



Direct Solvent Liquefaction of Tropical Hardwood Bark and Characterization of the Resulting Bio-Oil

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Authors' contributions

This work was carried out in collaboration among the authors. Author YBO, is the main author wrote the protocol, drafted the manuscript and performed the literature search. Author OAO gave technical correction to the manuscript. Author LL helped to probe the chemistry aspect of the work. Author AB designed the study and performed the statistical analysis. All the authors read and approved the final manuscript.

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ABSTRACT

Ethanol, water and ethanol/water mix were used to directly liquefy *Detarium senegalense* bark at 500°C for 15 min. Ethanol/water mix at 50/50% weight by weight showed synergistic effect on biomass direct liquefaction, and was found to be the most effective solvent for the liquefaction of *Detarium senegalense* bark. Water was more active than Ethanol when both mono-solvents were evaluated. Liquefaction with 100% water yielded 46% by weight of the bio-oil, compared with 30% by weight of bio-oil yield when 100% ethanol was used. The result however, show that 50% ethanol/water showed a synergistic effect and work best to obtain 52% bio-oil on the liquefaction

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whereas water was found hence more active than ethanol as a single solvent with 46% and 30% bio-oil respectively.

The GC-MS analysis of the obtained bio-oils from the three matrices confirmed the presence of phenolic compounds and aromatics such as benzenes, followed by aldehydes, long chain ketones and cyclic ketones and alcohol, esters, organic acids and ether compounds. The detected phenolic compounds were 4-ethyl-guaiacol, 2-methoxy-4-(2-propenyl)-phenol, 2-methoxy-phenol, and 2-methoxy-4-vinyl-phenol., formed from the cleavage of guaiacyl and hydroxyphenyl-type lignin with varying degrees of alcohol substitution. Understanding and evaluating the liquefied products obtained from hardwood barks, could offer valuable information on the utilization of the biomass-liquefaction products for chemical or energy production.

Keywords: Biomass direct liquefaction; GC-MS analysis; liquefaction solvents; bio-oil.

1. INTRODUCTION

Solvolytic liquefaction among others is a method of converting lignocellulosic biomass into bio-phenolic compounds or precursors for the production of PF resins [1] and is more preferable to the pyrolysis processes with respect to energy efficiency and the quality of the oily products. As such, the solvolytic liquefaction technologies of lignocellulosic materials have attracted increasing interest for the production of bio-phenol precursors for synthesis of bio-based phenolic resins and heavy oils (bio-crude) for bio-fuel production. Several solvents had been experimented for the liquefaction procedure such as acids and phenols. Strong acids had limitations which includes partial carbonization of biomass during liquefaction and corrosion of the equipment whereas phenols could yield such problems as environmental issues among which are, Increasing world energy consumption [2] and growing carbon dioxide emissions that have contributed to the promotion of sustainable energy development.

Solvent with low boiling points such as alcohols and water [3] and [4] had been explored for low-temperature liquefaction of biomass instead of the use of acids and phenol due to the fact that they could be recycled easily by distillation/evaporation after liquefaction and are much cheaper. Another advantage of using alcohols as the solvent for biomass liquefaction is that they are renewable due to the fact that they can be readily produced from biomass. In addition, they have higher solubility for the liquid products derived from cellulose, hemicelluloses, and lignin due to their lower dielectric constants compared with that of water [5]. Water, on the other-hand is a unique transport properties (gas-like diffusivity and liquid-like density) and ability to dissolve materials not normally soluble in either liquid or gaseous phase of the solvent, and

hence to promote the gasification/liquefaction reactions. Phenol-formaldehyde (PF) resins are widely used as an adhesive in the wood products industry for the manufacture of particleboard and other composite products because of its high strength and moisture resistance [3,6].

