

EFFECT OF SOLVENTS ON *DETARIUM SENEGALENSE* BARK AND CHARACTERIZATION OF THE RESULTING BIO-OIL FOR PF RESIN SYSTEM

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Abstract:

Ethanol, water and ethanol/water mix were used to directly liquefy Detarium senegalense bark at 500°C for 15min. 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 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.

Key words: Biomass direct liquefaction; GC-MS analysis; Liquefaction solvents; Bio-oil.

INTRODUCTION

Solvolytic liquefaction among others is a method of converting lignocellulosic biomass into bio-phenolic compounds or precursors for the production of PF resins (Effendi *et al.* 2008), 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 (Ragauskas *et al.* 2006) 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 (Hassan and Shukry 2008) 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 (Yamazaki *et al.* 2006) 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 (Shiraishi *et al.* 1993; Wang *et al.* 2009). 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 Hock *et al.* (1944). 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 (Russel *et al.* 1985).

The lignocellulosic biomass liquefied is the bark *Detarium senegalense* wood, a lesser-utilized tropical hardwood species in Nigeria, medium-sized tree that may grow up to 40m tall (Adenkunle *et al.* 2011). Like many trees in the *Caesalpinioideae*, they have thick, irregularly placed branches. The bark of *Detarium senegalense* had been studied and successfully recommended in terms of bark abundance, to sustainably utilize the wood bark in biorefineries and chemical industries (Ogunwusi 2012, Ogunwusi 2013). Tree bark

usually refers to all external tissues surrounding the vascular cambium of the tree. Generally, it takes up about 9-15% of a typical log by volume Harkin and Rowe (1971). Bark has a similar chemical composition to wood, only that it contains more extractives, higher lignin content, and a smaller amount of holocellulose than wood. Bark phenolic 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 (Kleinert *et al.* 2009; Wang *et al.* 2009). In this regard, lignocellulosic bark biomass can be a source of as precursor in chemical industries.

Liu and Zhang (2008), 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 20min 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 26.5wt% 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 (Vassilev *et al.* 2010). 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.

MATERIALS AND METHOD

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 3.175mm (1/8 In.) sieve size for particle reduction. It was then oven dried at 105°C for 2h. 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 T249cm-85 (for cellulose and hemi-cellulose). The liquefaction of the hammer-milled *D. senegalense* bark was carried out in a 1000mL stainless steel autoclave reactor equipped with a stirrer and a water-cooling coil. Liquefaction procedure of Chen *et al.* (2011) was employed.

SOLVENT LIQUEFACTION OF *DETARIUM SENEGALENSE* BARK

The bark was hammermilled using New Holland grinder model 358, with 3.175mm (1/8 in.) sieve size for particle reduction (Fig. 1). It was then oven dried at 105°C for 12hrs and kept in a desiccator at room temperature before use. Solvolytic Liquefaction of the hammer-milled *D. senegalense* bark was carried out in a 1000ml stainless steel autoclave reactor equipped with a mechanical stirrer (500rpm) and a water-cooling coil (Fig. 2 a). The solvents used for the liquefaction were: water, ethanol and ethanol/water mix on weight-to-weight basis. The solvents were used differently in each run. In a typical run, the reactor was charged with 10g *D. senegalense* bark and 100g water or 100g ethanol or ethanol/water co-solvent 50/50%(v/v), after which the reactor was sealed, and the air inside the reactor was displaced by high-purity nitrogen.

The reactor was pressurized to 2.0MPa and heated to the desired temperature of 300°C at a steady rate of 10°C per minute while being constantly stirred. The reaction was stopped after 30 minutes completion of the liquefaction process. The reactor was cooled to room temperature of 25 °C by means of the water-cooling coil. The gaseous products (**GAS**) inside the reactor were thereafter vented. The resulting suspension inside the reactor was completely rinsed with acetone and collected in a glass bowl. The suspension was filtered under reduced pressure through a pre-weighted Whatman No. 5 filter paper to obtain the solid residue (**SR**) on the filter paper while the aqueous soluble products (**AP**), (Fig. 2b) consisting of bio-oil, in the form of liquid oily product and other non-oily liquid products were obtained as filtrate. The SR and filter paper were dried at 105°C for 2h before weighing.

