reaction, we aimed at finding a way to remove the water in the actual bio-oil experiments. In a successive study, we opted for an improved reactor concept (equivalent to a Dean Stark) using a molecular sieve in the condensate chamber to sequestrate water more effectively, thus accelerating the kinetics and shifting the equilibrium, further. By using a molecular sieve, the choice of alcohol is not limited to have a biphasic behaviour to separate water, as it is the case with *n*-BuOH. We employed tetra-hydrofurfuryl alcohol (THFA), a furfural derived alcohol with a high boiling point (178 °C) that is obtained by two successive hydrogenation reactions of furfural, through furfuryl alcohol [44]. Therefore this upgrading route, using THFA, can be considered a green biomass derived route.

The reaction was carried out in a batch reactor at the reflux temperature, ~178 °C (Fig. 3). The conditions were such that the vapours produced (water, and low molecular weight volatile organics) were subsequently condensed. The condensate liquid drains down to a vessel containing the 3Å molecular sieve (previously thermally activated at 350 °C overnight). There, water is selectively adsorbed. The remainder of the condensate is continuously recycled to the reaction vessel.

It was found that the reaction proceeds very well with both Amberlyst 16 and Beta-pyr550 (Table 1, entries 2 and 3). The total

ACCEPTED MANUSCRIPT

acid number of the upgraded oil was reduced from 25 to 6-10 mg KOH/g with a water content depletion from 8.2 to 2.6-4.3 *wt.* %. In order to decrease the TAN and water content further, the reaction was carried out for 48 h, with a replacement of the molecular sieve after 24 h. Under such conditions the TAN was reduced to a marginal value of 2 mg KOH/g, whereas almost no water was detected in the upgraded oil.

The product yield per carbon basis was calculated by the mass ratio between the recovered upgraded liquid to the starting water-free pyrolysis oil, *i.e.* BcPO where pristine water was subtracted. The calculated ratios were about 90% (for 24 h reaction time, entry 3) and 75% (for 48 h reaction time, entry 4), which means that a fraction of these light compounds is held up within the molecular sieve. Effective means to recover this fraction, as well as reducing the alcohol use, are areas for optimization.

It is concluded that using a reactor concept where reaction and water separation are decoupled, and employing a biomass derived high-boling temperature alcohol, tetrahydrofurfuryl alcohol, a free-flowing upgraded pyrolysis oil with marginal TAN and water content can be obtained.

Experimental Section

Experimental Details can be found in the **electronic supporting information**.

Acknowledgements

This research has been carried out within the framework of the CatchBio program. The authors thank the support of the Smart Mix Program of the Netherlands Ministry of Economic Affairs, Agriculture and Innovation and the Netherlands Ministry of Education, Culture and Science.

Keywords: Bio-fuels • bio-energy • green chemistry • zeolite catalysis • adsorption

