Upgrading Fast Pyrolysis Bio-Oil Quality by Esterification and Azeotropic Water Removal

3 AUTHORS:

Tom Sundqvist
VTT Technical Research Centre of Finland
3 PUBLICATIONS   **2** CITATIONS

SEE PROFILE

Anja Oasmaa
VTT Technical Research Centre of Finland
83 PUBLICATIONS   **2,911** CITATIONS

SEE PROFILE

Ari Koskinen
Aalto University
210 PUBLICATIONS   **2,610** CITATIONS

SEE PROFILE

Upgrading Fast Pyrolysis Bio-Oil Quality by Esterification and Azeotropic Water Removal

Tom Sundqvist,*,[†] Anja Oasmaa,[†] and Ari Koskinen[‡]

[†]Catalysis and Synfuels, VTT Technical Research Centre of Finland, P.O. Box 1000, 02044 Espoo, Finland
[‡]Department of Chemistry, School of Chemical Technology, Aalto University, P.O. Box 16100, 00076 Espoo, Finland

ABSTRACT: Fast pyrolysis bio-oil has unfavorable properties that restrict its use in many applications. Among the main issues are high acidity, instability, and water and oxygen content, which give rise to corrosiveness, polymerization during storage, and a low heating value. Esterification and azeotropic water removal can improve all of these properties. In this work, low acidity bio-oils were produced from fast pyrolysis bio-oil via esterification with methanol or *n*-butanol. Esterification conversion was enhanced by azeotropic water removal prior to and/or during esterification. An additional hydrocarbon entrainer (*n*-heptane or petroleum ether) was required for efficient water removal. The product oils had total acid numbers ranging from 5 to 10 mg KOH/g and pH values from 4.0 to 5.6. The best results were obtained with 1:0.9:0.1 wt ratio of bio-oil, *n*-butanol, and *n*-heptane and *p*-toluenesulfonic acid (*p*-TSA) as catalyst. Removal of homogeneous catalyst (2 wt % *p*-toluenesulfonic acid (*p*-TSA)) was attempted by precipitation, centrifugation, and water washing, but only 41−82 wt % of the catalyst could be recovered from the product oil based on sulfur content. Solid acid catalysts were more efficient with methanol than *n*-butanol in dry conditions. An organic base (triethylamine) was tested for neutralizing the methanol esterified bio-oil's residual acidity. Nitrogen content increased by 0.1−0.4 wt % when pH values of 6−8 were obtained.

■ INTRODUCTION

Fast pyrolysis is a low-cost thermal liquefaction method for converting wood, forest residues, and other renewable and nonedible biomass to a free-flowing brown liquid, called bio-oil or pyrolysis oil.[1] Bio-oil can be burned to produce heat and electricity or upgraded to higher value products, such as transportation fuels or chemicals.[2] It can partly replace diminishing fossil resources in the future. However, fast pyrolysis bio-oil has challenging chemical and physical properties that currently prevent its economical use in most stationary and transportation fuel applications.[3] The main limitations are low heating value, corrosiveness, instability, and high water and solids content, in no particular order. Various upgrading methods have been introduced to improve those properties, the best-known ones being catalytic pyrolysis and hydrotreatment.[4−6]

Esterification of bio-oil refers to an upgrading method, the objective of which is to neutralize acidity. It typically comprises alcohol addition (30−100 wt %), mild heating (60−120 °C) under strong acid catalyst, and water (20−40 wt %) removal by distillation. To achieve complete conversion, water removal is essential because two types of equilibrium reactions occur between bio-oil and added alcohols: (1) esterification of carboxylic acids to esters and (2) acetalization of aldehydes, ketones, and sugars to acetals (Scheme 1).[7,8] Water is produced as a side product, and it participates in the reverse reaction, hydrolysis of esters and acetals back to the starting materials. Besides lowered acidity, the main benefits of the method are increased heating value due to alcohol addition and water removal, improved stability due to alcohol addition,[9,10] and more stable chemical composition that is driven closer to equilibrium by the catalyst and heat.

Scheme 1. Main Reactions between Fast Pyrolysis Bio-Oil and Alcohols: Esterification of Acids and Acetalization of Aldehydes, Ketones, and Sugars[a]
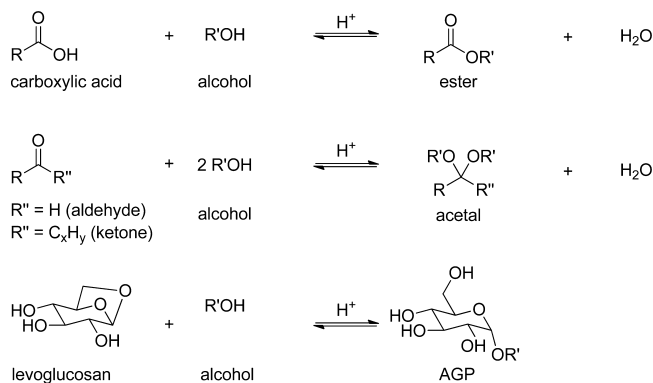
[a]AGP = alkyl D-glycopyranoside.

There have been several reported attempts to esterify fast pyrolysis bio-oil with methanol, ethanol, or *n*-butanol during the last 8 years or so.[11−19] Many of them have reported improvements in physical properties, such as increased heating value, lower viscosity, or a slower increase of viscosity during aging. Those are obvious improvements of the alcohol addition and, therefore, should not be regarded as a consequence of a successful esterification. The main objective for the addition of a large amount of alcohol (30−100 wt %), strong acid catalyst, and heat should be the complete neutralization of acidity.

