



Maderas. Ciencia y tecnología

ISSN: 0717-3644

ISSN: 0718-221X

Universidad del Bío-Bío

Kumar, Anil; Sethy, Anil; Chauhan, Shakti
Liquefaction behaviour of twelve tropical hardwood species in phenol
Maderas. Ciencia y tecnología, vol. 20, no. 2, 2018, pp. 211-220
Universidad del Bío-Bío

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LIQUEFACTION BEHAVIOUR OF TWELVE TROPICAL HARDWOOD SPECIES IN PHENOL

Anil Kumar¹, Anil Sethy¹, Shakti Chauhan^{1,}*

ABSTRACT

Liquefaction of ligno-cellulosic biomass is one of the chemical conversion technologies for developing new materials, adhesives and energy systems. The liquefaction process also provides an opportunity to utilize ligno-cellulosic wastes such as saw-dust, woody wastes, branches and twigs, agro-residues, etc. for the development of value added products. This paper presents the liquefaction behaviour of wood meal of twelve tropical hardwood species in phenol as liquefying media to produce chemically active liquid which has potential to be used as a raw material for developing different products. The liquefaction was carried out at 140°C temperatures for 120 minutes at different liquid ratios. In all the cases, a viscous and sticky black liquid was obtained after the stipulated reaction time. The liquefaction efficiency was found to vary with species and liquid ratio. The highest liquefaction efficiency of 93% was achieved in balsa wood at 1:3 (wood: phenol) liquid ratio. The liquefied wood and residues were characterized by FTIR spectroscopy. The liquefied wood was found to be highly acidic in nature. Viscosity of liquefied wood at higher liquid ratio was independent of wood species. Correlation analysis revealed a strong negative relationship between wood basic density and liquefaction efficiency.

Keywords: Ash content, density, extractives, Fourier transform infrared analysis, lignin, wood chemical properties.

INTRODUCTION

In recent years, the utilisation of lignocellulosic biomass has become appealing because of versatility, renewable nature and environmental concerns. One of the promising approaches of utilizing lignocellulosic wastes is its liquefaction and converting the liquefied wood into value added products (Worthy 1990). In liquefaction process, macromolecule compounds in biomass are degraded into micro molecules and the obtained small molecules are unstable, reactive and can re-polymerize into oily products with a wide range of molecular weight distribution (Demirbas 2000).

Strong network of cellulose, hemicellulose and lignin and the crystalline structure of some regions of cellulose make wood extremely resistant to liquefaction, even under severe reaction conditions. Pu and Shiraishi 1993, Pu and Shiraishi 1994) reported that liquefaction of lignocellulosic biomass wastes, especially in presence of organic solvents e.g. phenols, alcohols, glycols and ketones using acid catalysts at temperatures of 120°C – 180°C or without catalysts at temperatures of 180°C - 250°C. Yao (1996), in his studies with birch wood, reported the initial stages rapid liquefaction due to dissolution of easily accessible components of lignin, hemicelluloses and cellulose, followed by the slow liquefaction

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Received: 17.01.2017 Accepted: 29.11.2017

of hard-to-access cellulose. Thereafter several studies have been carried out on liquefaction of wood in different liquefaction systems and product development from liquefied wood (Alma *et al.* 1998, Alma and Acemioğlu 2004, Yamazaki *et al.* 2006, Honglu and Tienju 2006, Lin *et al.* 2014, Petrič *et al.* 2015). Lin *et al.* (2001, 2004) have studied the mechanism of liquefaction of lignin model compound and cellulose in phenol to understand wood liquefaction mechanism.

Research on wood liquefaction has primarily focussed on effects of catalysts, solvents, temperature, and other factors on liquefaction efficiency. Studies on accelerating liquefaction using microwave and ultrasonication has also been attempted (Pan *et al.* 2011). In most of these studies, specific wood species has been used as the source of woody biomass.