[1] A. Oasma, S. Czernik, *Energ. Fuel.,* **1999**, *13*, 914-921.
[2] D. Mohan, C.U. Jr. Pittman, P.H. Steele, *Energ. Fuel.,* **2006**, *20*, 848-889.
[3] S. Czernik, A.V. Bridgwater, *Energ. Fuel.*, **2004**, *18*, 590-598.
[4] A.V. Bridgwater, Upgrading Fast Pyrolysis Liquids, in R.C. Brown (Ed.) Thermochemical Processing of Biomass into Fuels, Chemicals and Power, John Wiley & Sons, **2011**.
[5] A. Oasmaa, S. Czernik, *Energ. Fuel.*, **1999**, *13*, 914.
[6] A. V. Bridgwater, G. V. C. Peacocke, *Renew. Sust. Energ. Rev.* **2000**, *4*, 1.
[7] D. Mohan, C. U. Pittman, P. H. Steele, *Energ. Fuel* **2006**, *20*, 848-889
[8] J. Diebold, J. Scahil, S. Czernik, *Proceedings of Specialist Workshop on Biomass Pyrolysis Oil Properties and Combustion, Estes Park, CO*, **1994**, pp 90-108.
[9] M. Ikura, S. Mirmiran, M. Stanciulescu, H. Sawatzky, *US patent 5,820640*, **1998**.
[10] M. Ikura, M. Stanciulescu, E. Hogan, *Biomass Bioenerg.* **2003**, *24*, 221-232.
[11] D. Diebold, S. Czernik, *Energ. Fuel.* **1997**, *11*, 1081-1091.
[12] F. d. M. Mercader, M. J. Groeneveld, S. R. A. Kersten, R. H. Venderbosch, J. A. Hogendoorn, *Fuel* **2010**, *89*, 2829
[13] J.D. Adjaye, N.N. Bakhshi, *Biomass Bioenerg*. **1995**, *8*, 131.
[14] S. Vitolo, M. Seggiani, P. Frediani, G. Ambrosini, L. Politi, *Fuel* **1999**, *78*, 1147.
[15] H. J. Park, H. S. Heo, J. K. Jeon, J. Kim, R. Ryoo, K. E. Jeong, Y. K. Park, *Appl. Catal. B*, **2010**, 95, 365 – 373.
[16] Y.T. Cheng, J. Jae, J. Shi, W. Fan, G.W. Huber, *Angew. Chem. Int. Ed.* **2012**, *51*, 1387 –1390.
[17] D.C. Elliott, E.G. Baker, *Biotechnol. Bioeng.* **1984**, *14*, 159-174.
[18] R. Maggi, B. Delmon, in G.F. Froment, B. Delmon, P. Grange *Hydrotreatment and Hydrocracking of Oil Fractions*. **1997**. pp. 99-113.
[19] J. Wildschut, I. Melian-Cabrera, H.J Heeres, *Appl. Catal. B-Environ.,* **2010**, *99*, 298-306.
[20] J. Wildschut, M. Iqbal, M. Farchad, I. Melián-Cabrera, R.H. Venderbosch, H.J. Heeres, *Energ. Environ. Sci.,* **2010**, *3*, 962-970.
[21] F.D. Mercader, M.J. Groeneveld, S.R.A. Kersten, C. Geantet, G. Toussaint, N.W.J. Way, C.J. Schaverien, K.J.A. Hogendoorn, *Energ. Environ. Sci.,* **2011**, *4*, 985-997.
[22] A. Oasma, E. Kuoppala, J.F. Selin, S. Gust, Y. Solantausta, *Energ. Fuel.* **2004**, *18*, 1578-1583.
[23] D. Radlein, J.K. Piskorz, P.A. Majerski, EP0718392, **1996**
[24] V.A. Doshi, H.B. Vuthaluru, T. Bastow, *Fuel Process. Technol.,* **2005**, *86*, 885–897.
[25] S. Miao, B. H. Shanks, *Appl. Catal. A-Gen.,* **2009**, *359*, 113.
[26] J. J. Wang, J. Chang, J. Fan, *Energ. Fuel.,* **2010**, *24*, 3251.
[27] X. Li, R. Gunawan, C. Lievens, Y. Wang, D. Mourant, S. Wang, H. Wu, M. Garcia-Perez, C. Z. Li, *Fuel* **2011**, *90*, 2530.
[28] L. Moens, S. K. Black, M. D. Myers, S. Czernik, *Energ. Fuel.*, **2009**, *23*, 2695.
[29] W. Li, C. Pan, Q. Zhang, Z. Liu, J. Peng, P. Chen, H. Lou, X. Zheng, *Bioresource Technol.*, **2011**, *102*, 4884.
[30] W. Li, C. Pan, L. Sheng, Z. Liu, P. Chen, H. Lou, X. Zheng, *Bioresource Technol.,* **2011**, *102*, 9223
[31] Q. Zhang, J. Chang, T. Wang, Y. Xu, *Energ. Fuel.,* **2006**, *20*, 2717.
[32] J. Peng, P. Chen, H. Lou, X. Zheng, *Energ. Fuel.,* **2008**, *22*, 3489.
[33] X. Junming, J. Jianchun, S. Yunjuan, L. Yanju, *Biomass Bioenerg.* **2008**, *32*, 1056.
[34] J. Peng, P. Chen, H. Lou, X. Zheng, *Bioresource Technol.* **2009**, *100*, 3415
[35] W. M. Xiong, M. Z. Zhu, L. Deng, Y. Fu, Q. X. Guo, *Energ. Fuel.* **2009**, *23*, 2278.
[36] M. Song, Z. Zhong, J. Dai, *J. Anal. Appl. Pyrol.* **2010**, *89*, 166.
[37] F. H. Mahfud, I. Melian-Cabrera, R. Manurung, H. J. Heeres, *Process Saf. Environ. Prot.* **2007**, *85*, 466.
[38] Z. Zhang, Q. Wang, P. Tripathi, C. U. Pittman Jr, *Green Chem.* **2011**, *13*, 940.
[39] P. Weerachanchai, C. Tangsathitkulchai, M. Tang-sathitkulchai, *Korean J. Chem. Eng***.** **2012**, *29*, 182.
[40] A.H. Zacher, Mariefel V. Olarte, D.M. Santosa, D.C. Elliott and S.B. Jones, *Green Chem.*, **2014**, *16*, 491-515.
[41] T.A. Peters, N.E. Benes, A. Holmen, J.T.F. Keurentjes, *Appl. Catal. A: General* **2006**, *297*, 182.
[42] Y. Liu, E. Lotero, J.G. Goodwin Jr, *J. Molec. Catal. A-Chem.* **2006**, *245*, 132.
[43] A. Oasmaa, E.Kuoppala, Energ. Fuel., **2003**, 17, 1075-1084.
[44] N. Merat, C. Godawa, A. Gaset, *J. Chem. Technol. Biot.* **1990**, *48*, 145-159.