Table 1. Summary of Literature Results: How Esterification Affects the Acidity of Bio-Oil

method	author	pH		TAN (mg/g)		number of product phases
		initial	final	initial	final	
esterification without distillation	Zhang et al.[11]	3.6	1.1			1
	Wang et al.[16]	3.7	2.0	26	6	1
	Moens et al.[14]			94	22	1
	Wang et al.[19]	3.5	0.5			1
	Zhang et al.[17]	2.6	3.5			1
	Xiong et al.[15]	2.9	5.1			2
reactive distillation (60−80 °C)	Xu et al.[13]	2.8	1.1−7.1			3
	Moens et al.[14]			94	21	2
azeotropic distillation (70−120 °C)	Mahfud et al.[12]	3.0	3.2			2
	Moens et al.[14]			94	5−20	2

However, esterification has not had the desired effect on the acidity of bio-oil. Table 1 summarizes the literature results on how the acidity of bio-oil has changed after esterification. The results are divided in three categories based on the type of applied distillation: no distillation, reactive distillation (60−80 °C), and azeotropic water removal (70−120 °C). In general, the conversion has been at most 80% based on the change in the total acid number (TAN). The pH value has not significantly increased, and in some instances, decreases in the pH value have also been observed due to leaching of the catalysts.[20,21] The original bio-oils had pH values from 2.6 to 3.7, and none of the single-phase product oils reached a value above 3.5. In a couple of cases, the bio-oil separated into two or more phases. For example, removal of solvents by distillation yielded a light distillate, a water-insoluble oil phase, and an aqueous phase.[13] At least one of the phases was almost acid-free, but carboxylic acids were found in another phase and were not completely converted to esters. Li et al. reported bio-oil's individual acids (e.g., acetic acid) reaching up to 90% conversion during esterification, but the TAN or pH value were not reported.[18]

Radlein et al.[22] were the first group to report esterification of pyrolysis products (slow pyrolysis tars). They used sulfuric acid as the catalyst at room temperature and removed water with 3 Å molecular sieves. The initial mixtures had water content between 1.74 and 11.9 wt %, and the final content was 0.05−0.20%. The esterification supposedly went to completion, but the acidity was not characterized by TAN, pH value, or other quantitative methods.

Two studies reported using azeotropic water removal to improve conversion of acids to esters. In brief, azeotropic distillation means adding alcohol and/or another entrainer that forms a low boiling (70−80 °C) azeotropic mixture with water. The entrainer solvent is ideally water-insoluble and forms a separate layer in the distillate which flows back to the reactor. Mahfud et al.[12] at the University of Groningen esterified fast pyrolysis bio-oil while utilizing simultaneous azeotropic water removal with water-insoluble alcohols, such as n-butanol and 2-ethylhexyl alcohol (Figure 1A). After distillation, the water content had decreased to 4.9−8.7 wt % (value of mixture) from the original content of 31.5 wt %. It was a significant decrease but not enough to enhance complete conversion of acids to esters. The pH value of the bio-oil−n-butanol mixture increased only by 0.2 units, which indicates that the mixture was still substantially acidic. Moens et al. at the National Renewable Energy Laboratory (NREL) used cyclohexane as the entrainer solvent while esterifying fast pyrolysis bio-oil with methanol or ethanol.[14]
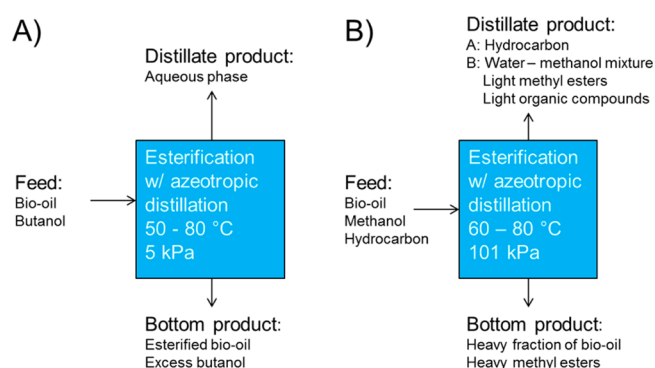

Figure 1. Esterification with azeotropic water removal at (A) University of Groningen[12] and (B) NREL.[14]

Figure 1B shows a flowchart of how the bio-oil fractionated in the process. Due to the low boiling point and water-solubility of methanol, it accumulated into the aqueous distillate instead of the bottom product. In the end, all solvents were distilled off under vacuum. The distillation had a dramatic effect on the acidity and water content: the TAN decreased as much as 95% and water was completely drained in the process. The aqueous distillate was also not significantly acidic indicating that almost all carboxylic acids did convert to esters. The disadvantage of the process, however, could be considered to be the water−methanol distillate that needs an additional separation step to recover the excess methanol.

In this work, esterification and azeotropic water removal of fast pyrolysis bio-oil was further studied. First, the effect of various entrainer solvents to azeotropic water removal of a fast pyrolysis bio-oil−n-butanol mixture was investigated. In the second part, fast pyrolysis bio-oil was esterified with n-butanol using simultaneous azeotropic water removal. The amount of n-butanol and efficiency of low-cost homogeneous and solid acid catalysts were compared. Removal of the p-toluenesulfonic acid (p-TSA) catalyst was attempted with precipitation and water washing. In the last part, dry bio-oil was esterified with methanol and the residual acidity was neutralized with amine base.

■ EXPERIMENTAL SECTION

Bio-Oil Production. The fast pyrolysis bio-oil was produced from forest thinnings in VTT's 20 kg h^{-1} process development unit.[23] The top phase of the bio-oil (about 10 wt %) that contains most of the wood extractives and solids was separated before upgrading experiments.[24] Bio-oil was stored in the freezer right after production.

Apparatus. Esterification and azeotropic distillation was carried out in a 500 or 2000 mL 3-neck flask equipped with a Dean-Stark

apparatus[25] that consisted of a distillation thermometer, a reflux condenser, and a 20 mL distillation column with a 3-way cock for online removal of the aqueous distillate. The reaction temperature was monitored with a glass ground joint thermometer. The third neck was reserved for addition of reagents or taking samples. The flask was heated in a silicon oil bath with a hot plate magnetic stirrer, and the temperature of the bath was controlled with a Pt-1000 sensor which was connected to the hot plate.

Water Removal and Reaction Conditions. Azeotropic water removal was used in three instances: (1) in comparison of hydrocarbon entrainers, (2) during esterification with n-butanol, and (3) prior to esterification with methanol. In the first two instances, mixtures contained typically 120 g of bio-oil, 60–132 g of n- or isobutanol, and 12 g of n-heptane or petroleum ether (90–100 °C fraction). In the last instance, mixtures contained 240–250 g of bio-oil and 12–25 g of petroleum ether. The temperature of the oil bath was kept constant at 130 °C (without n-butanol) or 140 °C (with n-butanol).

The reaction time of a typical esterification with n-butanol was between 2 and 3 h. The water was distilled as an azeotrope until water formation to distillate stopped. The reaction temperature was 100 °C in the beginning and increased to about 120 °C after all the water had been depleted. In some cases, the completion of the reaction was also confirmed by periodically measuring the TAN and water content of 2 g samples withdrawn from the reaction mixture.

