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# Catalytic depolymerisation of suberin rich with precious metal catalysts

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## Abstract

Hydrogenolysis of cork has been examined using a range of precious metal catalysts studying the effect of the support, added base and solvent used. The addition of a catalyst and a base resulted in a bio-oil increase of 9.3 – 158 % compared to when no catalyst was used along with an increase in lipid yield of 113-258 %. The solvent change to 2-methyl tetrahydrofuran from the original dioxane solvent system<sup>1</sup> allowed for a change to a “greener” solvent as well as an increased yield from 11.5 wt% bio-oil yield to 42.6 wt% bio-oil yield, in the absence of base.

## Introduction

Fossil derived oil is a finite resource and, therefore, a replacement for it must be found as it provides not only fuels but most platform chemicals as well. Suranovic<sup>2</sup> compared the issue of climate change and fossil fuels to that of a smoker and their body, with the risk that the necessary changes will not occur until irreparable damage has already happened. This global challenge has led to governments forming panels such as the IPCC<sup>3</sup> and making policies<sup>4</sup> to reduce emissions with increased renewable resource use.<sup>5</sup>

Biomass feedstocks are a potentially inexhaustible and inexpensive natural resource, readily available everywhere in the world. The sheer volume of biomass sources has the potential to be a substitute for at least some currently used non-renewable chemical raw materials.<sup>6</sup> A significant amount of biomass originates outside the food chain, for example wood products. Up to 60 % felled wood is left on the forest floor to rot, typically in the form of branches, twigs and other smaller off-cuts, although it is desirable for some material to remain for soil fertility and erosion control a significant amount could be utilised.<sup>7</sup> It is also known that 20-30 % of all processed wood by-products, for example sawdust, is unsuitable for high value commercial applications.<sup>8</sup> Typically this biomass waste is used for low grade uses such as cement binders or is burned to provide heat.<sup>6</sup> Consequently, much focus has now been applied to the valorisation/upcycling of such waste to value added products such as bio-fuels or chemicals useful for industries as varied as plastic manufacture, food flavourings, fragrances and pharmaceuticals.<sup>6, 7</sup>

This paper reports on the catalytic hydrogenolysis of wood biomass, in particular the conversion of suberin within cork. The dry weight composition of cork is suberin (ca. 40%), lignin (ca. 20%), polysaccharides (ca. 20%) and solvent extractable fraction (ca. 15%).<sup>8,9</sup> This unique chemical composition combined with the cellular structure of cork make it an ideal material for wine stoppers, insulation, composites and ornamental uses.<sup>8</sup>

The issue with cork is that due to the high suberin (See ESI) content it does not biodegrade and with many of these applications being single and/or low grade use.<sup>10</sup> Currently cork has an annual worldwide production 201 ktonnes<sup>11</sup>, with 40% of this is used as wine stoppers. 66 % of used wine stoppers go to landfill.<sup>12</sup> Despite increasing schemes to promote recycling of cork wine stoppers<sup>10</sup> only 3 % are ever recycled<sup>12</sup> which is granulated and used as low grade application alongside the 25 % of produced cork which is designated as by-products/waste of the initial processing.<sup>10</sup>

It has been shown<sup>1</sup> that the use of a heterogeneous Rh/C catalyst in the depolymerisation of suberin increased the yield of bio-oil over threefold compared to the control (no catalyst), with increased yields of both aromatic and lipid components. This work has recently been compared with other depolymerisation methods in the literature.<sup>11</sup> Furthermore, recent reports demonstrate ongoing research into the addition of sodium hydroxide as a promoter for lignin/biomass depolymerisation<sup>12-14</sup>, which has been reported since the 1850s.<sup>15</sup> Sodium hydroxide as a promoter tends to create undesired by-products accompanied with a decrease in lipid yield.<sup>11,16</sup> Therefore, the investigation of other bases for biomass conversion is a logical step towards raising the yield of desired products.<sup>16</sup> In terms of the green chemistry paradigm it is advantageous to carry out reactions with heterogeneous catalysts due to ease of separation, facilitating the retrieval of products by filtration and recovery of catalyst. For example, the use of solid acids and bases, such as hydrotalcite (Htc)<sup>17-20</sup>, dolomite (Dol)<sup>21-23</sup> and HZSM-5<sup>24</sup> have been shown to be effective heterogeneous promoters for depolymerisation. This has been both as additional solids as well as a solid support for precious metal catalysts.<sup>24,25</sup>