Electronic Supporting Information

Mild Upgrading of Bio-crude Pyrolysis Oil. A Concept based on Bio-based Alcohols with Selective Water Adsorption.

R. Kumar Pazhavelikkakath Purushothaman,‡ [a] T. Buntara,‡ [a] Z. Zhang,[a] I.J. Vehoff,[a]

C. Boyadjian,[a] L. Falco,[a,c] K. Seshan,[b] N. Gómez,[c] H.J. Heeres,[a]
I. Melián-Cabrera [a,c] *

[a] *Chemical Reaction Engineering, ENTEG, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands.*
[b] *Catalytic Processes and Materials, University of Twente, 7500 AE Enschede, The Netherlands.*
[c] *European Bioenergy Research Institute (EBRI), School of Engineering and Applied Science, Aston University, Aston Triangle, Birmingham B4 7ET, United Kingdom.*

‡ Equal contribution.

Corresponding author:
i.melian-cabrera@aston.ac.uk (Ignacio Melián-Cabrera)

1. Materials and methods

1.1. Materials

Pinewood pyrolysis oil was obtained from University of Twente, Sustainable Process Technology Group, The Netherlands (pH = 2.9, water content = 25.4 *wt.*%, density = 1.15 g/ml). Acetic acid (glacial, 100%) was purchased from Merck. n-butanol (99%) and glycerol (99.6%) were purchased from Acros while tetrahydrofurfuryl alcohol (98%) was purchased from Aldrich. Sulfuric acid (95-97%) was purchased from Merck. Nafion SAC-13 (Aldrich), Nafion NR50 (Aldrich), Amberlyst 15 H^+ (moisture $\leq$ 1.5%, Aldrich), Amberlyst-16 wet (Fluka), beta zeolite (CP806E) from Zeolyst (modified afterwards in house, details in 1.2.1), Dowex 50WX8 Na^+ (Fluka), Dowex 50WX8 H^+ (Fluka), Dowex Marathon MSC H^+ (Aldrich), Lewatit K2621 (Bayer), Smopex 101 (Johnson Matthey) and Amberlite IR-120 (Fluka). Sulfonated carbonized glucose was prepared in house (details in 1.2.3). A 3Å molecular sieve from Merck was employed.

1.2. Methods

1.2.1. Preparation of pyrolysed beta zeolite catalyst

In a tubular oven (Nabertherm), beta zeolite containing the TEA template (Zeolyst, CP806E, Si/Al = 12.5) was heated under N_2 flow to 550 ºC (5 ºC/min heating rate) and kept at this temperature for 1 h to give the pyrolyzed beta zeolite (Beta-pyr550).