The dried bio-oils (water content 1.5–6.0 wt %) were esterified with methanol under reflux condenser. Nothing was removed or added during the reaction. Typical mixtures contained 185 g of dry bio-oil, 80–125 g of methanol, and 10 g of Amberlyst 15 catalyst. The reaction time was 16 h at 70 °C. In some cases, residual acidity was neutralized with triethylamine (Alfa Aesar 99 wt %).

Catalysts. Both homogeneous and solid acid catalysts were used in the esterification with n-butanol and methanol. Homogeneous catalysts used were p-TSA (Alfa Aesar 98.5 wt %) and sulfuric acid (Merck 95–97 wt %). They were neutralized with an equimolar amount of sodium hydroxide or sodium bicarbonate after the reaction in order to compare changes in acidity. After neutralization, the p-TSA formed a poorly soluble salt (sodium p-toluenesulfonate) that was partly separated by centrifugation. Solid acid catalysts, Amberlyst-15 and Amberlyst-36 (wet hydrogen form, Dow), and Smopex-101 (Johnsson Matthey) were used as such without pretreatment and separated by filtering after reaction.

Characterization. The TAN was determined according to the ASTM standard D664 potentiometric titration,[26,27] except the titration base was replaced with tetrabutylammonium hydroxide (0.1 M in methanol/isopropanol, Merck) and titration solvent was replaced with isopropanol. Water content was measured with Karl Fischer titration according to ASTM E203-96, pH value with Mettler Toledo Inlab 413 pH-electrode, carbonyl content with hydroxylamine titration,[28] and sulfur content with a Leco SC-432 apparatus.

Average molecular weights were measured with a Waters 515 HPLC pump equipped with a UV detector at 280 nm and PSS MCX columns (porocity 1000 Å and 100 000 Å sequentially). Eluent was 0.1 M NaOH with a flow rate of 0.5 mL/min at 25 °C. Sample (4 mg) was dissolved in 0.1 M NaOH (4 mL) overnight and filtered with 0.45 μm PTFE membrane syringe filters. Average molecular weights were calculated relative to sodium polystyrenesulfonate standards.

Quantitative changes in individual compounds (e.g., acetic acid) were analyzed by gas chromatography equipped with a flame ionization detector (GC-FID, Agilent 7890A) using an HP-Innowax cross-linked polyethylene glycol capillary column (length 60 m, diameter 0.25 mm, film thickness 0.25 μm) and n-butanol as internal standard. Bio-oil and product oils were extracted with water (1:10) for 30 min in an ultrasonic bath prior to GC-FID analysis. Qualitative changes in chemical composition were analyzed using gas chromatography−mass spectrometry (Shimadzu GCMS-QP2010). The interpretation of chromatograms was based on NIST11 library and literature data and the references contained therein.[29] Samples were dissolved in a mixture of methanol and dicholoromethane (1:1) prior to the analysis. The column was HP Ultra 1 fused silica capillary

column (length 50 m, diameter 0.32 mm, film thickness 0.52 μm). The oven temperature was initially 30 °C and increased 3 °C/min to 290 °C.

■ RESULTS AND DISCUSSION

Esterification of Bio-Oil with n-Butanol and Simultaneous Azeotropic Distillation. Azeotropic water removal from fast pyrolysis bio-oil was first tested in the absence of catalyst to determine adequate distillation conditions for water removal during esterification. Figure 2 compares the efficiency
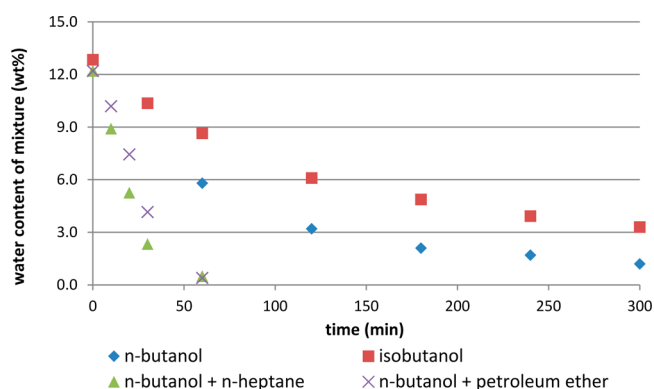
Figure 2. Azeotropic water removal from a bio-oil−n-/isobutanol mixture (1:1 wt ratio) or from a bio-oil−n-butanol−hydrocarbon mixture (1:1:0.1 wt ratio) at 90−120 °C.

of butanol and butanol−hydrocarbon mixtures as entrainer solvents in azeotropic water removal from a 120 g batch of bio-oil at a 100−120 °C temperature. After 5 h of distillation, azeotropic water removal from bio-oil with n- or isobutanol (1:1 wt ratio) decreased the water content from 12.2 wt % to 1.2 and 3.3 wt %, respectively. Butanol−hydrocarbon mixtures (1:1:0.1 wt ratio) were significantly more efficient, removing almost all water (water content <0.5 wt %) in a 1 h distillation. The reactor temperature was 90−100 °C when distillation started and gradually increased to 120 °C when the water content became low. The water content of the aqueous distillate was 87 wt %, which indicates that a small amount of n-butanol or light organic compounds of the bio-oil dissolved in the aqueous distillate. The results show that n-heptane or petroleum ether was needed for efficient water removal from bio-oil. However, the hydrocarbon solvent can be recycled because it forms a separate layer from the distillate.

The main objective of esterification was to attain a carboxylic acid-free bio-oil with close to neutral pH value. Fast pyrolysis bio-oil was esterified with n-butanol at 120 °C, and water was simultaneously removed as an azeotrope with n-heptane (Figure 3). n-Butanol was chosen because it is the smallest alcohol that is relatively water-insoluble and therefore suitable for azeotropic water removal.