In the current work, we have investigated the addition of base to the Rh/C catalysed process for depolymerisation of suberin, and the effect this has on yields. A number of greener solvent alternatives were also investigated; 2-Methyl-tetrahydrofuran (MeTHF), ethylene glycol (EtGlyc), methanol (MeOH) and ethanol (EtOH) have all been identified as potential green alternatives.<sup>25-31</sup>

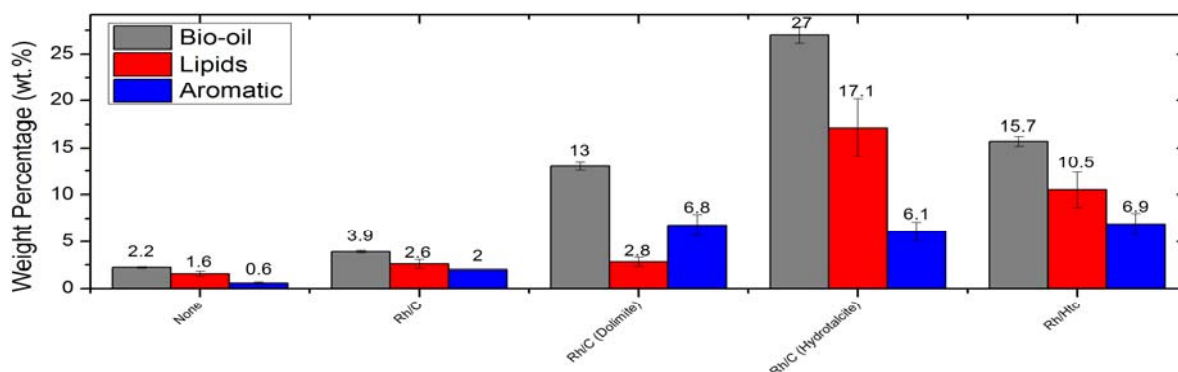
The experimental and analysis methods are reported in ESI.

## Results and Discussion

### Effect of bases on the hydrogenolysis of cork

Results will be directly compared with previous work<sup>1</sup>, while further comparison can be made from a review in literature.<sup>11</sup> Figure 1 shows the effect of the addition of a base in the hydrogenolysis of cork. Therein, a significant increase in the yield of both the aromatic and

aliphatic product streams was observed. Firstly, the yield of organic soluble bio-oils are compared with previous (base-free) studies<sup>1</sup>, which reported crude yields of 0.6 wt.% to 2 wt.%. The yields in this study were greatly increased, reaching between 13 wt.% and 27 wt.% of bio-oil. This was matched by an increase in the conversion of the solid material, from 33-48% by weight without base compared to 42-57% in the presence of a base.



**Figure 1:** Effect of Base Change

Additionally, further comparison can be drawn between the aromatic yields reported in the current work and the previously reported work<sup>1</sup>. The addition of hydrotalcite to the Rh/C reaction led to an aromatic yield of 6.1 wt.%, while the addition of dolomite yielded 6.8 wt.% aromatics. These are both a marked increase compared to the 2.0 wt.% obtained for Rh/C in the absence of a base. The addition of dolomite to the Rh/C did not have a significant impact on the lipid yield (increase to 2.8 wt.% from 2.6 wt.%). The reported results, therefore, have identified the potential for base-catalysed depolymerisation of suberin, in agreement with the successes previously reported for lignocellulosic biomass.<sup>26,33</sup> The effect of the addition of a solid base as a catalyst support may be due to the proximity of activated potential sites on the alkaline and the transition metal. Conversely, any blocking of sites by residual lipids might have an increased inhibitory effect on the system.

Figure 1 also shows the use of Rh supported on hydrotalcite (Rh/Htc) in the hydrogenolysis of cork. When compared with the Rh/C catalyst without base, there is a reduction in starting material as the solid material extracted was from 33.0 wt% to 55.3 wt% with the the Rh/Htc. In fact this increase in conversion was also higher than that observed for the Rh/C catalyst even in the presence of Htc and dolomite. Interestingly while the bio-oil yield from Rh/Htc was higher than for Rh/C without base, this was still lower than the bio-oil yield obtained for Rh/C with the addition of Htc; i.e. Rh/C/Htc > Rh/Htc > Rh/C/D > Rh/C. This trend also applies in the yields for lipids, while the yields for aromatics (6.1-6.9 wt.%) from Rh catalysts with base are similar, and were higher than the yield without base (2.0 wt.%).