1.2.2. Preparation of sulfonated carbonized glucose

In a tubular oven (Nabertherm), D-Glucose was heated under N_2 flow to 400 °C (5 ºC/min heating rate) and kept at this temperature for 15 h. The resulting char was then sulfonated in an OmniStation MKII set-up with concentrated H_2SO_4 at 150 ºC under N_2 during 15 h. After cooling to ambient temperature, the solid was filtered using 1000 cm^3 of distilled water and the black precipitate was washed repeatedly with hot distilled water (T > 80 ºC) until no acidity was detected in the residual water. The final material was dried overnight in an oven at 90 ºC.

1.2.3. General reaction procedure for the esterification of acetic acid with n-butanol

Acetic acid (29 ml, 0.5 mol), *n*-butanol (47 ml, 0.5 mol), water (14 ml, 0.78 mol), catalyst (0.8 g), and a Teflon stirring bar were added to a 250 ml three-neck round bottom flask. The flask was placed in an electric heating plate. A condenser was placed above the flask and a soxhlet, in case of soxhlet configurations, was placed between the flask and the condenser. The reaction was performed at 110 °C, 1 bar for 24 h. Then, the reaction mixture was allowed to cool to ambient temperature. The catalyst was filtered and the filtrate was subjected to GC analysis. In some experiments (when stated in the text), no water was added to the reaction mixture. Figure S-1 shows the two configurations employed for the model reaction.

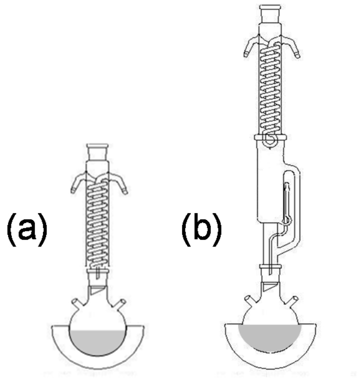

Figure S-1. Configurations used in a model compound reaction: **a)** conventional and **b)** *in-line* Soxhlet that serves to hold the distillate, containing water.

1.2.4. General reaction procedure for the esterification of pyrolysis oil equipped with an in-line soxhlet system

Pyrolysis oil (30 ml, 34.5 g), n-butanol (60 ml, 48.6 g), catalyst (1.65 g, 2 wt.%), and a Teflon stirring bar were added to a 250 ml three-neck round bottom flask. The flask was placed in an electric heating plate. A condenser was placed above the flask and an empty soxhlet was placed between the flask and the condenser. The reaction was performed at 110 °C, 1 bar for 7 h. Then, the reaction mixture was allowed to cool to ambient temperature.

The catalyst was filtered and the filtrate was subjected to pH, water content and 2D-GC analyses.

1.2.5. General reaction procedure for the esterification of pyrolysis oil including water separation in a modified Dean-stark trap

Pyrolysis oil (30 ml, 34.5 g), tetrahydrofurfuryl alcohol (THFA, 90 ml, 94.9 g), catalyst (1.65 g), and a Teflon stirring bar were added to a 250 ml three-neck round bottom flask. The flask was placed in an electric heating mantle. A condenser was placed above the flask and a Dean-stark. The reaction was performed at ca. 180 ^{o}C and 1 atm. The reactor contents were heated under magnetic stirring for the desired reaction time. Then, the reaction mixture was allowed to cool to ambient temperature. The catalyst was filtered and the filtrate was subjected to pH, water content and TAN analyses.

1.2.6. Gas chromatography analysis

2D-GC analyses were performed on a trace 2D-GC from Interscience equipped with a cryogenic trap system and two columns: a 30 m x 0.25 mm i.d. and 0.25 μm film of sol-gel capillary column connected by a melt fit to a 150 cm x 0.1 mm i.d. and 0.1 μm film Restek 1701 column. An FID detector was applied. A dual jet modulator was applied using carbon dioxide to trap the samples. The lowest possible operating temperature for the cold trap is 60 ^{o}C. Helium was used as the carrier gas (continuous flow 0.6 ml/min). The injector temperature and FID temperature were set at 250 ^{o}C. The oven temperature was kept at 40 ^{o}C for 5 minutes then heated up to 250 ^{o}C at a rate of 3 ^{o}C/min. The pressure was set at 70 kPa at 40 ^{o}C. The modulation time was 6 seconds. Products were identified with a home-made database using external standards.

1.2.7. Water content analysis by Karl Fischer titration

The water content was determined using a Karl-Fischer titration using a Metrohm 702 SM Titrino titration device.