Table 2 presents the results from the esterification of fast pyrolysis bio-oil with different amounts of n-butanol at 120 °C with p-TSA catalyst. A homogeneous product with maximum reduction in acidity was attained when 90 wt % of n-butanol was used. The TAN decreased by 95%, and the pH value increased by more than two units from 3.3 to 5.5. No phase separation or solid deposits were observed. More than 90 wt % of n-butanol did not have a significant impact anymore. On the other hand, when the n-butanol amount was 70 wt %, solid deposits were noticed, and with 50 wt % of n-butanol,
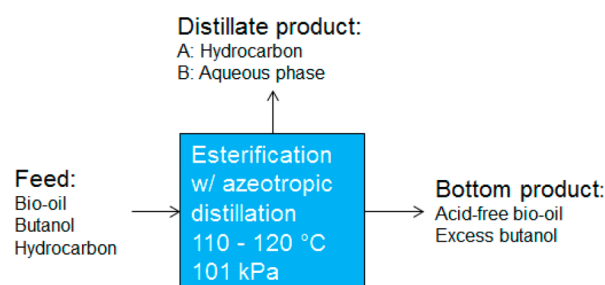
Figure 3. Production of acid- and water-free bio-oil by simultaneous esterification and azeotropic water removal.

Figure 4. Mass balance example of esterification of bio-oil with *n*-butanol.

precipitation was even more distinct. Polymerization side reactions were apparently unavoidable in the presence of a strong acid catalyst at 120 °C. The average molecular weight of heavy oligomers increased from 1260 to 2290–2480 g/mol after esterification. Both the increase in molecular weight and loss of some solvents in the distillation compromised the homogeneity of the bio-oil. To compensate for the altered composition, a large (residual) amount of *n*-butanol was apparently required to avoid phase separation.

The presence of the catalyst and water removal was fundamental to obtain the maximum reduction in acidity (Table 2). Without the addition of the catalyst (sample 5), TAN decreased only 42% and the pH value did not change. Without water removal (sample 6), TAN decreased only 73%, and the pH value increased merely by 0.7 units.

Figure 4 shows a mass balance example of esterification of 500 g of bio-oil with 90 wt % of *n*-butanol. In total, 181 g (36 wt %) of water was removed, of which 120 g (24 wt %) was the bio-oil's original water content, and 61 g (12 wt %) was formed in the chemical reactions.

Experimental results for the required amount of alcohol can be compared to an estimation based on the quantitative characterization of carboxyl and carbonyl groups. The bio-oil that was used in these experiments contained 1.8 mol/kg carboxylic acids and 3.7 mol/kg aldehydes and ketones. On the basis of Scheme 1, their neutralization should require 9.2 mol/kg of alcohol, which corresponds to 68 wt % of *n*-butanol. The required amount of *n*-butanol was slightly higher than was estimated, probably because a small amount of *n*-butanol was lost with the aqueous distillate phase during distillation because *n*-butanol is not completely water-insoluble.

The catalyst, *p*-TSA, was neutralized with an equimolar amount of base before the products were characterized. Three different types of bases were tested. A weak inorganic base (bicarbonate) did not dissolve in the product oil and was therefore inefficient; neutralization was incomplete after stirring
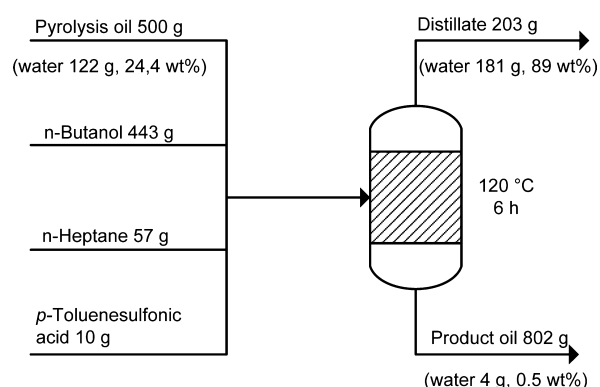
overnight. A strong inorganic base (sodium hydroxide) dissolved moderately in the product oil and neutralized the catalyst in about 1 h. A weak organic base (triethylamine) dissolved immediately and neutralized the catalyst in a few minutes.

Removal of *p*-TSA from the bio-oil after esterification was attempted by precipitation with sodium hydroxide because the salt, sodium *p*-toluenesulfonate, is poorly soluble in organic solvents. The precipitate was separated by centrifugation and filtration and washed with acetone. It was white, crystalline, and water-soluble. Table 3 presents the results of *p*-TSA (2 wt %)

Table 3. Removal of *p*-TSA Catalyst from Bio-Oil by Precipitation and Water Washing

sample	sulfur content, wt %	water content, wt %	organic loss, wt %
original bio-oil	<0.01	24	
esterified bio-oil	0.17	<1	
neutralized bio-oil	0.10–0.11	<1	1
water washed bio-oil	0.03–0.06	9	11–14

removal from two samples that were esterified with 90 wt % of *n*-butanol. The whole catalyst could not be recovered. The sulfur content of the esterified bio-oil was 0.17 wt % (due to the sulfurous catalyst), and the content decreased at most to 0.10 wt % after separation of the precipitated sulfonate salt. The product oil apparently still contained traces of polar solvents (e.g., water and methanol) that could dissolve part of the catalyst. In contrast to the original bio-oil, the product bio-oil was relatively immiscible with water. Addition of water (50 wt %) to the esterified bio-oil led to the formation of two clear

Table 2. Product Properties after Esterification of Fast Pyrolysis Bio-Oil with Different Amounts of *n*-Butanol[a]

butanol, wt %	catalyst	water removal by distillation	TAN, mg/g	pH	homogeneous oil	M_w, g/mol
0		no	104	2.6	yes	1260
50–110		no	50–69	3.1–3.3	yes	
50	*p*-TSA	yes	11	3.5	no	
70	*p*-TSA	yes	9	4.3	no	2480
90	*p*-TSA	yes	5	5.5	yes	2360
110	*p*-TSA	yes	5	5.6	yes	2290
90	no catalyst	yes	52	3.3	yes	
90	*p*-TSA	no	28	4.0	yes	

[a]The catalyst was neutralized with an equimolar amount of sodium hydroxide.

phases: a heavier, dirty yellow aqueous phase and a dark-colored organic phase. Water washing further decreased the sulfur content to 0.03−0.06 wt % depending on the number of washes (1−3 times). There were two downsides to the water washing: 9 wt % of water dissolved in the product oil and 11−14 wt % of organic compounds were lost to the aqueous phase during washes.