The acetone in the filtrate was then removed by rotary evaporation under vacuum (Fig. 2c) at 40°C. When co-solvent mixture of ethanol-water was used, this treatment removed the alcohol co-solvent in addition to acetone. The remaining liquid solution was extracted with ethyl acetate. Separatory funnel was used to separate the liquid oily products, denoted as bio-phenolic oil from water and aqueous soluble

products (**AP**) (Fig. 2d). Ethyl acetate soluble phase was then evaporated under a reduced pressure at 57°C to remove ethyl acetate; and recover the remaining aqueous soluble product (**AP**). Yield of bio-oil, SR was calculated by the percentage weight of the mass of each product to the mass of the dry *Detarium senegalense* bark loaded into the reactor at each run.

The biomass conversion was simply calculated using (Eq. 1). Being a common challenge for the biomass liquefaction studies, quantification of aqueous products (AP) was difficult not only because it is hard to separate the aqueous soluble products from water due to the high point boiling of water but the complexity of the aqueous products (a mixture of carboxylic acids, carbohydrates, aldehydes etc.) was also a challenge. Since our major interest in this research was the bio-oil products, the aqueous products were not analysed.

MEASUREMENT OF THE BIO-OIL YIELD

The yield of the Bio-oil was quantified as:

$$\% \text{ Bio-oil yield} = \frac{\text{Weight of bio-oil}}{\text{Weight of oven-dried raw } D.\text{senegalense}} \times 100 \quad (1)$$

bark before liquefaction



Fig. 1.
Hammer-milling of *D. senegalense* bark of *D. senegalense*.



Fig. 2.
Liquefaction reactor (a) used to separate the liquefied fraction under vacuum (b) and subsequent separation with the use of separatory funnel (c) to obtaining the bio-oil (d).

RESULTS AND DISCUSSIONS

Table 1

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

Elemental 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; ^c On a dry and ash-free basis; ^dBy difference.

ELEMENTAL CHEMICAL ANALYSIS AND STRUCTURAL CHEMICAL COMPOSITIONAL ANALYSIS OF *D. SENEGALENSE* BARK

The results of the elemental chemical analysis and structural chemical compositional analysis of the *D. senegalense* bark are presented in Table 1. The value of the percentage means 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. 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 (Cheng et al. 2011).

Table 2

Detected compounds and their relative percentage area From GC-MS chromatographs

Relative composition per area percentage					
Peak no	Retention time/min	100 % Ethanol	100 % Water	50 % Ethanol/ Water (wt/wt)	Compounds name
1	3.04	3.95 ^g	a	a	Ethyl 2-hydroxypropanote
2	3.52	3.23 ^f	a	a	2-Furanmenthanol
3	4.02	a	a	2.05 ^f	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 ^f	Ethanol, 2-(ethenyloxy)-
8	4.75	a	a	10.56 ^m	Benzene (1- methylethl)-
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 ^f	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- methylethl)-
21	8.39	a	5.56 ^j	a	-methyl-1,2-cyclopentanedione
22	8.46	a	2.38 ^j	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 ^l	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-ethylsulfanyl)-Propanoic acid
29	10.22	8.33 ^d	a	4.45 ^k	Phenol, 2-methoxy-4-(2-propenyl)-
30	10.33	a	4.65 ^l	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,
36	13.34	6.02 ^d	a	2.13 ^k	-4hydroxy- alpha - [(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-methoxyphenl)
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%	
^a Not including the small peaks with an area less than 2 % of the total area.					

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.

