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A Breakthrough Is Something You Don't See Coming Preface

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BIOMASS TO FUELS

Upgrading of Flash Pyrolysis Oil by Reactive Distillation Using a High Boiling Alcohol and Acid Catalysts

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Abstract: We here report our studies on the upgrading of flash pyrolysis oil using an improved alcohol treatment method. The method consists of treating pyrolysis oil with a high boiling alcohol like n-butanol in the presence of a (solid) acid catalyst at 323–353 K under reduced pressure (<10 kPa). Using this approach, the water content of the pyrolysis oil is reduced significantly. Variables like the type of alcohol (n-butanol, ethylene glycol, 2-ethyl-hexyl-alcohol) and liquid and solid acids were explored and the product properties of the resulting upgraded pyrolysis oil (kinematics viscosity, water content, pH and heating value) were determined. On the basis of these screenings studies, n-butanol and the solid acid Nafion SAC13 seem to have the highest potential. The product properties of the upgraded pyrolysis oils, and particularly the heating value and the acidity are considerably improved. These improvements are not only due to blending effects but also the result of the occurrence of chemical reactions (a.o. esterification).

Keywords: flash pyrolysis oil; upgrading; reactive distillation; acid-catalysts; esterification; acetalization.

INTRODUCTION

Anticipated future energy shortages and environmental concerns have boosted research on alternatives for fossil energy carriers (Ssen, 2004). This has encouraged the exploration of renewable resources like biomass for energy generation. Flash pyrolysis oil, also known as bio-oil (BO), is a biomass-derived liquid energy carrier. It is produced via flash pyrolysis technology in yields up to 75 wt% (Agblevor *et al.*, 1995; Bridgwater *et al.*, 1999; Bridgwater and Grassi, 1991; Czernik *et al.*, 1995; Oasmaa *et al.*, 2003; Onay and Kockar, 2003). A large variety of applications for BO have been proposed (Czernik and Bridgwater, 2004). Examples are the use as a fuel in boiler systems, stationary diesel engines, gas turbines, and Sterling engines. However, poor volatility, high viscosity, coking and corrosiveness of crude BO have limited the applicability for the application mentioned above. A number of BO upgrading technologies have been proposed to improve the product properties and to increase the range of possible applications. Examples are a.o. hydrocracking or hydrodeoxygenation

(Adjaye and Bakhshi, 1995; Bridgwater, 1996; Elliott and Baker, 1984; Maggi and Delmon, 1997). For the latter, hydrogen consumption is excessive which negatively affects the economics of this process.

Alternatively, a number of studies have been reported dealing with chemical upgrading of crude bio-oil by reacting it with an alcohol (e.g., ethanol) at mild conditions using a liquid mineral acid catalyst, like sulphuric acid (Boucher *et al.*, 2000; Doshi *et al.*, 2005; Oasmaa *et al.*, 2004; Radlein *et al.*, 1996). From a chemical point of view, it is anticipated that reactive molecules like organic acids and aldehydes are converted by the reactions with alcohols to esters and acetals, respectively (Figure 1). Removal of water is essential to drive the equilibria to the right (product) side. For this purpose, Radlein *et al.* (1996) have proposed the use of molecular sieves to capture the water (reactive-adsorption). Analyses of the derived bio-oil product show that the product properties were significantly improved by this alcohol treatment.

We here propose an alternative upgrading technology for BO based on reactive

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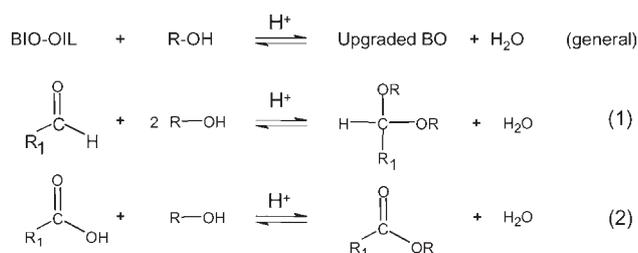


Figure 1. Reactions involved in bio-oil alcoholysis: (1) acetalization, (2) esterification.