Industrial woody wastes are generally mixtures of various wood species softwoods, hardwoods, composite wood, other ligno cellulosic material from forest, agricultural residues, weeds, shrubs, lops and tops of plantation species. Liquefaction behaviour of different species and, the physical and chemical properties of liquefied wood have not been studied much. Kurimoto *et al.* 1999, Kurimoto *et al.* 2001 reported strong influence of wood species on liquefaction process using Poly Ethylene Glycol as the liquefying agent at 3:1 liquid ratio and 120 minutes of reaction. The softwood species exhibited higher residual content as compared to hardwood species. Within hardwood species also significant differences were observed in liquefaction efficiency Ertas *et al.* (2014) compared liquefaction efficiency of Eucalyptus and pine wood in PEG-400 /glycerine system and found significant differences in characteristics of liquefied wood from two species. Hardwood species are highly variable in terms of their anatomical structure, density and extractive content which can influence the liquefaction process. There is hardly any study on liquefaction process of tropical hardwood species. Chauhan and Karmarkar (2009) studied the liquefaction efficiency of *Hevea brasiliensis* wood in phenol with hydrochloric acid as a catalyst and found liquefaction efficiency of 49% to 82% under different reaction conditions.

In this study, liquefaction efficiency of 12 tropical hardwood species and their mixture was determined using phenol as the liquefying agent and HCl as the catalyst. The liquefaction was carried out at different liquid ratio. The liquefied wood was characterized for properties like viscosity and pH. The wood characteristics namely wood density, ash content, extractive content, and lignin content were determined and related to liquefaction efficiency. The liquefied wood and residues were chemically characterized by FTIR spectroscopy.

MATERIALS AND METHODS

Wood species and chemicals

Wood species were selected based on various density classes and these were

- I. Low Density class (below 500 kg/m³): *Ochroma pyramidale*, *Delonix regia*
- II. Moderate Density Class (500-650 kg/m³): *Melia dubia*, *Leucania leucocephala*, *Hevea brasiliensis*,
- III. High Density Class (above 650 kg/m³): *Prosopis juliflora*, *Azadirachta indica*, *Tectona grandis*, *Eucalyptus tereticornis*, *Dalbergia latifolia*, *Terminalia tomentosa*, *Casuarina equisetifolia*
- IV. Mixture of all wood species

Wood material of each of the selected species was collected from local sawmills and chipped into small pieces. The chips were air dried and pulverized using a laboratory scale pulveriser. The pulverized wood meal was sieved through 150 mesh sieve (BSS specification, ~80 µm particle size) and oven dried at 105°C for 24 h.

Phenol (LR grade) was used as the liquefying media and hydrochloric acid (LR. Grade) was used as a catalyst. For characterizing the liquefied wood, laboratory grade reagents namely; 1-4 Dioxane,

phthalic anhydride, pyridine, KOH and methanol were used. All the reagents and solvents were procured from Nice Chemicals, Kochi, India and used as received.

Liquefaction of wood powder

Oven dry sawdust of various wood species was used for the preparation of liquefied wood. Wood liquefaction was carried out in phenol as the dissolving agent and HCl as the catalyst. The liquid ratio i. e. wood to solvents ratio were 1:1, 1:2, 1:3 and catalyst content was 3 wt% of the wood content. Liquefaction reaction was performed for 120 minutes in a glass reactor equipped with a stirrer and a condenser. The reactor was immersed in an oil bath that was preheated to 140°C. For each liquefaction reaction, 10 g of oven dried meal was taken in the glass reactor. The pre-determined quantity of phenol and HCl was added to the wood meal. The mixture was kept as such without any stirring at 140°C for 30 minutes. Thereafter, stirring was started and continued for 90 minutes. After the liquefaction reaction process, the liquefied wood was diluted thoroughly with excess methanol and filtered through glass filter paper under reduced pressure on G1 filtration apparatus. Methanol from the filtrate was recovered by distillation and the liquefied wood was obtained. The residues were dried in an oven at 105°C until it reached to a constant weight. Liquefaction efficiency (LE, %) was calculated from the initial weight of wood meal and residual weight using Equation 1.

$$LE(\%) = \frac{m_0 - m_1}{m_0} \times 100 \quad (1)$$

Where m_0 is oven-dry weight of the initial wood (g) and m_1 is oven-dry weight of the residue content (g).