The chemical composition of the raw product oil was further analyzed with GC-FID. The original and upgraded bio-oils (1:0.9 wt isobutanol) were separately extracted with water (1:10) and the water-soluble fraction was analyzed with GC-FID. Table 4 shows the changes in the most abundant carboxyl

Table 4. Change in Concentration of Common Carboxylic Acids, Aldehydes, and Ketones after Esterification with Isobutanol (1:0.9 wt ratio) Based on Quantitative GC-FID Analysis

chemical compound	bio-oil, wt %	esterified bio-oil, wt %
acetic acid	6.46	0.16
propanoic acid[a]	0.22	
butanoic acid	0.08	0.00
1-hydroxyacetaldehyde[b]	6.59	0.17
1-hydroxy-2-propanone[b]	2.12	0.78
1-hydroxy-2-butanone[b]	0.34	0.15
furfural	0.31	0.01
5-(hydroxymethyl)furfural	0.55	0.07

[a]The amount of propanoic acid in product oil could not be analyzed because of overlapping with a new peak. [b]Compounds with additional hydroxyl groups give wide peaks, which increases the margin of error.

and carbonyl compounds after esterification. Carboxylic acids decreased by 98%, aldehydes by 97%, and hydroxy ketones by 62%. The changes in chemical composition were also compared with qualitative GC-MS analysis (Figure 5). Acetic acid and

other typical degradation products of hemicellulose and hemicelluloses (colored red) were abundant in the original bio-oil but absent in product oil. Clear new signals of butyl esters and acetals and residual n-butanol (colored green) were detected in product oil. The chromatogram also shows the distillation entrainer n-heptane (colored yellow), because it was not separated.

Esterification with n-butanol was attempted with two solid acid catalysts, Amberlyst 36 and Smopex 101 (5 wt %). Figure 6 compares the efficiency of the solid acid catalysts to homogeneous catalysts in terms of the product's acidity. With solid acid catalysts, the product remained significantly more acidic compared to homogeneous catalysts. TAN was approximately 5 times higher with Amberlyst 36 and Smopex 101 compared to p-TSA and H_2SO_4, and the pH value did not notably increase from the initial diluted value. The low conversion may be explained by the lack of swelling polar solvents, such as water and methanol. After the water removal, the solid acid catalysts shrank, which probably hindered access of reactants to the catalyst's acidic sites. The unchanged pH value indicates that some acid leaching from the solid acid catalysts may have occurred. The most likely reason is ion exchange between the bio-oil's alkali and alkali earth metals and the catalyst's acidic sites, which in turn releases acidic protons to bio-oil.

Sulfuric acid and p-TSA were equally efficient, but an unwanted side reaction was observed between sulfuric acid and bio-oil at 120 °C. The color of bio-oil turned pitch-black, and the odor changed to being burned and liquorice-like. Concentrated sulfuric acid is known to react vigorously with small carbohydrates producing solid carbonaceous residue and water.[30] Apparently, anhydro sugars of bio-oil (e.g., levoglucosan) dehydrated to elemental carbon, which caused the color to change. Although high conversion of wood bio-oil's carboxyl and carbonyl compounds to esters and acetals was demon-
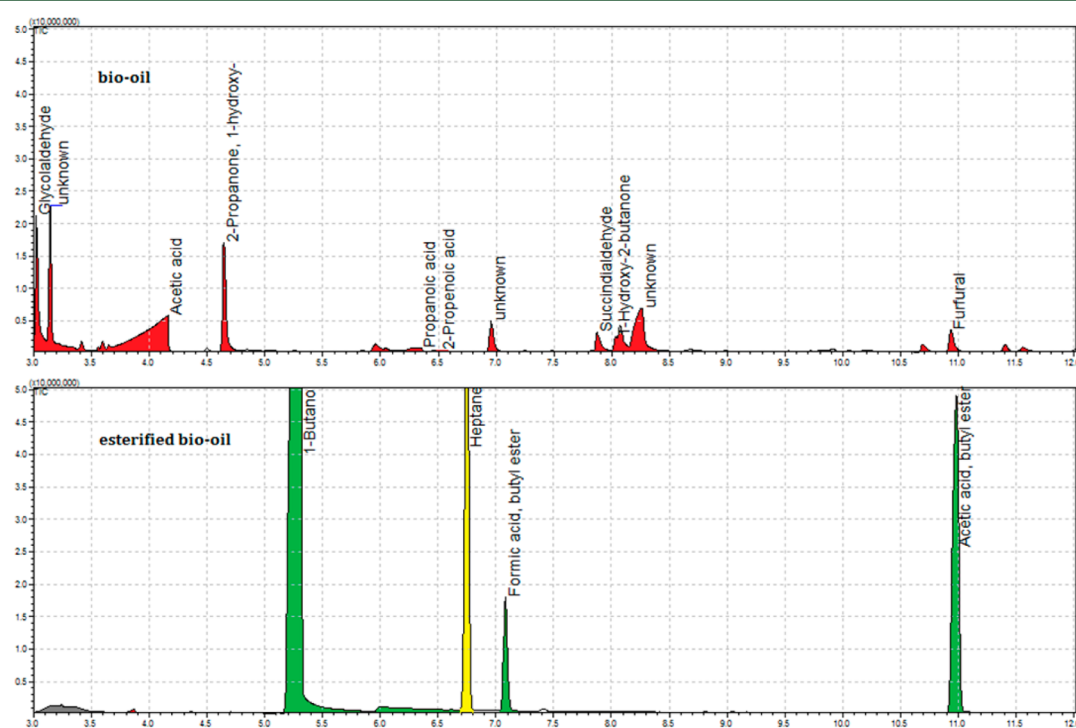