distillation using a high boiling alcohol in the presence of an acid catalyst. The objective is to produce an upgraded BO with improved properties like a higher heating value, a lower water content, lower viscosity and lower free acid content. In this new concept, the water in the crude BO as well as the water produced by the various chemical reactions (Figure 1) are removed simultaneously (by distillation) in a single step. This will drive the equilibria to completion and is expected to lead to *a.o.* reduced acidity. To prevent excessive alcohol evaporation, alcohols with a boiling point higher than water are required. n-Butanol was selected as the alcohol of choice as it is available from renewable resources by fermentation processes (Ezeji *et al.*, 2005, 2007).

A solid catalyst, instead of a liquid inorganic acid, can also be employed and this significantly simplifies product work-up. Our study will focus on: (1) demonstration of the concept, (2) screening studies on the type of high-boiling alcohols and acid catalysts and (3) determination of the product quality of the upgraded pyrolysis oil (kinematics viscosity, water content, pH, density and heating value).

EXPERIMENTAL

Materials

Bio-oil

The crude BO was kindly provided by the Biomass Technology Group (BTG), Enschede (The Netherlands), using rotating cone flash pyrolysis technology. The oil employed in this study originated from beech (production date: 19-04-2004) and was used as received. The properties of the crude bio-oil are summarized in Table 1.

Table 1. Properties of crude BO.

Property	Value	Unit
Water content	31.5	wt%
Density	1.17	kg L ⁻¹
pH	3.0	
Elemental analysis (wet basis)		
C	35.80	wt%
H	8.38	wt%
N	—	wt%
O (by difference)	55.82	wt%
High heating value (HHV), dry basis	20.6	MJ kg ⁻¹
Kinematics viscosity ^{313K}	17	mm ² s ⁻¹
Flash point	326	K

Alcohols

Ethylene glycol, n-butanol and 2-ethyl-hexyl alcohol (EHA) from Acros Organics (purity >99%) were used in this study.

Catalysts

Potassium hydroxide pellets (>99%, Merck), sulphuric acid (95–97 wt%, Merck) and hydrochloric acid (37 wt%, Merck) were used as purchased. The solid acid catalyst Nafion[®] SAC-13 was obtained from Aldrich (99%).

Reactive-Distillation Setup and Procedures

The reactive-distillation experiments were carried out in a Dean-Stark laboratory set-up consisting of a three-neck round bottom glass flask (250 ml) equipped with magnetic stirrer, a Dean Stark set-up and a glass condenser. The temperature in the reactor was measured using a thermometer; the pressure in the set-up was controlled using a vacuum-controller (Vacuum-Controller 220). The reaction mixture was maintained at the desired temperature using a water bath. A schematic diagram of the reactive distillation set-up is shown in Figure 2.

Typically, BO (50 ml) and n-butanol (50 ml) were charged into the reactor vessel. The reaction mixture was heated to the desired temperature (323–353 K). Subsequently, the catalyst (1.6 wt%) was added. The pressure was reduced to the desired setting, typically 5 ± 0.05 kPa. The starting of the reaction was set at the time for formation of the first drop of distillate in the condenser. A typical reaction time was 60–120 min.

After reaction, the product was analysed not later than one day to avoid possible changes in the product composition. All samples were stored at 255 K in a refrigerator to prevent further reactions upon storage.

Analytical Methods and Terminology

Water content

The water content of the samples was determined using a Karl-Fischer titration (702 SM Titrimo, Metro-Ohm). The