Phenol, the most costly chemical raw material for the manufacturing of PF resins, is primarily produced from petroleum-derived benzene by the cumene process developed by [7]. Dwindling of petroleum resources as well as increasing demands for petroleum by developing economies, political and environmental concerns over fossil-based resources has necessitated the interest in exploring and developing alternative renewable resources for both energy and chemical production [8]. The lignocellulosic biomass used as precursor in the production of bio-phenol is *Detarium senegalense*, a lesser-utilized tropical hardwood species in Nigeria, composed of lignin, amorphous micromolecule, which comprises of three phenyl-propanol macromolecules, namely p- hydroxy-phenylpropanol, guaiacyl-propanol and syringyl-propanol, that can be decomposed into the oligomeric and monomeric phenolic compounds through thermochemical technology such as solvolytic liquefaction [9,6]. In this regard, lignocellulosic biomass can be a potential source of bio-phenolic compounds to replace petroleum-based phenol in the production of PF resins.

Among the properties that will qualify wood bark as a potential raw material in the developing biorefinery and chemical industries are the percentage bark composition as well as the percentage variation of bark within and between species. Hard wood species were studied for variation in their bark percentages within trees of the same species and those of different species, *D. senegalense* performed best [10,11] compared the effect of various solvents (water,

acetone and ethanol) on pinewood (soft wood specie) liquefaction for producing fuels and chemical feedstocks. The experiments were conducted in an autoclave at temperatures ranging from 250°C to 450°C for 20 min with a biomass-to-solvent ratio of 1/6 (wt/wt). The results showed that the yield and composition of the liquefaction products were greatly affected by the solvent type. The highest oil yield of 26.5 wt% was obtained in ethanol. Ethanol was favorable for the formation of 2-methoxy-4-(1-propenyl)-phenol and 2-methoxy-4-methyl-phenol, while the composition of bio-oil from the liquefaction using water solvent was rich in 2-methoxy-phenol, organic acids and furans. However, the focus was essentially on softwood bark because of its composition of both guaiacyl and syringyl units derived from trans-coniferyl and *trans*-sinapyl alcohols. Notwithstanding, it has been established that the weight percentage of lignin, cellulose, and hemicellulose in any type of biomass as well as the composition of syringyl, guaiacyl and p-hydroxyphenyl is affected by several factors among which are: geographical location, soil type, climatic conditions, plant species, pH level, soil nutrients and the Age of Plant Species [12]. The aim of this study, therefore, is to investigate the effect of solvents on *Detarium senegalense* bark and characterization of the resulting bio-oil for PF resins system.

2. MATERIALS AND METHODS

2.1 Bark Collection and Sample Preparation

The bark of *Detarium senegalense* was obtained from Aiyegun sawmill, New Garage, Ibadan Nigeria. Reliable information from the sawmillers was that the log was collected from Gambari Forest Reserve. Gambari Forest Reserve which is located on latitude of 70.25° N and 7.55° E and the longitude 3.53° N and 3.9° E within the low land semideciduous forest belt of Nigeria and covers a total land area of 17,984 ha. The air-dried bark samples of *D. senegalense* was hammer milled using New Holland grinder model 358 (New Holland, PA) with 3.175 mm (1/8 In.) sieve size for particle reduction. It was then oven dried at 105 °C for 2 h. Elemental composition of carbon, hydrogen, nitrogen, and sulfur in the *D. senegalense* samples was analyzed with a CHNS Flash Elemental Analyzer 1112 series. Compositional analysis for its contents of cellulose, hemicelluloses and lignin content was done in accordance with the TAPPI T249 cm-85

(for cellulose and hemi-cellulose). The liquefaction of the hammer-milled *D. senegalense* bark was carried out in a 1000 mL stainless steel autoclave reactor equipped with a stirrer and a water-cooling coil. Liquefaction procedure of [13] was employed.

3. RESULTS

3.1 The Proximate and Elemental Chemical Analysis as well as Structural Chemical Compositional Analysis of *D. senegalense* Bark

The results of the proximate, elemental chemical analysis and structural chemical compositional analysis of the *D. senegalense* bark are presented in Table 1. The value of the percentage means of volatile matter, fixed carbon and ash content were: 16.5%, 83.2% and 0.4%, respectively. It was observed that fixed carbon made up the bulk of the biomass. Also for the elemental compositional analysis the percentage composition of C, H, O, N, were 53.82%, 7.52%, 36.8% and 0.14%, respectively. Carbon had the highest value, followed by oxygen, hydrogen and then nitrogen. The percentage composition of sulphur was at trace level (0.08%). Likewise, for the structural chemical compositional analysis, the percentage by weight of cellulose, hemicelluloses and lignin were 46.2%, 18.0% and 35.2%, respectively. Cellulose has the highest percentage followed by hemicelluloses and the least was lignin.