1.2.8. Acidity analysis

The pH was determined using a pH meter (pH 315i) from WTW, Germany. The TAN number analyses were performed using a Metrohm Titrino Plus 848.

1.2.9. Elemental analysis

Elemental analyses were performed using a EuroVector EA3400 Series CHNS-O analyzer with acetanilide as reference. All analyses were performed twice and the average value is reported.

1.2.10. Definition

Average pH ($\mathrm{pH}^{\mathrm{AV}}$) was calculated using the following equation:

$$\mathrm{pH}^{\mathrm{AV}} = \sum x_i . pH_i \qquad \text{(eq. 1)}$$

where x_i is the mass fraction of each phase and pH_i is the pH of each phase. When using *n*-BuOH we identified 3 phases: heavy oil, light oil (organic) and light oil (aqueous). The reason for including all the fractions in the calculation is to include the possible absorption of the unreacted carboxylic acids in the light oil (aqueous).

1.2.11. TAN determination

The TAN number of pyrolysis oil samples was determined by potentiometric titration following the method reported by J. J. Wang et al, Energ. Fuel. 2010, 24, 3251 but using acetone as co-solvent, using a Metrohm 702 SM Titrino titration device. Varying amounts of PO samples (0.50 to 1 g, depending on the acidity levels) were dissolved in a 1:1 mixture of acetone and water (40 mL) and were titrated using 0.1 M standard aqueous solution of KOH (Sigma-Aldrich). Each sample was analyzed twice and a mean value is reported.

2. Additional results

2.1. Model compound reaction of acetic acid and *n*-butanol using pyrolyzed beta in various reactor configurations

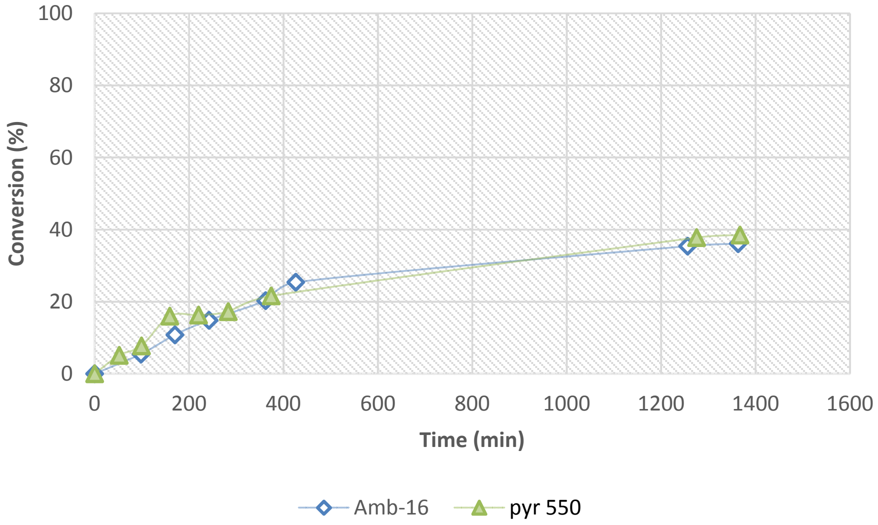

Figure S-2. Performance in a conventional system, Fig. S-1a, (+H_2O). Conditions: Acetic acid (0.5 mol), *n*-butanol (0.5 mol), water (0.78 mol), catalyst (0.8 g).