Figure 5. GC-MS total ion chromatogram (3−12 min) for wood bio-oil and esterified bio-oil (1:0.9 wt ratio n-butanol).
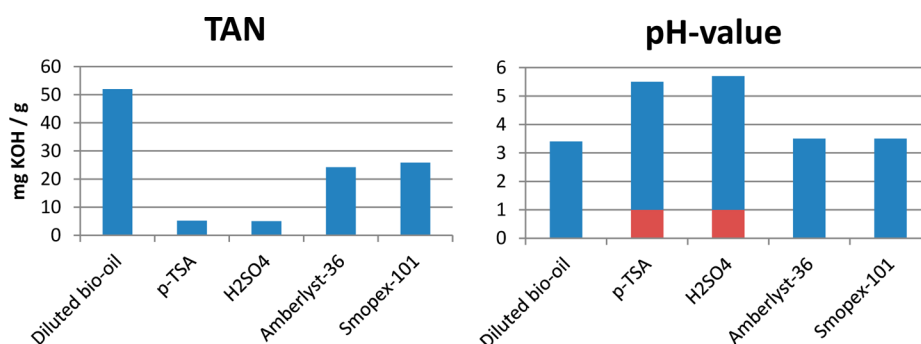
Figure 6. Efficiency of various catalysts in the esterification of dry bio-oil with 90 wt % of *n*-butanol at 120 °C. The red color indicates pH value before neutralization of catalyst.
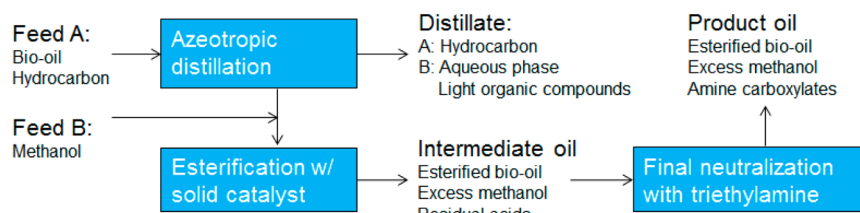

Figure 7. Production of acid-free bio-oil in three steps: (1) azeotropic water removal, (2) esterification with methanol, and (3) final neutralization with triethylamine.

Table 5. Mass Balance of Azeotropic Water Removal of Bio-Oil with Petroleum Ether at 90 °C Temperature[a]

	distillation conditions			bottom product			distillate			
entry	bio-oil, g	petrol, g	time, h	amount, g	water, wt %	TAN, mg/g	amount, g	water, wt %	TAN, mg/g	balance, %
1	240	12	2	183	6.0	104	65	80	90	99
2	250	25	3	186	1.5	64	88	74	129	99

[a]Initial bio-oil had water content of 24.4 wt % and TAN of 104 mg KOH/g.

strated with *n*-butanol and *p*-TSA catalyst, the low efficiency with solid acid catalysts and current market price of *n*-butanol prompted us to seek an alternative approach.

Esterification of Bio-Oil with Methanol and Solid Acid Catalyst. The acidity of the fast pyrolysis bio-oil was neutralized in three steps (Figure 7): water removal, esterification, and final neutralization. The bio-oil was first dried to have a water content of 1.5−6.0 wt %. Water removal was done by azeotropic distillation with petroleum ether. Methanol was added to the dry bio-oil, and the mixture was esterified with an Amberlyst 15 solid acid catalyst at 70 °C to obtain a bio-oil with substantially reduced acidity. In this case, methanol was introduced after the water removal in order to avoid the need to separate the methanol from the aqueous distillate. Finally, the residual acidity was neutralized with an amine base to obtain a product oil with a neutral pH value.

Table 5 shows the mass balance and changes in water content and acidity during azeotropic distillation. Two experiments were carried out with slightly different conditions leading to bio-oils with water contents of 1.5 and 6.0 wt %. Petroleum ether (5−10 wt %) was added to the bio-oil and used as an entrainer solvent, because it greatly accelerates the distillation of water and is poorly soluble in both bio-oil and aqueous distillate and, therefore, is easily recyclable. The second run had twice the amount of petroleum ether and a 1 h longer distillation time, which caused more distillate to accumulate. Loss of organics to the aqueous distillate was 7 and 12 wt %, respectively. A noteworthy difference is that substantially more carboxylic acids were distilled off in the

second run. TANs of the bottom products were 104 and 64 mg/g, and TANs of the distillates were 90 and 129 mg/g, respectively.

The dried bio-oils were esterified with methanol at 70 °C with a solid acid catalyst (Amberlyst 15). Table 6 presents the results and compares them to the esterification of wet bio-oil at the same conditions. Without water removal prior to esterification, the TAN decreased 73% and the pH value remained unchanged. With dry bio-oil, a higher conversion and lower TAN was obtained compared to wet bio-oil, even though less methanol was used. The TAN decreased 74−81% and was

Table 6. Change in Acidity after Esterification with Methanol at 70 °C

sample name	methanol,[a] wt %	water content, wt %	TAN, mg KOH/g	pH value
bio-oil		24	104	2.6
bio-oil, diluted	100	12	52	3.3
bio-oil, esterified	100	17	14	3.2
dry bio-oil 1, diluted	30	2	78	4.1
dry bio-oil 1, esterified	30	9	15	4.2
dry bio-oil 2, diluted	50	1	39	4.1
dry bio-oil 2, esterified	50	5	10	4.0

[a]Methanol amount is calculated on the basis of the amount of initial wet bio-oil.

10 mg/g at the lowest. If the dilution effect of methanol is ignored, the difference between dry and wet esterified bio-oils is more significant; the TAN for wet bio-oil would be about 2-fold compared to dry bio-oil after esterification, 28 and 15, respectively. The pH value of dry esterified bio-oil increased by approximately one unit to approximately 4, but the improvement did not seem to be caused by esterification, but rather by water removal. The water content of both wet and dry bio-oils increased 4−5 wt % during esterification with methanol.

Residual acidity of the methanol esterified dry bio-oil was neutralized with an organic base (triethylamine) to obtain higher pH values. Figure 8 shows the effect of triethylamine on
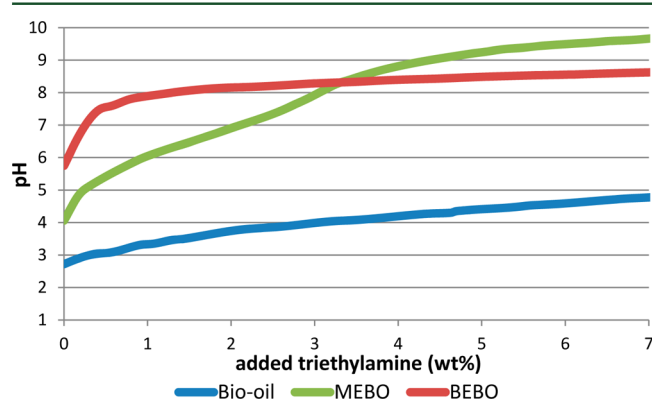

Figure 8. Neutralization of (residual) acidity of bio-oil, methanol esterified bio-oil (MEBO), and n-butanol esterified bio-oils (BEBO) with amine base.