From these results it is clear that the addition of base promotes the depolymerisation reaction, as reported elsewhere<sup>11-16</sup>, and the solid bases utilised can be deemed suitable for this purpose. Another hypothesis for this would be that the breaking of ester linkages between the layers of suberin depolymerised via a base catalysed reaction results in the formation of lipids and aromatics. This is similar to the effect acid or base has for the depolymerisation of lignin or cellulose.<sup>11-16, 24</sup> It is also clear that although bases obviously

promote the reaction, the use of Htc as a catalytic support is not as viable for this process when compared to the Rh/C catalyst in the presence of Htc as an additive.

### Effect of solvent on hydrogenolysis of cork

Figure 2 shows the effect of a change in solvent system on the hydrogenolysis. The solvent system can greatly affect the conversion of the solid, increased bio-oil yield and change both the aromatic and aliphatic product distribution. The highest bio-oil yield achieved was with MeTHF:water in a 6:4 ratio, which also had the highest wt.% of lipids. However, the highest aromatic yield was achieved with MeOH (8.7 wt.% versus 6.1 wt.% in 1,4-dioxane). This was not matched by the reduction in the mass of the solid. It was also found that the overall reduction of the solid material was lowest in 4:6 MeTHF system (27.6 wt.%), and was highest in the EtOH system (51.2 wt.%).

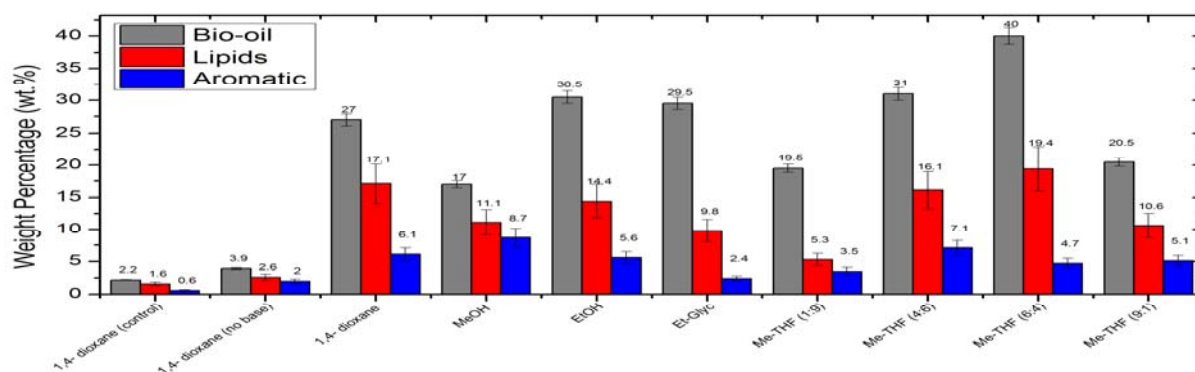


Figure 2: Effect of Solvent Change

The increase in solid yield can be related to the effect of a solvent as a hydrogen donor. It should be noted that the increase in the bio-oil yield in the EtGlyc system was a result of residual ethylene glycol. Using the review of solvent effects by Jessop *et al.*<sup>34</sup> along with other studies on Kamlet-Taft parameters it was found that there was no particular solvent effect with only a weak effect of the H-bonding on the solvent. However, given the immiscibility of Me-THF with water this is not a concern with our chosen system [See Fig S2-S4]. The effect of the solvent was also equally important in the separation of products. In the previously reported work<sup>1</sup>, ca. 200 mL of chloroform was used as the extraction method. The use of a solvent which is immiscible with water, MeTHF, allowed for the extraction of the organic soluble products without the use of an additional solvent.

The use of additional solvents can result in the loss of potentially valuable products. With this in mind, MeTHF was chosen as the preferred solvent and therefore different ratios of MeTHF and water (1:9, 4:6, 6:4 and 9:1) were used to investigate the effect of increasing organic and aqueous solvent has on the system.

## Conclusions

This paper reports environmental improvements for the valorisation of suberin rich biomass via the use of base and alternative solvents. The current work reports an increased bio-oil yield (to 42.6 wt%) and increased conversion of solid material (48.7% by weight) compared to those previously reported<sup>1</sup>, which can be attributed to the addition of a base. The change in solvent system to MeTHF also allowed for the elimination of chloroform extraction improving the overall environmental impact.