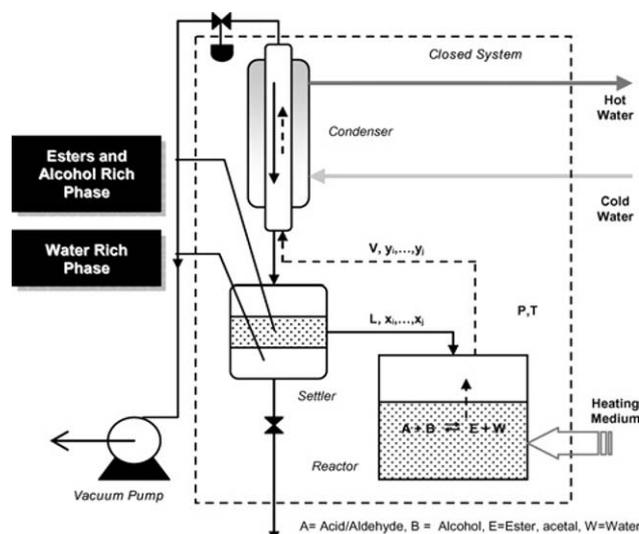


Figure 2. Batch reactive distillation setup.

samples were dissolved in Hydranal solvent (Riedel-de-Haen) and titrated using Hydranal Composite 5 (Riedel-de-Haen). The amount of water produced during the reaction (W_R) was used to evaluate catalysts performance [Equation (1)]. It is based on a water mass balance, and it takes into account the water present in the initial BO-n-butanol mixture (x_o), product (x_p) and distillate (x_d):

$$W_R = W_p x_p + W_d x_d - W_o x_o, \text{ ing} \quad (1)$$

The amount was normalised on the initial amount of water in the BO-n-butanol mixture

$$\Delta W_R = \frac{W_p x_p + W_d x_d - W_o x_o}{W_o x_o}, \text{ in wt\%} \quad (2)$$

where, W_i is the mass of a certain fraction i (g) and x_i is water amount (wt%) in a fraction i and subscripts R , p , d and o stand for water produced during reaction, in the product, distillate, and initially present in the BO-n-butanol mixture, respectively. The overall mass balance calculations indicate that losses were always less than 2 wt% of the total intake. In the mass balance calculations, it is assumed that the losses were due to evaporation and as such were included in the distillate fraction.

Viscosity

The dynamic viscosity of the product was measured at 313 K using a cone and plate rheometer (Rheolyst AR-1000 N). The kinematics viscosity was calculated using

$$\nu = \frac{\eta}{\rho}, \text{ in mm}^2 \text{ s}^{-1} \quad (3)$$

where ν is kinematic viscosity ($\text{mm}^2 \text{ s}^{-1}$, or cSt), η is dynamic viscosity (mPa s) and ρ is density (kg dm^{-3}). Density was determined by weighing a predetermined volume of products.

Acidity

The acidity was evaluated by direct pH measurement of the product using a pH-meter (Metro-Ohm) with a KCl electrode for ion-poor media. The electrode was directly immersed into the samples.

Flash point

The flash point was determined using a Miniflash FLP (Grabner Instruments). The measurement was based on ASTM method D6450. Each sample was measured twice and the average values are reported.

Elemental analysis and higher heating value (HHV)

The elemental compositions of the main elements in the samples (C and H) were determined using an Elemental

Analyzer (Flash EA 1112, CE Instruments). The oxygen content was calculated from the differences.

The high heating value (HHV in MJ kg^{-1}) of the product samples was calculated using the following relation (Cho *et al.*, 1995).

$$\text{HHV} = 33.82 \cdot x_c + 144.28 \cdot \left(x_H - \frac{x_O}{8} \right) \quad (4)$$

where x_c , x_H and x_O are the carbon, hydrogen and oxygen content (wt%), respectively.

RESULT AND DISCUSSION

Introduction of the Reactive-Distillation Concept for Bio-Oil Upgrading

The method consists of performing the reaction between BO and the alcohol by reactive distillation. The method requires an alcohol with a boiling point higher than water. To prevent solidification/polymerization of the BO at elevated temperatures, the procedure is applied under reduced pressure. Our proposal is conceptually different from the concept reported by Radlein *et al.* (1996), which is an example of reactive adsorption using molecular sieves to remove the water. A comparison between both methods is given in Table 2.