3.2 Effect of Solvent Types: Ethanol, Water and 0% (wt/wt) of Ethanol on Percentage Bio-oil Yield

The results of the effect of solvent types: ethanol, water and 50/50% weight by weight ethanol/water mix on the yield of bio-oil from the liquefaction at 300°C at solvent-to-biomass ratio of 10:1 (wt/wt), are shown in Fig. 1. As a single solvent, water provided better bio-oil yield (46%) than ethanol (30%); however, 50% wt/wt ethanol gave the best yield of 52%.

3.3 Chemical Compositional Characterization of Bio-oil Obtained from the Solvolysis Liquefaction Using Ethanol, Water and Ethanol/Water Mix

The chemical compounds as identified using the WILEY8 library based on the GC-MS

chromatographs. The detected compounds and their relative percentage area for the major compounds are summarized in Table 2. The relative percentage area for each compound was defined by the percentage of the chromatographic area of the specific compound

out of the total area of 50 largest identified peaks. The major compounds identified in the bio-oil products were phenolic compounds, benzenes, aldehyde, long-chain and cyclic ketones, alcohols, esters, carboxylic acids and ether compounds.

Table 1. Proximate, ultimate analysis and structural compositional analysis of *D. senegalense* bark

Proximate analysis, wt%	
^c Vm	16.5
^c Fc	83.2
^a Ash	0.4
Ultimate analysis, wt%	
C	53.82
H	7.32
N	0.14
S	0.08
O ^d	36.8
Structural composition, wt%	
^b Total lignin	35.2
^d Cellulose	46.8
^d Hemicelluloses	18.0

Note: ^aOn a dry basis; ^bDetermined by thermogravimetric analysis (TGA) in N₂ at 10°C/min to 900°C; ^cOn a dry and ash-free basis; ^dBy difference

Table 2. Chemical compositional characterization of bio-oil showing the relative percent area for each compound identified and the total percent for all of the identified compounds obtained

Peak no	Retention time/min	Relative composition per area percentage			Compounds name
		100% Ethanol	100% Water	50% Ethanol/ Water (wt/wt)	
1	3.04	3.95 ^g	a	a	Ethyl 2-hydroxypropanoate
2	3.52	3.23 ^f	a	a	2-Furanmenthanol
3	4.02	a	a	2.05 ^l	Benzene, methyl-
4	4.21	3.01 ^g	a	a	Butanoic acid, 2-hydroxy-ethyl ester
5	4.23	a	a	2.13 ^o	2-amino-2-carboxy- ethyldisulfanyl)
6	4.40	2.5 ^f	a	a	-propionic acid
7	4.51	2.41 ^e	a	4.67 ^l	Ethanol, 2-(ethenyloxy)-
8	4.75	a	a	10.56 ^m	Benzene (1- methylethyl)-
9		a	a	2.01 ^g	Propanoic acid, 2-hydroxy- ethyl ester
10	5.73	2.56 ^o	a	2.03 ^o	Piperazine
11	6.24	a	a	2.38 ^l	Methoxy -1-Cyclopentene
12	6.47	a	a	2.08 ^m	Propanoic acid ,2-hydroxy-, methyl ester
13	5.05	a	19.56 ^h	2.21 ⁿ	2-Furancarboxaldehyde
14	6.53	a	a	2.05 ^l	Benzene, (1-methylethyl)-
15	6.59	2.43 ^o	a	a	Acetamide,n-(1-methylpropyl)-
16	6.66	2.95 ^o	a	a	Butanoic anhydride
17	6.83	6.07 ^c		4.56 ^k	Phenol, 2-methoxy-
18	7.10	a	13.01 ^h	3.19 ⁿ	-furancarboxaldehyde, 5-methyl-
19	8.21	3.22 ^e		5.16 ^l	1-hydroxy-2-methoxy-4-methylbenzene
20	8.30	a	a	3.21 ^l	Benzene (1- methylethyl)-
21	8.39	a	5.56 ^l	a	-methyl-1,2-cyclopentanedione