## Acknowledgements

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## In Memoriam

We dedicate this work to our colleague, Mark Garrett, who passed away on 25th April 2016. Mark began his PhD research with Gary Sheldrake more than 20 years ago and continued to be a close colleague and friend. He was always so full of vitality, good humour and boundless energy and he will be deeply missed.

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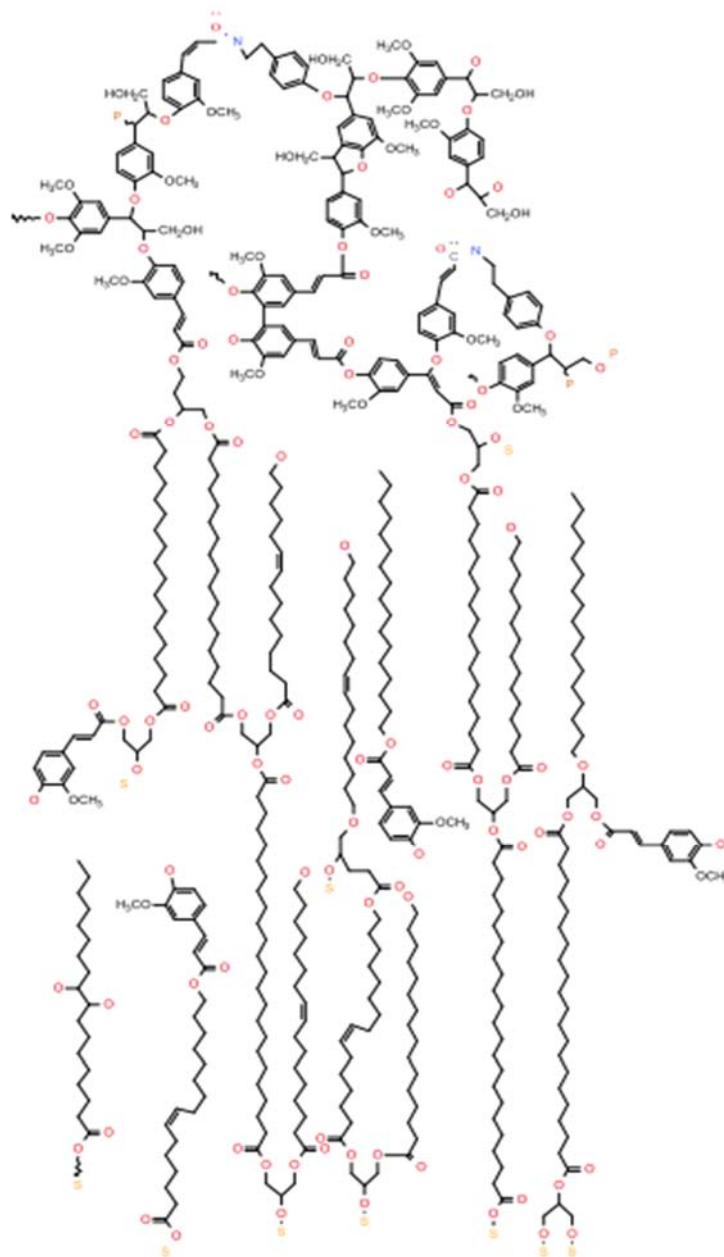
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## Electronic Supplementary Information (ESI) for

### Catalytic depolymerisation of suberin rich with precious metal catalysts

Christopher S. McCallum, Nicholas Strachan, Stephen C. Bennett, W. Graham Forsythe, Mark D. Garrett, Christopher Hardacre, Kevin Morgan and Gary N. Sheldrake

Suberin is a natural biopolymer with a structure, originally proposed by Bernards<sup>1</sup> (Figure S1), comprising two separate layers: poly-aliphatic layers (SPAD) and poly-phenolic layer (SPPD). The SPAD layer contains long chain  $\alpha,\omega$ -dicarboxylic acids,  $\omega$ -hydroxyacids and alkanolic acids with the SPPD layer containing mainly aromatic precursors such as lignin<sup>1</sup>