Initially, the concept was tested using n-butanol and H_2SO_4 as a catalyst at 333 K and 5 kPa pressure (base case). n-Butanol was selected as a green version is available by fermentation of renewable resources like corn based starch using *Clostridium beijerinckii* (Ezeji *et al.*, 2005; Parekh *et al.*, 1998, 1999; Qureshi and Blaschek, 2000, 2001). The results are compared with a blank experiment without catalyst addition. As BO is a complex matrix with more than 400 different chemical compounds present, it is difficult to evaluate the catalyst performance based on the conversions of individual components (Bridgwater, 1999). However, the amount of water can be accurately quantified by means of a Karl Fischer titration. Therefore, we employed the amount of water produced by the reactions per initial water contained in the crude BO as an indicator for catalyst performance [ΔW_R in wt%, see equation (2)].

Figure 3 shows the water produced by chemical reactions for two cases. Significant amounts of water were produced when H_2SO_4 was employed as the catalyst. An overall and water mass balance for the treatment procedure using sulphuric acid is schematically provided in Figure 4.

Even in the absence of a catalyst, such water producing reactions occur ($\Delta W_R = 6 \text{ wt\%}$), although to a significantly lesser extent than in the presence of H_2SO_4 . This is likely due to the inherent acidic nature of BO (pH ca. 3). The organic acids present in the matrix (acetic acid, propionic acid) likely also auto-catalyse the esterification and acetalization reactions.

Table 2. Comparison of BO upgrading methods by alcohol treatment: reactive adsorption and reactive distillation.

Process	Reactive adsorption using Molecular Sieve (Radlein, 1996)	Reactive distillation using high boiling alcohol (this work)
Alcohol	Low b.p. (<373 K): ethanol, propanol, etc.	High b.p. (>383 K). Butanol, ethylene glycol, etc.
Processing aid	Molecular sieves, relatively large amount per BO used	Catalyst, relatively small amount per BO used
Conditions	293–343 K, atmospheric	293–343 K, reduced pressure

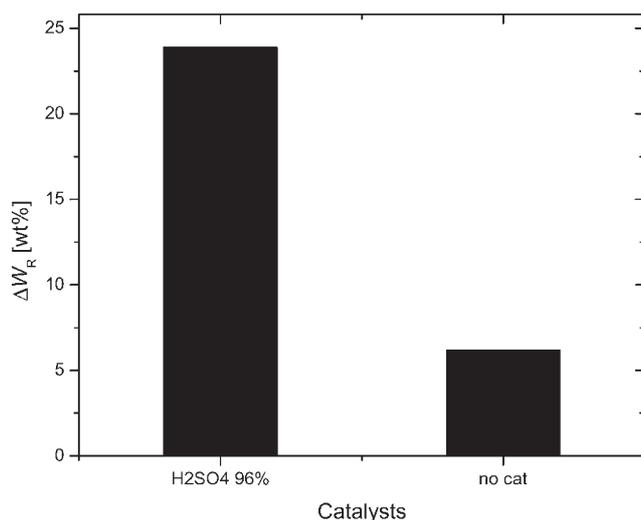


Figure 3. ΔW_R with and without catalyst. Conditions: $T = 333$ K, $P = 5.0$ kPa, $t_r = 60$ min.

Product Properties

The BO product properties (kinematic viscosity, pH, HHV and water content) were evaluated before and after treatment (Figure 5). Physical appearance (e.g., colour) of the products were close to that of the original pyrolysis oil. However, the odor changed dramatically, i.e., from smoky pungent to

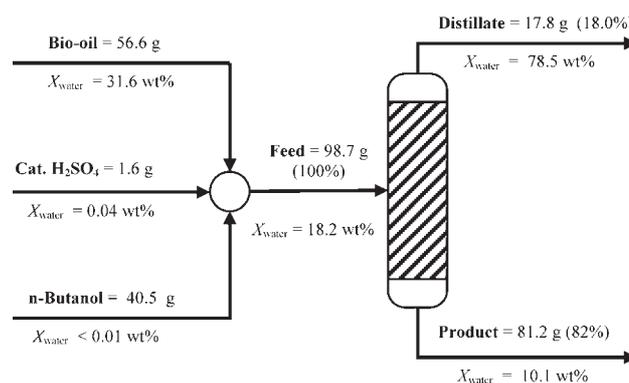


Figure 4. Schematic diagram of the reactive-distillation with mass balance data. Conditions: 1.6 wt% H_2SO_4 , $T = 333$ K, $P = 5.0$ kPa, $t_r = 60$ min.

banana like. This change is due to the formation of butyl esters of organic acids (*vide infra*) that have a very typical sweet, banana-like odour.