the pH value of the methanol esterified dry bio-oil and compares its behavior to the original and n-butanol esterified bio-oils. The pH value increased from 4 to 6 after 1 wt % addition and to 8 after 3 wt % addition, after which all residual carboxylic acids were completely neutralized. Triethylamine contains 14 wt % of nitrogen, so reaching a pH value of 6 or 8 would increase the nitrogen content of product by 0.14 or 0.42 wt %, respectively. In comparison, the addition of the base to the original bio-oil had a very limited impact on the pH value, whereas the n-butanol esterified bio-oil required less than 1 wt % addition of triethylamine to reach a pH value of 8. Thermal stability of methanol esterified bio-oil and amine neutralized products (1 and 3 wt % triethylamine) were tested by holding them for 72 h at 60 °C in closed containers. The stability of the methyl esters and amine salts were evaluated by comparing changes in pH value (Figure 9). The methanol esterified bio-oil retained its pH value at around four, indicating that the esters were relatively stable to mild heating. On the other hand, pH of the amine neutralized bio-oils decreased from 5.9 to 5.2 and from 8.8 to 6.6, which shows that the amine salts were not thermally stable and they partly decomposed back to carboxylic acids.

Clearly, any attempt to completely neutralize the normal fast pyrolysis bio-oil's acidity with the addition of an organic base would lead to very high nitrogen content. However, when water removal and methanol esterification were applied prior to the base addition, a much lower amount of base was needed. If moderate nitrogen content is acceptable in some fuel application that benefits from lower acidity, neutralization of residual acidity after esterification might be a viable option.
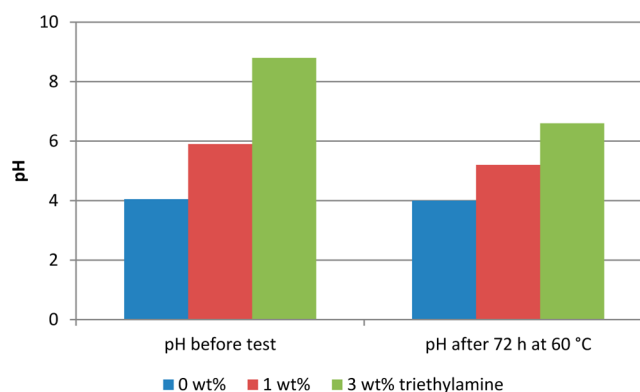

Figure 9. Thermal stability test (72h at 60 °C) of the methanol esterified bio-oil as such and two triethylamine neutralized products.

CONCLUSIONS

Production of carboxylic acid-free bio-oils from fast pyrolysis bio-oil was demonstrated via two alternative routes that were based on azeotropic water removal, esterification with alcohols, and optionally final neutralization. An additional hydrocarbon solvent (n-heptane or petroleum ether) was needed for efficient azeotropic water removal from bio-oil.

High conversion of carboxylic acids to esters required water removal during esterification, a water-insoluble alcohol (n-butanol), and an efficient homogeneous acid catalyst, such as p-TSA. With a 1:0.9 wt ratio of bio-oil and n-butanol, the product oils had TANs as low as 5 mg/g and close to neutral pH values. Lower amounts of n-butanol resulted in more residual acidity and nonhomogeneous products. Removal of p-TSA was attempted by precipitation, but only less than half of the catalyst could be recovered from the product oil. Therefore, esterification with n-butanol increased the bio-oil sulfur content by approximately 0.1 wt %. Commercial solid acid catalysts, Amberlyst 36 and Smopex 101, were ineffective under dry bio-oil conditions, resulting in 5 times higher TANs compared to homogeneous catalysts.

A moderate conversion (∼80%) of carboxylic acids to esters could be achieved with water removal prior to esterification and using a water-soluble alcohol (methanol) in esterification. With a 2:1 wt % ratio of bio-oil and methanol and Amberlyst 15 catalyst, the product oil had a TAN as low as 10 mg/g, and the pH value increased by one unit to about 4. Although the conversion was lower with methanol than n-butanol, it had two advantages: a lower amount of alcohol was needed and solid acid catalysts worked efficiently with methanol. To obtain neutral pH values (6−8) with methanol, neutralization of residual acidity with amine base was needed, which caused a 0.1−0.4 wt % increase in nitrogen content.

The esterification of fast pyrolysis bio-oil is an alternative step toward utilization in more demanding applications. Generally, internal combustion engines do not withstand the corrosiveness of carboxylic acids that are found in all thermal liquefaction products of lignocellulosic biomass. Conventionally, the carboxylic acids of bio-oil can be neutralized by hydrodeoxygenation, but we have showed the carboxylic acids can also be substantially or completely neutralized by esterification and azeotropic distillation without reduction of all oxygenated compounds to hydrocarbon or alcohol level. The esterified bio-oil could possibly be used in the more robust combustion engines, such as slow and medium-speed diesel

engines, that require lower acidity and water content than that found in the conventional fast pyrolysis bio-oil.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: tom.sundqvist@vtt.fi.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Bridgwater, A. V. Review of Fast Pyrolysis of Biomass and Product Upgrading. *Biomass Bioenergy* **2012**, *38*, 68−94.

(2) Alonso, D. M.; Bond, J. Q.; Dumesic, J. A. Catalytic Conversion of Biomass to Biofuels. *Green Chem.* **2010**, *12*, 1493−1513.

(3) Mohan, D.; Pittman, C. U., Jr.; Steele, P. H. Pyrolysis of Wood/Biomass for Bio-Oil: A Critical Review. *Energy Fuels* **2006**, *20*, 848−889.

(4) Butler, E.; Devlin, G.; Meier, D.; McDonnell, K. A Review of Recent Laboratory Research and Commercial Developments in Fast Pyrolysis and Upgrading. *Renewable Sustainable Energy Rev.* **2011**, *15*, 4171−4186.

(5) Xiu, S.; Shahbazi, A. Bio-Oil Production and Upgrading Research: A Review. *Renewable Sustainable Energy Rev.* **2012**, *16*, 4406−4414.

(6) Zhang, L.; Liu, R.; Mei, Y. Upgrading of Bio-Oil from Biomass Fast Pyrolysis in China: A Review. *Renewable Sustainable Energy Rev.* **2013**, *24*, 66−72.