**Figure S1** - Suberin Structure (drawn based on Bernards<sup>1</sup>)



## Experimental

### Materials

All cork samples were obtained from commercial wine bottles and pulverised and sieved to <0.2 mm using a Kinematica Polymix PX-MFC 90D. The samples were used without any pre-extraction. 1,4 dioxane was supplied by Alfa Aesar. Double distilled water was used in all reactions. All other solvents and reagents used were obtained from Sigma Aldrich and used as received, unless otherwise stated. Commercial rhodium on carbon (5 wt.% Rh, 64 % wet) was supplied by Johnson Matthey. 5 wt.% rhodium supported on hydrotalcite was prepared by adding synthetic hydrotalcite (0.5 g) to a mortar and concentrated Rh(acac) (0.025 g, 5 wt%) in chloroform (0.25 mL) solution was pipetted evenly over the hydrotalcite. This mixture was then ground thoroughly with a pestle. This solid was left in an oven at 60 °C overnight to dry, and then calcined at 500 °C under air for 5 hours (heated at 1 °C min<sup>-1</sup>, cooled at 10 °C min<sup>-1</sup>).

### Batch reaction conditions for cork hydrogenolysis

Under identical conditions to those reported in the previous study<sup>1</sup> the catalyst (Rh/C; 0.5 g or Rh/Htc; 0.5 g), cork powder (0.2 mm, 2.0 g) and the appropriate solvent system were added together in a mini-reactor (Hastelloy® 100 mL volume, Autoclave Engineers). Air was expelled from the reactor by exchange of the headspace with hydrogen, and the pressure was set to 40 bar H<sub>2</sub> with the stirring set to 1000 rpm. Thereafter, the temperature was increased to 200 °C (at a rate of 10 °C min<sup>-1</sup>) and, thereafter, this temperature was maintained for 4 h.

Using the previously reported conditions<sup>1</sup> of a 1:1 dioxane: water (44 mL) solvent system, the effect on the hydrogenolysis by the addition of base (0.25-0.5 g of hydrotalcite or dolomite) was investigated.

Additionally, five different solvent systems have been investigated for the hydrogenolysis of cork; 1,4-dioxane, 2-methyl-tetrahydrofuran (MeTHF), ethylene glycol, methanol and ethanol. For the comparison of solvent systems a solvent to water ratio of 6:4 was used unless otherwise stated.

## Product Extraction Methods

After cooling, the reaction mixture was filtered and the filter cake washed. For the dioxane, ethylene glycol, ethanol and methanol solvent systems, the filter cake was washed with 1 : 1 dioxane : water (3 × 20 mL). The combined filtrates were extracted with chloroform (3 × 200 mL), dried over anhydrous magnesium sulphate and concentrated under vacuum resulting in the isolation of the bio-oil. This bio-oil was dissolved in 1 : 1 dioxane: water (30 mL) to which sodium hydroxide (0.5 g) was added to neutralise free acids. After refluxing for 4 hours the mixture was extracted with chloroform (3 × 100 mL). For the MeTHF solvent system, the resulting biphasic mixture was separated and the aqueous layer was extracted with 2-MeTHF (2 × 100 mL).

In all cases, the organic phase was then dried with anhydrous magnesium sulphate and filtered. The solvent was then removed under reduced pressure and remaining traces of solvent removed under high vacuum. This extraction process resulted in the production of a brown bio-oil (the crude product) for each of the solvent systems.

## Analysis and Characterisation

Analysis of the crude yield for all reactions investigated has identified two main product streams, namely lipids and aromatics.

Quantitative GC-MS analysis of the lipids in the bio-oil was performed using a Perkin-Elmer autosystem XL GC with a Perkin-Elmer Turbomass detector and BP5 column. The bio-oil (20 mL) was dissolved in a solution of 1.25 M hydrochloric acid (HCl) in anhydrous methanol (2 mL). This mixture was heated under reflux for 4 h under nitrogen after which the methanol was removed by evaporation using a nitrogen stream. The residue was suspended in water (5 mL) and extracted with chloroform (3 × 5 mL). The organic layer was dried and concentrated using a nitrogen stream to an oily residue which was further dried under vacuum for 2 h. After this time the bio-oil was dissolved in anhydrous pyridine (0.3 mL), *N,O*-bis(trimethylsilyl)-trifluoroacetamide (0.5 mL containing 10% chlorotrimethylsilane) was then added. This mixture was heated at 70 °C with agitation for 1 h under nitrogen. After cooling, 0.2 mL of a standard of 1 mg mL<sup>-1</sup> (trimethylsilyl)cholesterol was added. This mixture was injected directly into the GC-MS for characterisation.