The water content of the treated bio-oil with H_2SO_4 was reduced from 30 wt% to 10.1 wt% [Figure 5(d)]. Evidently, this reduction is due to blending with n-butanol as well as due to removal of water by evaporation. Further reduction in the water content of the product to 4.9 wt% was obtained at prolonged reaction times (2 h).

Significant reductions in the water content of the product (to 14 wt%) were also observed in the absence of a strong

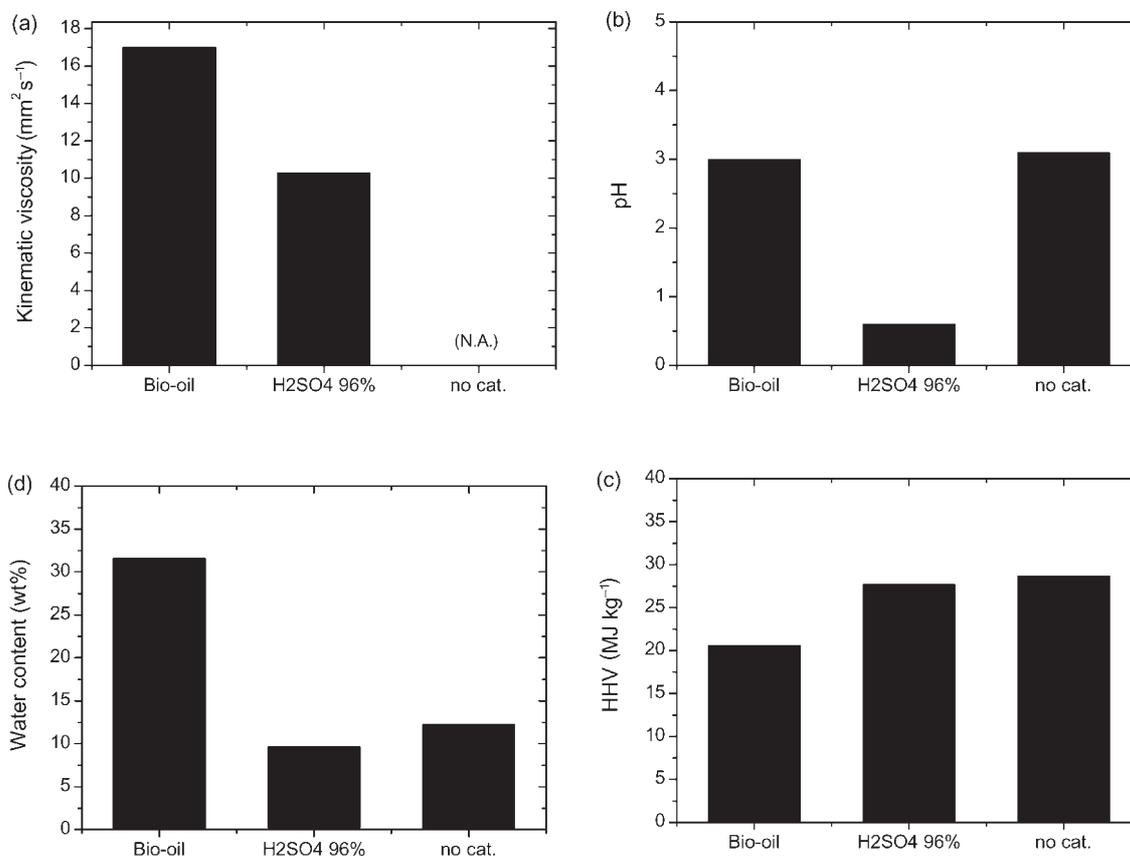


Figure 5. Product properties before and after reactive distillation with n-butanol. (a) Kinematic viscosity, (b) pH, (c) HHV (dry bases) and (d) water content. Conditions: $T = 333$ K, $P = 5.0$ kPa, $t_r = 60$ min.

mineral acid catalyst [Figure 5(d)], although less than with added catalyst. Here, also a liquid product without solid deposits was obtained. This is rather remarkable as it is well known that fractionation of crude BO is difficult and invariably leads to excessive decomposition and the formation of large amounts of solid by-products (Bridgwater, 1999). This work implies that distillative work-up with a co-diluent even in the absence of a mineral acid is possible without negatively affecting the product properties.