Viscosity of the Liquefied wood

The viscosity of the liquefied wood was measured using a Ford viscosity cup N° 4 (B4 cup). The viscosity cup was fully filled with the liquid under the test, and the flow time through standard orifice was measured. Equation 2 was used to convert the time of flow in seconds, t to kinematic viscosity V_4 ;

$$V_4 = 3,85(t - 4,49) \quad (2)$$

Where; V_4 = kinematic viscosity using orifice N° 4 and t is flow time of liquid through orifice in seconds

FTIR analysis of the Liquefied wood and residues

The changes of components of the liquefied biomass based polyols during the liquefaction were analyzed using Bruker make Fourier transform infrared (FTIR) spectrometer (Tensor 27 model). Spectra were recorded for wood meal, liquefied wood and wood residue, with a co-addition of 64 scans at a spectral resolution of 4 cm^{-1} . Each spectrum was recorded in a frequency range of 400–4000 cm^{-1} using potassium bromide (KBr) disc. KBr was previously oven-dried at 105°C to reduce the interference of water.

Wood chemical analysis

Wood meal of all the studied species was analyzed for ash content, extractive content and lignin content. For ash content estimation, 10 g wood sample (oven dried and cooled) was weighed in a ceramic crucible and kept in a muffle furnace at 650°C for 8 hours. Ash content was determined from the initial and final weight of the sample. Extractive content was determined by extracting 10 g wood

meal (oven dried and cooled) with a mixture of toluene, acetone and ethanol (4:1:1 wt ratio) using soxhlet extraction until colour less solution in the extraction unit was obtained. The extractive free wood was oven dried and weighed. Extractive content was estimated from the initial weight and final weight after extraction. Lignin estimation was carried out from the extractive free wood as per Tappi method (T222-om 15:1988). Air-dry density of wood was determined from the air-dried mass and volume of wood samples of each species.

RESULTS AND DISCUSSION

Wood characteristics namely air dry density, ash content, extractive content and lignin content of the species are given in Table 1. Wood density among the species was varying from 178 kg/m³ to 831 kg/m³. Ash content was ranging from 0,84% to 5,27% extractive content was ranging from 1,92% to 16,81% and acid-insoluble lignin content was ranging from 18,84% to 31,86%.

Table 1. Air-dry density, ash content, extractive content and lignin content in wood.

No.	Species	AD density (kg/m ³)	Ash content (%)	Extractive content (%)	Lignin content (%)
1	<i>Ochroma pyramidale</i>	178	1,69	1,92	18,84
2	<i>Delonix regia</i>	432	5,09	7,42	29,59
3	<i>Melia dubia</i>	510	0,84	8,11	31,86
4	<i>Hevea brasiliensis</i>	535	1,17	6,66	21,17
5	<i>Lecanea leucocephala</i>	578	2,00	10,49	28,75
6	<i>Prosopis juliflora</i>	655	2,04	9,94	28,75
7	<i>Eucalyptus treticornis</i>	668	1,79	10,20	27,08
8	<i>Tectona grandis</i>	675	2,30	11,76	29,40
9	<i>Azadirachta indica</i>	692	3,84	8,02	31,17
10	<i>Dalbergis latifolia</i>	737	5,27	13,31	30,91
11	<i>Casurina equisetifolia</i>	773	1,11	9,49	30,83
12	<i>Terminalia tomentosa</i>	831	2,50	16,81	31,84

The liquefaction efficiency and characteristics of liquefied wood namely viscosity and pH at different liquid ratio are given in Table 2. Within a species, liquefaction efficiency increased with the increasing liquid ratio. The role of solvent is to dissolve the liquefied products and prevent them from re-polymerizing. At lower liquid ratio, during the initial stages of the process, the dissolving agent was wetting only a small part of wood meal and the stirring was difficult in the reactor vessel. However as the reaction proceeded with slow and careful stirring for longer time, it resulted in photolysis of lignin which initiated the liquefaction process resulting in satisfactory liquefaction. Liquefaction efficiency of 68,89% to 78,53% was achieved for different species at 1:1 liquid ratio.

At 1:2 liquid ratio, there was no concern with respect to stirring as the quantity of phenol was enough to wet wood surface and the liquefaction reaction proceeded smoothly. The liquefaction efficiency at this liquid ratio was nearly 10% higher than as observed at 1:1 liquid ratio. Increasing phenol content further at 1:3 liquid ratio did not result in any remarkable increase in the liquefaction efficiency. At 1:3 liquid ratio, the liquefaction efficiency was only about 3-4,5% higher than at 1:2 liquid ratio irrespective of species. Overall, liquefaction efficiency of wood varied from 69% to 93% under different reaction conditions and at different liquid ratio. Chauhan and Karmarkar (2009) observed