Peak no	Retention time/min	Relative composition per area percentage			Compounds name
		100% Ethanol	100% Water	50% Ethanol/ Water (wt/wt)	
22	8.46	a	2.38 ^l	a	Ethanone, 1-(5-methyl-2-furanyl)-
23	8.51	a	a	6.40 ^m	Pentanoic acid ,4-oxo-, ethylester
24	8.94	4.67 ^d	17.08 ⁱ	8.46 ^k	Phenol, 2-methoxy-
25	9.29	6.24 ^d	a	a	Guaiacol,4-methoxy-
26	9.45	2.03 ^o	a	2.56 ^o	Formamide, n -dimethyl-
27	9.71	2.81 ^d	a	a	2-methoxy-4-vinylphenol
28	9.84	2.53 ^o	3.34 ^o	a	2-amino-3-(2-amino-2-carboxy-ethyl-disulfanyl)-Propanoic acid
29	10.22	8.33 ^d	a	4.45 ^k	Phenol, 2-methoxy-4-(2-propenyl)-
30	10.33	a	4.65 ⁱ	2.96 ^l	-hydroxy-2methoxy-4-methylbenzene
31	10.72	5.58 ^d	a	a	Guaiacol, 4-propyl-
32	11.25	a	a	3.45 ⁿ	-furancarboxaldehyde, 5-(ethoxymethyl)-
33	11.39	20.07 ^b	a	a	Phenol, 2-methoxy-4-(2-propenyl)-
34	12.79	4.01 ^d	a	4.92 ^k	Guaiacol, 4-ethyl- tetrahydro-pyran-3-ol
35	13.18	a	10.64 ^h	4.48 ⁿ	Benzaldehyde, 4-hydroxy-3-methoxy- Benzenemethanol, -4hydroxy- alpha -
36	13.34	6.02 ^d	a	2.13 ^k	[(methylamino)methyl]-
37	13.74	a	a	8.01 ^p	Phenol, 2-methoxy-4-(2-propenyl)-
38	14.20	a	4.42 ^j	a	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)
39	15.81	a	3.01 ^h	a	2-propanone, (4-hydroxy-3-methoxyphenyl
40	16.30	a	a	a	1-(4-isopropylphenyl)-2-methylpropyl acetate
Total area %		94.62%	83.65%	96.11%	

^aNot including the small peaks with an area less than 2% of the total area

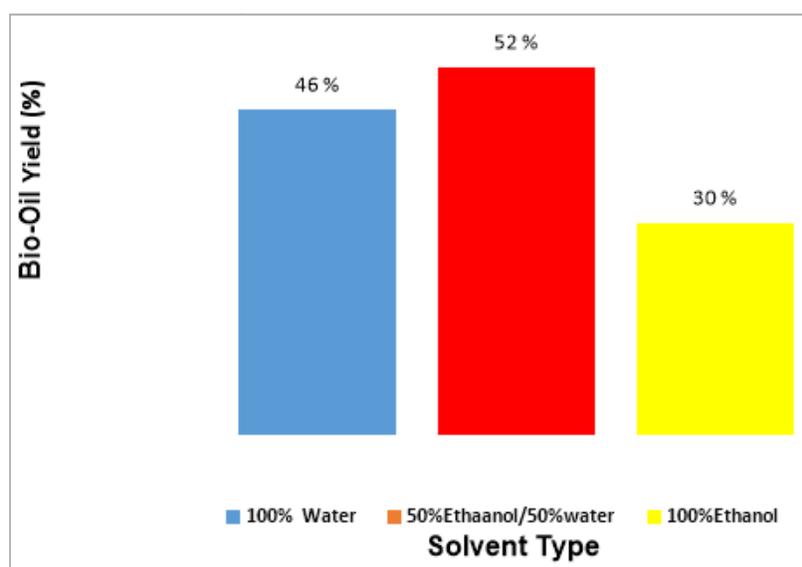


Fig. 1. Effect of solvent types: 100% Ethanol, 100% Water and 50/50% (weight by weight) Ethanol/Water mix on the yield of Bio-oil from the liquefaction at 300°C while the solvent-to-biomass ratio was fixed at 10:1 (wt/wt)

4. DISCUSSION

4.1 Elemental Analysis of *Detarium senegalense* Bark

The results of the Elemental analysis of depolymerised *D. senegalense* bark showed that sulphur and nitrogen compounds were reduced to the barest minimum as shown in Table 2, which invariably implies safer environmental conditions associated with products obtained from depolymerized *D. senegalense* bark. The nitrogen and sulphur compounds detected were likely to originate from the fuel-bound nitrogen and sulphur in the *D. senegalense* bark. The results fall within the range of previously reported values [14].