Quantitative  $^1\text{H}$  NMR spectroscopy was performed on a Bruker Avance spectrometer at 300 MHz with tetramethylsilane (TMS) as internal standard (unless indicated otherwise). The extracted bio- oil (50 mg) and vanillin (10 mg), as an internal standard, was measured into a sample vial, and dissolved in deuteriated chloroform (1 mL).

Errors were calculated via the following equation:

$$\text{Reported error} = \Delta x_{avg} \pm \frac{\text{Range}}{2\sqrt{\text{Number of samples}}}$$

### Quantification of yields from NMR

MestReNova (v.5.2.3.) NMR analysis software was used and the aldehyde hydrogen on vanillin was used to calibrate the spectra (set at 9.73ppm) and was integrated as 1.

### Determination of fatty acid yields

In the region between 2.0 ppm and 3.0 ppm there are resonances resulting from the  $\text{CH}_2$  groups alpha and beta to the benzene ring of the aromatic products, as well as alpha to the carboxylic acid of the lipid products. Previously, triplets have been assigned in this region<sup>[2]</sup>. The  $\text{CH}_2$  group adjacent to the carboxylic acid group of lipids is found at 2.24 (2H, t,  $J = x$  Hz); propyl-guaiacol  $\text{CH}_2$  alpha to the ring is found at 2.42 (2H, t,  $J = x$  Hz); dihydroconiferyl alcohol  $\text{CH}_2$  alpha to the ring is found at 2.55 (2H, t,  $J = x$  Hz). Previously not observed in the spectra is dihydroferulic acid {DFA/ 3-(4-Hydroxy-3-methoxyphenyl)propanoic acid}. The  $\text{CH}_2$  beta to the ring of DFA is found at 2.78 (2H, t,  $J = x$  Hz); further, the  $\text{CH}_2$  group alpha to the ring is observed at 2.50 (2H, t,  $J = x$  Hz). Each triplet can be integrated to calculate the mass of each individual product of the hydrogenolysis, this calculation is found in Equation S1:

$$\text{weight}\% = \frac{\left( \frac{\text{int.}}{2} \times n_v \times M_M \right) \times M_O}{M_C} \times 100$$

**Equation S1:** where: int. = integration of  $\text{CH}_2$  triplet;  $n_v$  = moles of vanillin in sample;  $M_M$  = molecular mass of species;  $M_S$  = mass of sample submitted;  $M_O$  = mass of oil (as crude yield);  $M_C$  = mass of cork used.

Molecular weights of the products can be found in Table S1. The wt% values calculated here are shown as weight percentages of the starting material (cork), allowing comparisons to be drawn across all of the results. To calculate the yield of the lipids an arbitrary weight of 170 g mol<sup>-1</sup> was used, based on in depth analysis of fatty acid chain length from previous work.<sup>2</sup>

### Determination of aromatic yields

In the region between 6.4 ppm and 7.4 ppm the aromatic hydrogens on the guaiacyl substituent are evident. The area of 6.5 – 6.8 was integrated and taken to represent 3 CH groups on the guaiacyl substituent of the aromatic products, this integration is used to calculate an arbitrary value representing the weight percentage of the aromatic products. To do this, an arbitrary molecular weight was taken to be 180 (the average M<sub>M</sub> of compounds 1-3) using Equation S2.

$$\text{weight}\% = \frac{\left( \frac{\text{int.}}{3} \times n_v \times 180 \right)}{M_s} \times M_o}{M_c} \times 100$$

**Equation S2.** where: int. = integration 3x aromatic hydrogens; n<sub>v</sub> = moles of vanillin in sample; 180 = molecular mass average; M<sub>s</sub> = mass of sample submitted; M<sub>o</sub> = mass of oil (as crude yield); M<sub>c</sub> = mass of cork used.

## GC-MS

### Crude product

**Table S1:** The identified products from GC-MS data of non-derivative oil

Time	m/z	Compound
11.7	124	guaiacol
13.46	138	methyl guaiacol
14.76	152	ethyl guaiacol
16.02	166	propyl guaiacol
17.88	220	C16 alcohol
19.51	182	DCA
20.11	240	C15 acid
20.84	240	C16 alkene acid
21.19	254	C16 acid
22.22	268	C17 acid

Time	m/z	Compound
22.8	256	C18 alkene acid
23.22	282	C18 acid
24.15	296	C19 acid
24.7	284	C20 alkene acid
25.06	310	C20 acid
25.93	324	C21 acid
26.79	338	C22 alkene acid
27.65	429	C22 epoxide acid
27.93	341	C20 diacid

GC-MS was performed crude yield. The gas chromatograph and mass spectra for 2 compounds are shown in the supporting information. Most of the identified products are listed in Table S1. Aromatic products, lipids and alcohols are observed.