77% liquefaction efficiency of rubber wood in phenol with 1: 3 liquid ratio at 140°C which was lower than the observed liquefaction of the same species in this study. Liquefaction efficiencies for birch wood was reported to be of 90% and 100% in the presence of hydrochloric and sulphuric acid catalyst respectively at 150°C in two hours of reaction (Acemioğlu and Alma 2002, Alma and Acemioğlu 2004) which is in agreement with this study. Lee and Chen (2008) also reported 82% liquefaction of Japanese cedar in phenol at 1:2.5 liquid ratio with HCl as catalyst with reaction carried out at 130°C. The liquefaction with sulphuric acid catalyst was nearly 95% under the same conditions. Hrastnik *et al.* (2013) obtained more than 90% liquefaction efficiency of black poplar wood at liquid ratio of 1:3 and more with ethylene glycol as the liquefying media and they did not find any significant improvement in liquefaction efficiency on increasing the liquid ratio beyond 1:3.

Among the species, the highest liquefaction efficiency was achieved in *Ochroma pyramidales* and the lowest was in *Terminalia tomentosa* at all the liquid ratios. These species were also found to be having the extreme values in terms of wood density, extractive content and lignin content. It was observed that high density wood exhibited relatively low liquefaction efficiency as compared to low density wood. However, it is to be noted that the liquefaction efficiency at 1:3 liquid ratio was varying within a small range from 83% to 93% though the air dry density was varying from 178 kg/m³ to 831 kg/m³, exhibiting nearly five- fold variation (Table 1).

The small difference in liquefaction efficiency of wood having extreme density differences may be attributed to the differences in anatomical structure and permeability which may influence the penetration of phenol in cell-walls and the mechanism of wood liquefaction. Once the depolymerisation of lignin takes place in the initial stages, the liquefaction process gets accelerated resulting in rapid liquefaction of other components of wood cell walls. This suggests that satisfactory liquefaction of wood can be achieved irrespective of wood species and density. This is further substantiated with the viscosity of the liquefied wood. At low liquid ratio i.e. 1:1 the viscosity of *Ochroma pyramidales* and *Delonix regia* liquefied wood was significantly lower than other species and this may be attributed to easy penetration of phenol into the cell wall resulting in rapid liquefaction of these two species. The viscosity at 1: 1 liquid ratio was ranging from 51,44 cp to 132,18 cp in different species. However at 1:3 liquid ratio, the viscosity of liquefied wood from different species was not varying much with its value ranging from 32,34 to 44,86 cp.

The pH value of liquefied wood is an indicator of hydrogen ions activity. pH value varied from 2,14 to 3,87 at 1:1 liquid ratio 1,84 to 2,86 at 1:2 liquid ratio and 1,53- 2,16 at liquid ratio 1:3. Within a species, pH values declined with increasing liquid ratio indicating that acidity increases with increase in phenol content. This was expected as the liquefied wood ought to be more acidic with more phenol.

Table 2. Effects of species on liquefaction efficiency at different liquid ratio.

No.	Species	Liquefaction efficiency (%)			Viscosity (cP)			pH		
		Liquid ratio 1:1	Liquid ratio 1:2	Liquid ratio 1:3	Liquid ratio 1:1	Liquid ratio 1:2	Liquid ratio 1:3	Liquid ratio 1:1	Liquid ratio 1:2	Liquid ratio 1:3
1	<i>Ochroma pyramidales</i>	78,53	88,36	93,02	51,44	42,20	32,34	3,6	2,8	1,86
2	<i>Delonix regia</i>	77,15	86,59	91,30	77,11	54,05	33,61	2,73	2,34	1,85
3	<i>Melia dubia</i>	76,29	86,25	90,78	99,83	87,93	44,01	3,02	2,86	2,16
4	<i>Hevea brasiliensis</i>	75,46	85,84	89,41	114,99	85,00	42,19	3,87	2,47	1,79
5	<i>Leucania leucocephala</i>	74,26	84,98	88,69	116,60	93,23	44,86	3,86	2,78	1,97
6	<i>Prosopis juliflora</i>	73,14	84,16	87,52	132,18	90,39	34,38	2,86	2,57	1,96
7	<i>Eucalyptus treticornis</i>	72,85	83,79	87,17	102,52	78,46	33,22	2,38	2,18	1,84
8	<i>Tectona grandis</i>	72,37	83,20	86,46	96,60	73,50	34,38	2,92	2,42	1,93
9	<i>Azadirachta indica</i>	71,41	82,68	85,79	97,60	71,88	32,65	2,87	2,62	1,83
10	<i>Dalbergia latifolia</i>	71,01	81,60	85,15	97,68	91,44	42,47	2,78	2,42	1,93
11	<i>Casuarina equisetifolia</i>	70,59	80,54	84,35	98,01	72,46	44,81	2,19	1,98	1,78
12	<i>Terminalia tomentosa</i>	68,89	79,57	83,09	97,71	89,20	40,75	2,14	1,84	1,64
13	Mixed hard wood	73,93	84,61	88,26	129,26	96,97	34,65	2,27	1,97	1,88