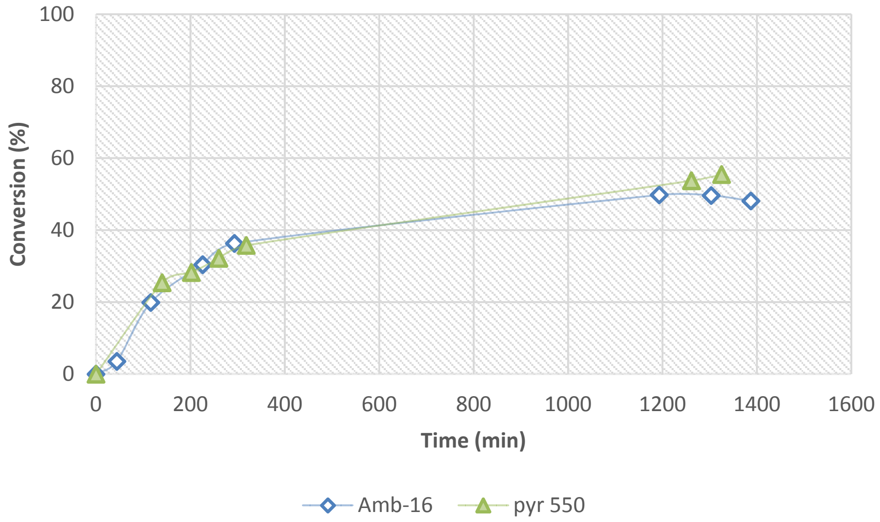

Figure S-3. Performance having an *in-line soxhlet* (+H_2O). Conditions: Acetic acid (0.5 mol), *n*-butanol (0.5 mol), water (0.78), catalyst (0.8 g).

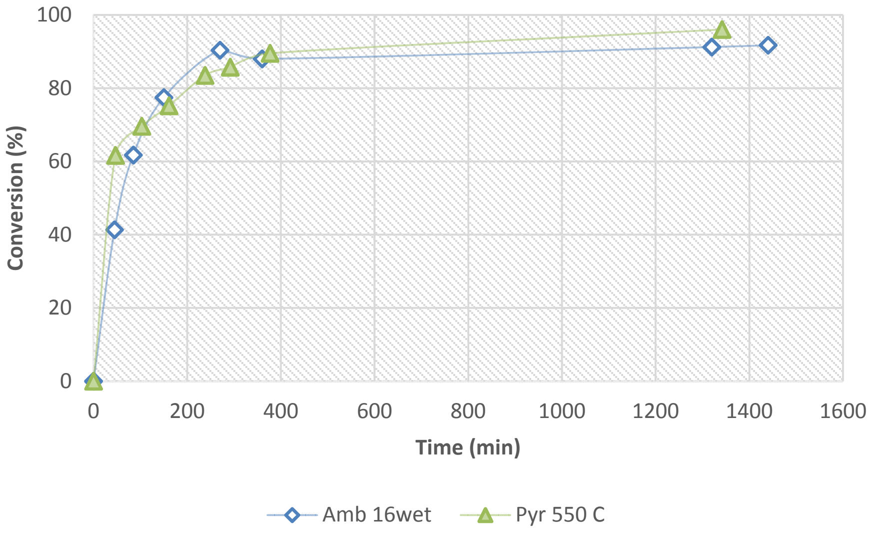

Figure S-4. Performance having an *in-line soxhlet* (-H_2O). Conditions: Acetic acid (0.5 mol), *n*-butanol (0.5 mol), water (0.78), catalyst (0.8 g)

2.2. Catalyst screening of the pyrolysis oil upgrading with *n*-butanol

Table S-1. Catalyst screening of the BcPO upgrading with *n*-butanol with an *in-line* soxhlet system.[a]

Catalysts	***pH* BcPO**	***pH* heavy fraction**	***pH* $^{AV\ c}$**
1 Dowex 50WX8 Na^+	2.9	4.2	4.0
2 Dowex 50WX8 H^+	2.9	3.9	3.8
3 Dowex Marathon MSC H^+	2.9	3.6	3.6
4 Lewatit K2621	2.1	2.9	2.9
5 Amberlyst 16 wet	2.1	3.4	3.7
6 Amberlyst 15 H^+	2.9	3.8	3.9
7 Smopex 101	2.9	2.7	2.8
8 Amberlite IR-120	2.9	3.7	3.6
9 Nafion SAC-13	2.1	3.7	3.7
10 Nafion NR50	2.9	4.2	4.0
11 Beta-pyr550	2.9	4.1	4.0
12 Sulfonated carbonized glucose	2.1	1.2	2.3
13 H_2SO_4	2.9	0.7	1.1

a. Conditions: Pyrolysis oil/*n*-butanol = 1/2 (vol.), cat. = 2 *wt*.%, time = 7 h.
b. ΔH_2O = water out (heavy fraction + light organic + light aqueous) – water in (initial pyrolysis oil).
c. $pH^{AV} = \sum x_i . pH_i$; where x_i is the mass fraction of each phase and pH_i is the pH of each phase.