### Derivative lipids

A derivatives sample was prepared and GC-MS was performed. The identified products are listed in Table S2. The derivation converted many of the acids into methyl esters, the alcohols were converted into trimethyl-silyl groups.

**Table S2:** The identified products from GC-MS data of derivative oil

Time	<i>m/z</i>	Compound
15.8	236	isoeugenol
16.71	238	propyl guaiacol
19.34	292	C16 alcohol - sime3
20.23	282	DFA - ester
20.62	326	DCA - ester
20.81	340	DFA - acid sime3

Time	<i>m/z</i>	Compound
21.74	270	C16 acid - ester
23.72	298	C18 acid - ester
24.89	341	C18 diacid - ester
26.8	384	C20 diacid
27.55	415	C22 acid

### Solvent Effect

**Table S3:** Kamlet Taft Parameters of Solvents

	Alpha	Beta	Mu	Bio-oil	Lipids	Aromatic
1,4-Dioxane <sup>4</sup>	0	0.37	0.35	27	17.1	6.1
MeOH <sup>4</sup>	0.93	0.66	0.58	17	11.1	8.7
EtOH <sup>4</sup>	0.52	0.16	-0.03	30.5	14.4	5.6
EtGly <sup>5</sup>	0.92	0.52	0.9	29.5	9.8	2.4
MeTHf <sup>4</sup>	0	0.58	0.53	40	19.4	4.7

Figure S2:  $\alpha$  (H bonding ability) of Solvent vs Weight Percentage of product