The pH of the treated BO drops from 3.0 to 0.5 when using 1.6 wt% H₂SO₄ as the catalyst. Therefore, an additional neutralization step will be required before application. This additional process step may be avoided when using a solid acid catalyst (*vide infra*). In the absence of sulphuric acid, the pH of the product is slightly higher than the original bio-oil (Figure 5). This is due to the diluting effect of n-butanol as well as the occurrence of esterification reactions, catalysed by organic acids present in BO (Figure 1).

The HHV of the product (27.7 MJ kg⁻¹) prepared using sulphuric acid is considerably higher than the HHV of the original BO (20.6 MJ kg⁻¹). This increase is the result of the reduced water content of the product and the presence of n-butanol (HHV: 37.5 MJ kg⁻¹).

The kinematic viscosity of the product after alcohol treatment is positively affected and is reduced from 17 to ca. 10 mm² s⁻¹ when H₂SO₄ is applied as the catalyst [Figure 5(a)]. This reduction is likely due to the diluting effect of n-butanol and less to the occurrence of chemical reactions.

Molecular Aspects

When the reactions depicted in Figure 1 occur, significant amounts of water will be formed. This was indeed the case when using sulphuric acid as the catalyst (Figure 3). Further evidence for the occurrence of the esterification reactions was obtained when analysing the distillate by GC/MS. Significant amounts of n-butylacetate as well as n-butylesters of higher organic acids like propionic- and butanoic acid,

were present, indicative for the occurrence of reactions between organic acids and n-butanol.

Alcohol Screening

Besides n-butanol, two other relatively high boiling alcohols were tested, i.e., ethyleneglycol (b.p. 470.6 K) and 2-ethylhexyl alcohol (EHA, b.p. 459 K). An experiment with EHA (333 K, 5 kPa) resulted in the formation of a liquid product. However, upon standing at room temperature for one day, solid deposits were formed, making EHA less suitable for applications.

More encouraging results were obtained with ethylene glycol (Figure 6). The amounts of water produced by reactions was similar to that for n-butanol (24 wt%) when using sulphuric acid. On the other hand, in the absence of catalyst, more water was produced by chemical reactions (12 wt%) compared to n-butanol (6 wt%). This finding may be related to the higher amounts of alcohol groups per mol of alcohol present for ethyleneglycol leading to higher reaction rates.

A major drawback of the application of ethylene glycol is the relatively high viscosity of the upgraded bio-oil, which is more than twice the value for n-butanol [Figure 6(b)].

Catalyst Screening

Besides sulphuric acid, also a base (KOH) was tested for a reactive distillation experiment with n-butanol. The results are given in Table 3. When using KOH, significant amounts of

Table 3. Catalyst screening.

Catalyst	ΔW_R , wt% ^a	Product pH ^a
H ₂ SO ₄ (96%)	23.9	0.5
no cat.	6	3.1
KOH	4	5.5

^aConditions: $T = 333$ K, $P = 5.0$ kPa, $t_r = 60$ min.