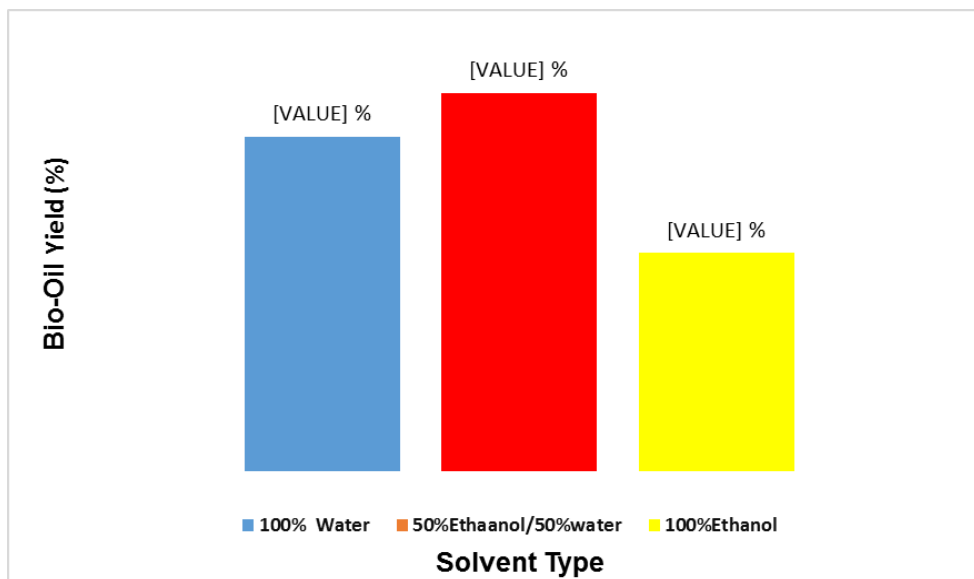


Fig. 3.

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).

EFFECT OF SOLVENT TYPES: ETHANOL, WATER AND ETHANOL/WATER MIX (WT/WT) 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. 3. 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%. 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 Cheng *et al.* (2010), where white pine sawdust was effectively liquefied in 50wt% ethanol-water medium, producing approximately 66wt% 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 (Savage 1999; Akiya and Savage 2002). As a result, the lower activity of the 100wt% 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 (Matsumura *et al.* 1999; Karagoz *et al.* 2004, 2005; Xu and Lad 2008). It has also been found to be very effective for promoting ionic, polar non-ionic and free-radical reactions 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 (Miller *et al.* 1999, Ogi *et al.* 1993). The lower yield of bio-oil in pure ethanol than water however, could be due to limited hydrolysis reaction.

However, from Fig. 3, 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 (Pasquini *et al.* 2005; Li and Kiran 1988) 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. 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.

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 50wt% co-solvent of ethanol-water was found to be the most effective solvent for the liquefaction of *Detarium senegalense* bark.

REFERENCES

- Adekunle A, Afolayan A, Okoh B, Omotosho T, Pendota C, Sowemimo A (2011) Chemical composition, antimicrobial activity, proximate analysis and mineral content of the seed of *Detarium senegalense* J.F Gmel. *African Journal of Biotechnology*, 10(48):9875-9879.
- Akiya N, Savage PE (2002) Roles of water for chemical reactions in high-temperature water. *Chemistry Review*, 102:2725-2750.
- Alma MH, Yoshioka M, Yao Y, Shiraishi N (1995a) Upgrading bitumen in supercritical fluids. *Mokuzai Gakkaishi*, 41:741-748.
- Alma MH, Yoshioka M, Yao Y, Shiraishi N (1995b) Preparation of sulfuric acidcatalyzed phenolated wood resin. *Journal of Wood Science Technology*. 30:39-47.
- Alma MN (1996) Several acids-catalysed phenolation of wood and its applications to molding materials. *Ph. D. Dissertation*. Kyoto University. Kyoto, Japan.
- Alma MH, Maldas D, Shiraishi N (1997) Liquefaction of several biomass wastes into phenol in the presence of various alkalis and metallic salts as catalysts. *Journal of Polymer Engineering*. 18:163.
- Alma MH, Yoshioka M, Yao Y, Shiraishi N (1998) Preparation of sulfuric acid-catalyzed phenolated wood resin. *Wood Science Technology*, 32:297-308.
- Alma MH, Basturk MA (2006) Liquefaction of grapevine cane (*Vitisvinisera* L.) waste and its application to phenol-formaldehyde type adhesive. *Journal of Industrial Crops Products*. 24:171-176.
- Amen-Chen C, Pakdel H, Roy C (2001) Production of monomeric phenols by thermochemical conversion of biomass: a review. *Journal of Bioresource Technology*, 79:277-299.
- Cheng S, D'cruz I, Wang M, Leitch M, Xu C (2010) Highly efficient liquefaction of woody biomass in hot-compressed alcohol-water co-solvents. *Energy Fuel* 24(9):4659-4667. "Critical literature review of relationships between processing parameters and physical".
- Cheng S, D'Cruz I, Yuan Z, Wang M, Anderson M, Leitch M, Xu C (2011) Using bio-crude derived from woody biomass to substitute for phenol at a high substitution level for production of bio-based phenolic resins. *Journal of Applied Polymer Science*.121:2743-2751.
- Effendi A, Gerhauser H, Bridgwater AV (2008) Production of renewable phenolic resins by thermochemical conversion of biomass: A review. *Renewable and Sustainable Energy Reviews*, 12(8):2092-2116.
- Hassan EM, Shukry N (2008) Polyhydric alcohol liquefaction of some lignocellulosic agricultural residues. *Industrial Crops Production*, 27:33-38.
- Karagoz S, Bhaskar T, Muto A, Sakata Y (2004) Effect of Rb and Cs carbonates for production of phenols from liquefaction of wood biomass. *Fuel*. 83:2293-2299.
- Karagoz S, Bhaskar T, Sakata Y (2005) Comparative studies of oil compositions produced from sawdust, rice husk, lignin and cellulose by hydrothermal treatment. *Fuel*. 84:875-884.
- Kleinert M, Barth T (2008) Phenols form lignin, *Chemical Engineering Technology*. 31:736-745.
- Li L, Kiran E (1988) Interaction of supercritical fluids with lignocellulosic materials. *Industrial Engineering Chemical Resources*. 27:1301-1312.
- Lin LZ, Yoshioka M, Yao YG, Shiraishi N (1994) Liquefaction of wood in the presence of phenol using phosphoric acid as a catalyst and the flow properties of the liquefied wood. *Journal of Applied Polymer Science*. 52:1629-1636.
- Lin LZ, Yoshioka M, Yao YG, Shiraishi N (1995) Preparation and properties of phenolated wood/phenol/formaldehyde cocondensed resin. *Journal of Applied Polymer Science*, 58:1297-1304.