(7) Radlein, D.; Piskorz, J. K. Method of Upgrading Biomass Pyrolysis Liquids for Use as Fuels and as a Source of Chemicals by Reaction with Alcohols. Patent EP0718392A1, 1996.

(8) Gunawan, R.; Li, X.; Larcher, A.; Hu, X.; Mourant, D.; Chaiwat, W.; Wu, H.; Li, C.-Z. Hydrolysis and Glycosidation of Sugars During the Esterification of Fast Pyrolysis Bio-Oil. *Fuel* **2012**, *95*, 146−151.

(9) Diebold, J. P.; Czernik, S. Additives To Lower and Stabilize the Viscosity of Pyrolysis Oils during Storage. *Energy Fuels* **1997**, *11*, 1081−1091.

(10) Oasmaa, A.; Kuoppala, E.; Selin, J.-F.; Gust, S.; Solantausta, Y. Fast Pyrolysis of Forestry Residue and Pine. 4. Improvement of the Product Quality by Solvent Addition. *Energy Fuels* **2004**, *18*, 1578−1583.

(11) Zhang, Q.; Chang, J.; Wang, T.; Xu, Y. Upgrading Bio-Oil over Different Solid Catalysts. *Energy Fuels* **2006**, *20*, 2717−2720.

(12) Mahfud, F. H.; Melián-Cabrera, I.; Manurung, R.; Heeres, H. J. Biomass to Fuels: Upgrading of Flash Pyrolysis Oil by Reactive Distillation Using a High Boiling Alcohol and Acid Catalysts. *Process Saf. Environ. Prot.* **2007**, *85* (B5), 466−472.

(13) Xu, J.; Jiang, J.; Sun, Y.; Lu, Y. Bio-Oil Upgrading by Means of Ethyl Ester Production in Reactive Distillation to Remove Water and To Improve Storage and Fuel Characteristics. *Biomass Bioenergy* **2008**, *32*, 1056−1061.

(14) Moens, L.; Black, S. K.; Myers, M. D.; Czernik, S. Study of the Neutralization and Stabilization of a Mixed Hardwood Bio-Oil. *Energy Fuels* **2009**, *23*, 2695−1699.

(15) Xiong, W.-M.; Zhu, M.-Z.; Deng, L.; Fu, Y.; Guo, Q.-X. Esterification of Organic Acid in Bio-Oil Using Acidic Ionic Liquid Catalysts. *Energy Fuels* **2009**, *23*, 2278−2283.

(16) Wang, J.-J.; Chang, J.; Fan, J. Upgrading of Bio-Oil by Catalytic Esterification and Determination of Acid Number for Evaluating Esterification Degree. *Energy Fuels* **2010**, *24*, 3251−3255.

(17) Zhang, Z.; Wang, Q.; Tripathi, P.; Pittman, C. U., Jr. Catalytic Upgrading of Bio-Oil Using 1-Octene and 1-Butanol over Sulfonic Acid Resin Catalysts. *Green Chem.* **2011**, *13*, 940−949.

(18) Li, X.; Gunawan, R.; Lievens, C.; Wang, Y.; Mourant, D.; Wang, S.; Wu, H.; Garcia-Perez, M.; Li, C.-Z. Simultaneous Catalytic Esterification of Carboxylic Acids and Acetalisation of Aldehydes in a Fast Pyrolysis Bio-Oil from Mallee Biomass. *Fuel* **2011**, *90*, 2530−2537.

(19) Wang, Q.; Hu, Y.; Chen, Q.; Lu, Q.; Jia, S. Bio-Oil Upgrading by Reactive Distillation Using p-Toluene Sulfonic Acid Catalyst Loaded on Biomass Activated Carbon. *Biomass Bioenergy* **2013**, *56*, 405−411.

(20) Hu, X.; Lievens, C.; Mourant, D.; Wang, Y.; Wu, L.; Gunawan, R.; Sang, Y.; Li, C.-Z. Investigation of Deactivation Mechanisms of a Solid Acid Catalyst During Esterification of the Bio-Oils from Mallee Biomass. *Appl. Energy* **2013**, *111*, 94−103.

(21) Dow. Ion Exchange Resins - Industrial Processess. http://www.amberlyst.com/faq_catalysis.htm#deactivation (accessed June 14, 2014).

(22) Radlein, D.; Piskorz, J. K.; Majerski, P. A. Method of Upgrading Biomass Pyrolysis Liquids for Use as Fuels and as a Source of Chemicals by Reaction with Alcohols. Patent EP0718392A1, 1996.

(23) Oasmaa, A.; Solantausta, Y.; Arpiainen, V.; Kuoppala, E.; Sipilä, K. Fast Pyrolysis Bio-Oils from Wood and Agricultural Residues. *Energy Fuels* **2010**, *24*, 1380−1388.

(24) Oasmaa, A.; Kuoppala, E.; Gust, S.; Solantausta, Y. Fast Pyrolysis of Forestry Residue. 1. Effect of Extractives on Phase Separation of Pyrolysis Liquids. *Energy Fuels* **2003**, *17*, 1−12.

(25) Dean, E. W.; Stark, D. D. A Convenient Method for the Determination of Water in Petroleum and Other Organic Emulsions. *Ind. Eng. Chem.* **1920**, *12*, 486.

(26) Oasmaa, A.; Elliott, D. C.; Korhonen, J. Acidity of Biomass Fast Pyrolysis Bio-Oils. *Energy Fuels* **2010**, *24*, 6548−6554.

(27) Mayer, A. M. *Annual Book of ASTM standards, Section Five: Petroleum Products, Lubricants and Fossil Fuels*; ASTM: West Conshohocken, PA, 2014; Vol. *05.01*.

(28) Oasmaa, A.; Korhonen, J.; Kuoppala, E. An Approach for Stability Measurement of Wood-Based Fast Pyrolysis Bio-Oils. *Energy Fuels* **2011**, *25*, 3307−3313.

(29) Sipilä, K.; Kuoppala, E.; Fagernäs, L.; Oasmaa, A. Characterization of Biomass-Based Flash Pyrolysis Oils. *Biomass Bioenergy* **1998**, *14*, 103−113.

(30) Helmenstine, A. M. Sulfuric Acid and Sugar Reaction. http://chemistry.about.com/b/2014/02/21/sulfuric-acid-and-sugar-reaction.htm (accessed June 17, 2014).