4.2 Effects of Solvent Types on Bio-Oil Yield

From Fig. 1, water was more active than Ethanol when both mono-solvents were evaluated. Liquefaction with 100% water yielded 46% by weight of the bio-oil, compared with 30% by weight of bio-oil yield when 100% ethanol was used. The result however, show that 50/50% (weight by weight) ethanol/water mix for the solvolytic liquefaction of *D. senegalense* bark yielded 52% bio-oil and was therefore much more effective than mono-solvent of either water or ethanol. The result was almost similar with the work of [14], where white pine sawdust was effectively liquefied in 50 wt% ethanol-water medium, producing approximately 66 wt% bio-oil. The difference in the yield from the tested solvents could be due to the fact that alcohols are slightly weaker acids than water. However, water in hot-compressed and sub-critical state has a number of special properties: a lower dielectric constant, fewer and weaker hydrogen bonds, a higher isothermal compressibility and an enhanced solubility for organic compounds than ambient liquid water [15,16]. As a result, the lower activity of the 100 wt% ethanol for biomass liquefaction than that of 100 % water may be expected. Also, hot-compressed water had been demonstrated to be an effective solvent for biomass hydrothermal liquefaction [17,18,19,20]. It has also been found to be very effective for promoting ionic, polar non-ionic and free-radical reactions [16], which make it a promising reaction medium for biomass direct liquefaction. Ethanol, however, could reduce the surface tension of the liquefied products and, hence, improve the diffusion of solvent to the lignin matrix. Ethanol, has also, been reported to have

the ability to readily dissolve relatively high-molecular-weight liquid products/intermediates derived from cellulose, hemicelluloses, and lignin because of their lower dielectric constants when compared to that of water [21,22]. The lower yield of bio-oil in pure ethanol than water however, could be due to limited hydrolysis reaction.

However, from Fig. 1, 50% wt/wt. co-solvent of ethanol-water was a much effective solvent than any constituent mono-solvent. These results strongly suggested synergistic effect on biomass direct liquefaction observed when the co-solvent of ethanol and water produced a higher yield of bio-oil as previously reported by [23,24] in organic solvent (organosolv) delignification of woody biomass at 190°C where 50% methanol to water solution or 50% ethanol to water solution was found to be very effective for wood delignification [25]. The co-solvent of ethanol to water has attracted more interests, simply because ethanol is a renewable resource, which can be obtained readily by fermentation of sugar.

5. CONCLUSION

The research revealed that the lignin in *D. senegalense* bark is composed of both guaiacyl and syringyl unit with small amount of *p*-hydroxyphenyl unit derived from transconiferyl and trans-sinapyl alcohol which could decompose into guaiacyl and hydroxyphenyl-type phenolic products during the liquefaction process. Ethanol and water showed synergistic effect on biomass direct liquefaction, and the 50 wt% co-solvent of ethanol-water was found to be the most effective solvent for the liquefaction of *Detarium senegalense* bark.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

REFERENCES

1. Effendi A, Gerhauser H, Bridgwater AV. Production of renewable phenolic resins by thermochemical conversion of biomass: A review. *Renewable and Sustainable Energy Reviews*. 2008;12(8):2092-2116.
2. Ragauskas AJ, Williams CK, Davison BH, Britovsek G, Cairney J, Eckert CA, Frederick WJ Jr., Hallett JP, Leak DJ, Liotta CL, et al. The path forward for biofuels and biomaterials. *Science*. 2006;311:484-489.