- Liu Z, Zhang F (2008) Effects of various solvents on the liquefaction of biomass to produce fuels and chemical feedstocks. *Energy Conversion Management* 49:3498-3504.
- Matsumura Y, Nonaka H, Yokura H, Tsutsumi A, Yoshida K (1999) Co-liquefaction of coal and cellulose in supercritical water. *Energy Fuel*. 78:1049-1056.
- Miller JE, Evans L, Littlewolf A, Trudell DE (1999) Bath microreactor studies of lignin and lignin model compound depolymerization by bases in alcohol solvents. *Energy Fuel*. 78:1363-1366.
- Ogi T, Yokoyama S (1993) Liquid fuel production from woody biomass by direct liquefaction. *Sekiyu Gakkaishi*, 36:73-84.
- Ogunwusi AA (2012) "Wood properties of *Detarium senegalense*, a lesser used tropical timber growing in Nigeria," *Journal of Biology, Agriculture and Healthcare*. 2(10).
- Ogunwusi AA (2013) "Variation in the percentages of bark of ten tropical hardwood species grown in Nigeria," *Journal of life sciences and Technology*; Vol 7:224-7181.
- Ohra-aho T, Tenkanen M, Tamminen T (2005) Direct analysis of lignin analysis lignin-like component from softwood kraft pulp by Py-GC/MS techniques. *Journal of Analytical Pyrolysis*, 74:123-128
- Pasquini D, Pimenta MTB, Ferreira LH, Curvelo AAS (2005) Extraction of lignin from sugarcane bagasse and *Pinus taeda* wood chips using ethanol-water mixtures and carbon dioxide at high pressures. *Journal Supercritical Fluids*. 36:31-39.
- Ragauskas AJ, Williams CK, Davison BH, Britovsek G, Cairney J, Eckert CA, Frederick WJ Jr, Hallett JP, Leak DJ, Liotta CL (2006) The path forward for biofuels and biomaterials. *Science* 2006, 311:484-489.
- Russell JA, Riemath WF (1985) Method for making adhesive from biomass. US Patent 4 508 886, USA as represented by the United States Department of Energy.
- Savage PE (1999) Organic chemical reactions in supercritical water. *Chemical Review*: 603621.
- Shiraishi N, Shirakawa K, Kurimoto Y (1992) Japanese Pat Appl. 106-128.
- Vassilev SV, Baxter D, Andersen LK, Vassileva CG (2010) An overview of the chemical composition of biomass. *Fuel* 89:913-933.
- Wang M, Leitch M, Xu C (2009) Synthesis of phenol-formaldehyde resol resins using organosolv pine lignins. *European Polymer Journal*, 12(45):3380-3388.
- Xu C, Lad N (2008) Production of heavy oils with high caloric values by direct liquefaction of woody biomass in sub-/near-critical water. *Energy Fuel*. 22:635-642.
- Xu C, Etcheverry T (2008) Hydro-liquefaction of woody biomass in sub- and supercritical ethanol with iron-based catalysts. *Energy Fuel*. 87(3):335-345.
- Yamazaki J, Minami E, Saka S (2006) Liquefaction of beech wood in various supercritical alcohols. *Journal Wood Science*. 52:527-532.