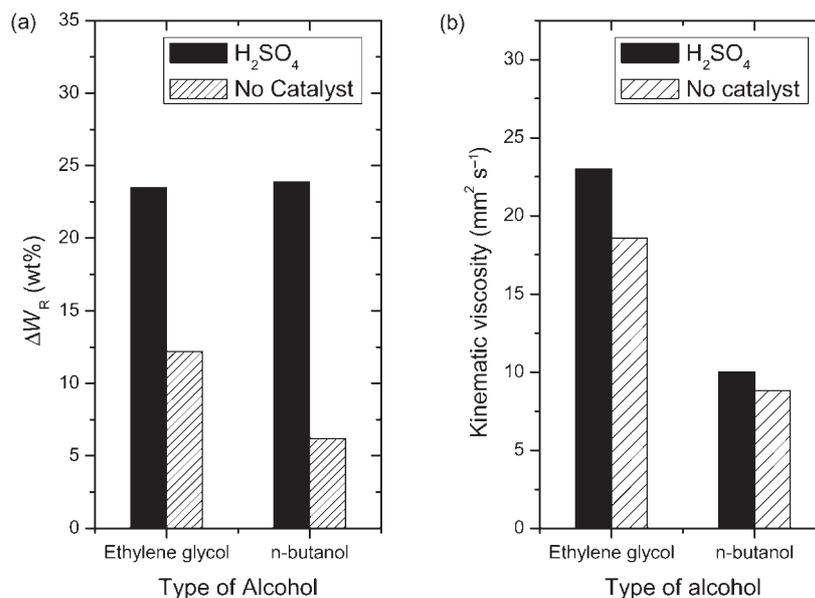


Figure 6. Effect of type of alcohol on water produced by reactions (a) and kinematic viscosity of the products (b). Conditions: $T = 333$ K, $P = 5.0$ kPa, $t_r = 60$ min.

water were produced by chemical reactions ($\Delta W_R = 4$ wt%). However, this amount was lower than for a reaction without catalyst ($\Delta W_R = 6\%$). The pH of the product using KOH was still slightly acidic. It implies that the amount of added KOH is insufficient to neutralize all the organic acids present in the BO. Hence, instead of creating a basic environment, the experiments were still performed under acidic conditions. Therefore, the water produced by chemical reactions likely originates from acid catalyzed esterification and acetalization reactions.

When using a mineral acid, the product pH is far from neutral and below target. To prevent a subsequent neutralization step, we envisaged the use of solid acid catalysts. Solid catalysts have been widely used to catalyse esterifications and other liquid phase acid catalysed reactions (Armor, 1991, 2001; Grieco, 1998; Harmer *et al.*, 1996, 2000; Harmer and Sun, 2001; Misono and Nojiri, 1990; Namba *et al.*, 1981; Okuhara, 2002; Tanabe and Holderich, 1999). For initial screening studies, Nafion[®] SAC13 (Harmer *et al.*, 1996, 2000; Harmer and Sun, 2001) was selected to overcome the low product pH and the catalyst recycle-ability problem when using homogenous acids like H₂SO₄. The results using 1.6 wt% of catalyst (on BO-n-butanol) are presented in Figure 7.

The performance for Nafion SAC 13 was lower than for sulphuric acid. Apparently, the catalytic effect of Nafion on the esterification and acetalization reactions depicted in Figure 1 is less than for sulphuric acid. However, there is a clear catalytic effect of Nafion as the amount of water produced is higher than for the blank without catalyst addition. This relatively low activity is likely due to the relatively low number of acid sites [ca. 0.2–1.0 meq g⁻¹ (Beltrame and Zuretti, 2003; Rios *et al.*, 2005)] on Nafion compared to H₂SO₄ (20.4 mmol [H⁺] g⁻¹ as calculated by de-protonation equilibria). Additionally, limited accessibility of the reactants to the active acid sites on the porous support may also affect the overall reaction rates.

Although the performance of Nafion is lower compared to sulphuric acid, the pH of the product is significantly higher (pH = 3.2 versus 0.5 for sulphuric acid). The pH of the product using Nafion is slightly higher than the starting BO, implying that conversion of the organic acids in the BO matrix is still far from quantitative. In conclusion, these screening studies indicate that solid acid catalysts have high potential for the reactive distillation concept, although optimization studies are required to achieve further reductions in product acidity and water content.