3. Shiraishi N, Shirakawa K, Kurimoto Y. Japanese Pat Appl. 1992;106-128.
4. Hassan EM, Shukry N. Polyhydric alcohol liquefaction of some lignocellulosic agricultural residues. *Industrial Crops Production*. 2008;27:33–38.
5. Yamazaki J, Minami E, Saka S. Liquefaction of beech wood in various supercritical alcohols. *Journal Wood Science*. 2006;52:527–532.
6. Wang M, Leitch M, Xu C. Synthesis of phenol-formaldehyde resol resins using organosolv pine lignins. *European Polymer Journal*. 2009;12(45):3380–3388.
7. Hock H, Lang S. *Ber Dtsch Chem Ges*. 1944;B77:257.
8. Russell JA, Riemath WF. Method for making adhesive from biomass. US Patent 4 508 886, USA as Represented by the United States Department of Energy; 1985.
9. Kleinert M, Barth T. Phenols form lignin. *Chemical Engineering Technology*. 2008;31:736-745.
10. Karagoz S, Bhaskar T, Muto A, Sakata Y. Effect of Rb and Cs carbonates for production of phenols from liquefaction of wood biomass. *Fuel*. 2004;83:2293–2299.
11. Ogunwusi AA. Variation in the percentages of bark of ten tropical hardwood specie grown in Nigeria. *Journal of Life Sciences and Technology*. 2013;7. 224-7181(Paper), ISSN 225-062x (Online)
12. Liu Z, Zhang F. Effects of various solvents on the liquefaction of biomass to produce fuels and chemical feedstocks. *Energy Conversation Management*. 2008;49:3498–3504.
13. Vassilev SV, Baxter D, Andersen LK, Vassileva CG. An overview of the chemical composition of biomass. *Fuel*. 2010;89:913–933.
14. Cheng S, D’cruz I, Wang M, Leitch M, Xu C. Highly efficient liquefaction of woody biomass in hot-compressed alcohol-water co-solvents. *Energy Fuel*. 2010;24(9): 4659–4667.
15. Cheng S, D’Cruz I, Yuan Z, Wang M, Anderson M, Leitch M, Xu C. Using bio-crude derived from woody biomass to substitute for phenol at a high substitution level for production of bio-based phenolic resol resins. *Journal of Applied Polymer Science*. 2011;121:2743–2751.
16. Savage PE. Organic chemical reactions in supercritical water. *Chemical Review*. 1999;60:3621.
17. Akiya N, Savage PE. Roles of water for chemical reactions in high-temperature water. *Chemistry Review*. 2002;102:2725-2750.
18. Matsumura Y, Nonaka H, Yokura H, Tsutsumi A, Yoshida K. Co-liquefaction of coal and cellulose in supercritical water. *Energy Fuel*. 1999;78:1049-1056.
19. Karagoz S, Bhaskar T, Muto A, Sakata Y. Effect of Rb and Cs carbonates for production of phenols from liquefaction of wood biomass. *Fuel*. 2004;83:2293–2299.
20. Karagoz S, Bhaskar T, Sakata Y. Comparative studies of oil compositions produced from sawdust, rice husk, lignin and cellulose by hydrothermal treatment. *Fuel*. 2005;84:875–884.
21. Xu C, Lad N. Production of heavy oils with high caloric values by direct liquefaction of woody biomass in sub-/near-critical water. *Energy Fuel*. 2008;22:635–642.
22. Miller JE, Evans L, Littlewolf A, Trudell DE. Bath microreactor studies of lignin and lignin model compound depolymerization by bases in alcohol solvents. *Energy Fuel*. 1999;78:1363–1366.
23. Ogi T, Yokoyama S. Liquid fuel production from woody biomass by direct liquefaction. *Sekiyu Gakkaishi*. 1993;36:73-84.
24. Pasquini D, Pimenta MTB, Ferreira LH, Curvelo AAS. Extraction of lignin from sugarcane bagasse and *Pinus taeda* wood chips using ethanol–water mixtures and carbon dioxide at high pressures. *Journal Supercritical Fluids*. 2005;36:31–39.
25. Li L, Kiran E. Interaction of supercritical fluids with lignocellulosic materials. *Industrial Engineering Chemical Resources*. 1988;27:1301-1312.

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