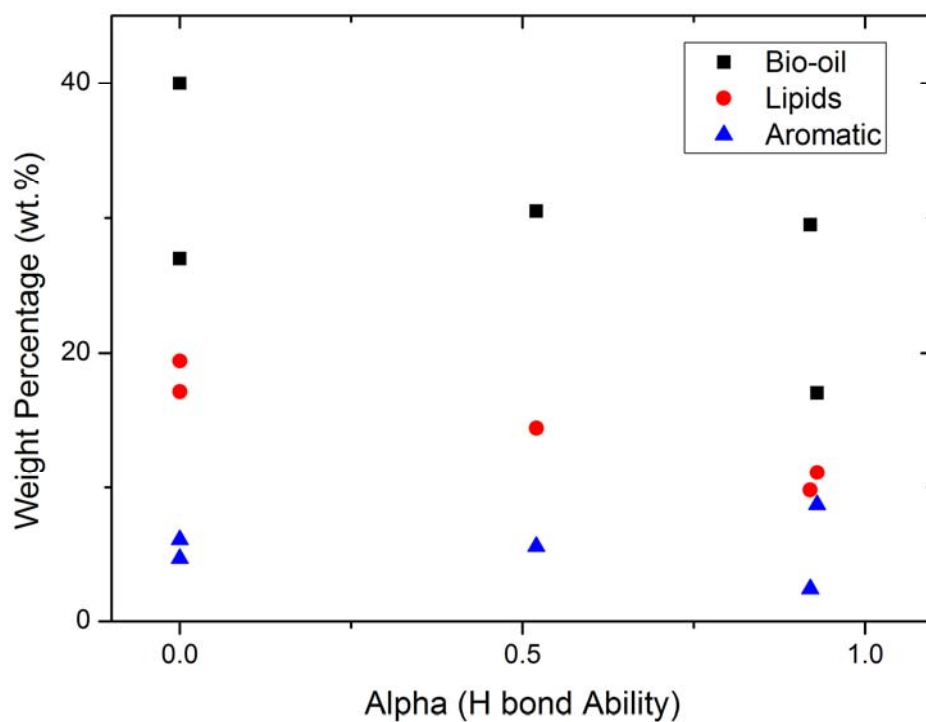


Figure S3:  $\beta$  (Basicity) of Solvent vs Weight Percentage of product

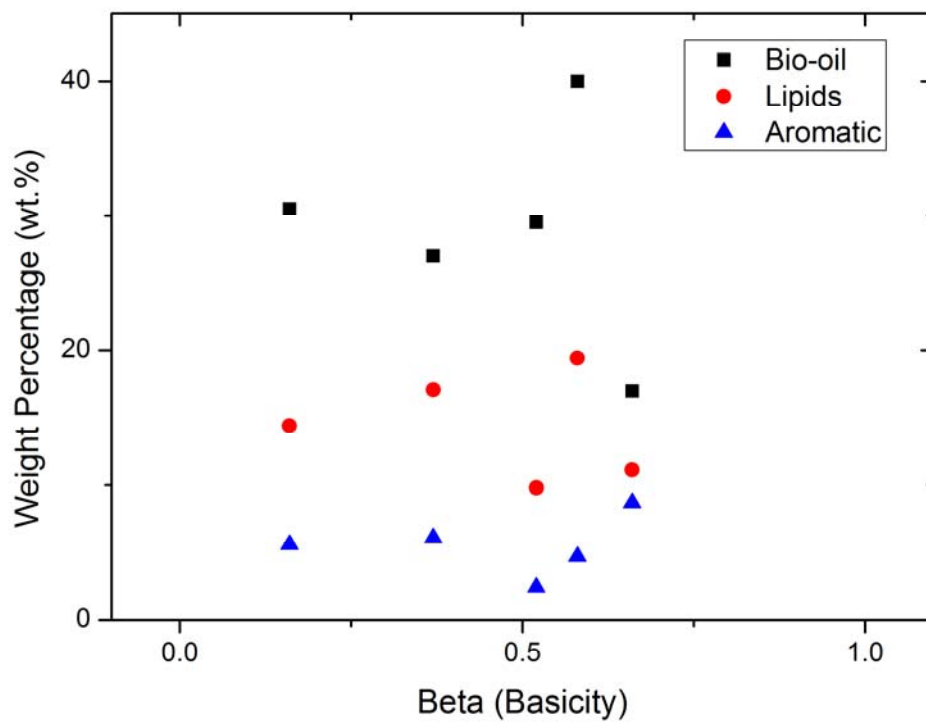
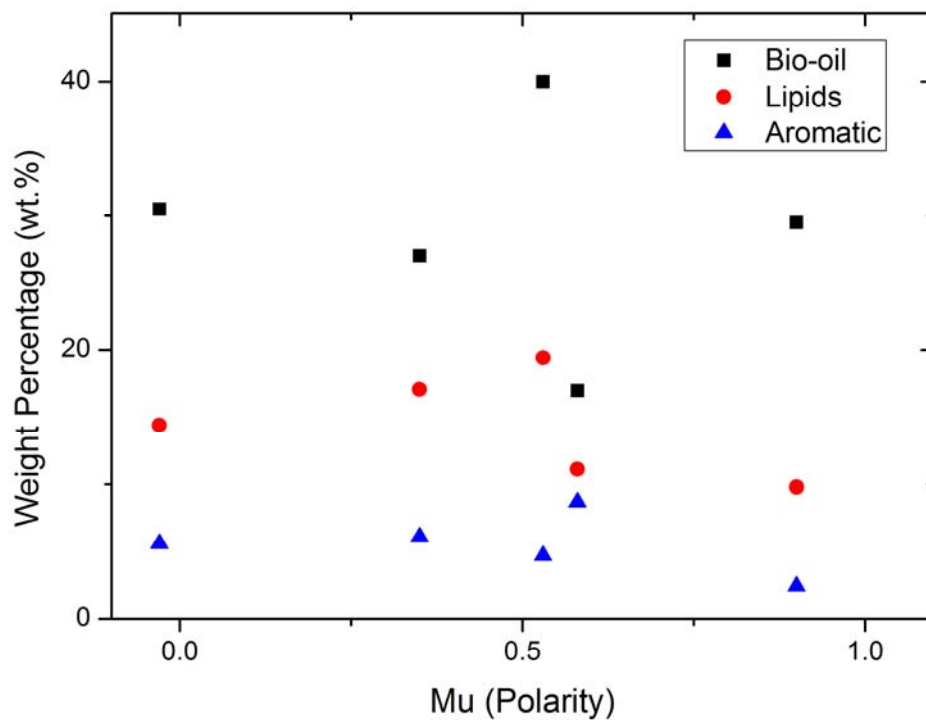


Figure S4:  $\mu$  (Polarity) of Solvent vs Weight Percentage of product



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