An overview of the product properties of the upgraded BO obtained using Nafion and H₂SO₄ are summarized in Table 4

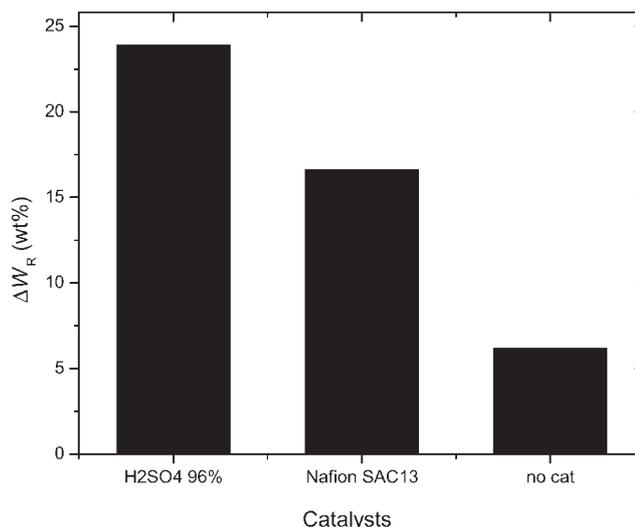


Figure 7. Catalyst performance (ΔW_R) for H₂SO₄ and Nafion SAC 13. Conditions: $T = 333$ K, $P = 5.0$ kPa, $t_r = 60$ min.

and compared with petroleum diesel and (FAME) bio-diesel. Some improvements are clearly shown when using Nafion SAC13. For example, the viscosity is reduced considerably and the water content is reduced to 8.7%, leading to a considerable improvement of the HHV to 28.7 MJ kg⁻¹.

CONCLUSIONS

A new method for upgrading BO is reported consisting of treating pyrolysis oil with a high boiling alcohol like n-butanol in the presence of a (solid) acid catalyst at 323–353 K under reduced pressure (<10 kPa). In this way, water can be continuously removed from the reaction medium, and the desired reactions (esterification and acetalisation) are driven to completion. Using this approach, the water content of the pyrolysis oil is reduced significantly and values less than 5 wt% were obtained using sulphuric acid.

Very promising results were also obtained with a solid acid catalyst, Nafion[®] SAC13. With this catalyst, a subsequent neutralization step after treatment is avoided. Further systematic experimental studies combined with extensive modeling studies will be required to optimize the concept and to determine the optimum process conditions. These studies as well as engine tests are currently in progress.

Table 4. Product properties of crude bio-oil, upgraded bio-oil, diesel and biodiesel.

Physical property	Bio-oil	Upgraded bio-oil ^a	Upgraded bio-oil ^a	Diesel	Bio-diesel
Catalyst	—	Nafion [®] SAC13	H ₂ SO ₄	—	—
Kin. viscosity 40°C, mm ² s ⁻¹	17.0	7.0	7.6	1.2–4.1	1.9–6.0
Water content, wt%	31.5	8.7	4.9	161 ppm	<0.05 vol%
Flash point, K	326	318	318	333–353	373–443
Density, kg L ⁻¹	1.17	0.95	0.96	0.85	0.88
pH	3.0	3.2	0.5	7.0	7.0
HHV (dry basis), MJ kg ⁻¹	20.6	28.7	27.7	n.a.	n.a.

^aConditions: 50vol% n-butanol, $T = 333$ K, $P = 5.0$ kPa, $t_r = 120$ min.

NOMENCLATURE

HHV	high heating value (on dry basis), MJ kg ⁻¹
ΔW_R	water produced by reactions, wt%
W_d	amount of distillate, g
W_o	amount of initial bio-oil-alcohol mixture, g
W_p	amount of product, g
x_C	C (carbon) content in the product, wt%
x_d	water fraction in distillate, wt%
x_H	H (hydrogen) content in the product, wt%
x_O	O (oxygen) content in the product, wt%
x_i	fraction of component <i>i</i> in the product, wt%
x_o	water fraction in the starting material, wt%
x_p	water fraction in product, wt%

Greek symbols

η_i	dynamic viscosity of component <i>i</i> , 10 ⁻³ Pa s
ρ_i	density of component <i>i</i> , kg L ⁻¹
ν_i	kinematic viscosity of component <i>i</i> , mm ² s ⁻¹

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