A correlation analysis was performed to understand the relationship between different parameters of the liquefied wood and wood characteristics. Table 3 represents the Pearson's correlation coefficients for 1:1, 1:2 and 1:3 liquid ratios with wood density, ash content, extractive content and lignin content.

Table 3. Pearson's correlation coefficients of liquefied wood parameters with wood characteristics. (ADD- air dry density, AC- Ash content, EC- extractive content, LC- lignin content, LE- liquefaction efficiency, V- Viscosity. Notation 1, 2, 3 represents liquid ratio of 1:2, 1:2 and 1:3, respectively).

Variable	LE1	LE2	LE3	V1	V2	V3	pH1	pH2	pH3
ADD	-0,95**	-0,94**	-0,96**	0,60*	0,67*	0,32	-0,63*	-0,64*	-0,29
AC	-0,15	-0,16	-0,15	-0,22	-0,14	-0,28	-0,21	-0,10	-0,13
EC	-0,83**	-0,83**	-0,82**	0,46	0,69*	0,33	-0,56	-0,60*	-0,23
LC	-0,63*	-0,65*	-0,61*	0,34	0,47	0,27	-0,64*	-0,31	0,15

**Significant at the 0,01 level, *Significant at the 0,05 level.

Liquefaction efficiency exhibited a strong negative relation with wood density at all liquid ratios. Wood density exhibited significant positive correlation with viscosity, and negative correlation with pH of liquefied wood at 1:1 and 1:2 liquid ratio but these relationships were not apparent at 1:3 liquid ratio. The varying correlation with liquid ratio may be attributed to limited liquefaction at low phenol content during the stipulated reaction time. Ash content of wood was not found to be associated with liquefaction efficiency and other liquefied wood parameters. Extractive content and lignin content of species were negatively correlated to liquefaction efficiency at all liquid ratio. Higher extractive and lignin content may hinder the penetration of phenol into the cell-wall ultra-structure and consequently slow defragmentation of cell-wall constituents. Wood density was positively correlated to extractive content ($r = 0,86$) and lignin content ($r = 0,72$) which was on the expected lines. There was no consistent correlation of viscosity and pH of liquefied wood with extractive content. Therefore any relationship observed at a specific reaction condition may not be generalized. No significant correlation was observed between viscosity and pH of liquefied wood at all liquid ratio.

The results suggest that wood species irrespective of having different densities can be liquefied at higher liquefying agent concentration without any significant influence on characteristics of liquefied wood and therefore mixing of wood species may not any significant impact on characteristics of liquefied wood. This is evident from the fact that for mixed hardwood species the liquefaction efficiency of 88% was achieved at 1:3 liquid ratio and other characteristics of liquefied wood were close to the average of species.

FTIR Characterization

FTIR spectra of wood and residuals shown in Figure 1 have been evaluated into two regions namely $3800\text{--}2700\text{ cm}^{-1}$ which is assigned to the O-H and C-H stretching vibrations and the $1800\text{--}900\text{ cm}^{-1}$ fingerprint region assigned to stretching vibrations of wood components. A strong broad band at $3000\text{--}3600\text{ cm}^{-1}$ is related to O-H stretching and a band at $2800\text{--}3000\text{ cm}^{-1}$ is related to asymmetric methyl and methylene stretching groups present in the wood (Poletto 2017). In the fingerprint region, band at 1740 cm^{-1} is assigned to non-conjugated carbonyl group in hemicellulose and the band at 1510 cm^{-1} and 1610 cm^{-1} have their origin in the aromatic ring of lignin. The bands at 1375 cm^{-1} , 1160 cm^{-1} and 898 cm^{-1} are mainly due to carbohydrates, while the band at 1460 cm^{-1} is attributed to syringyl aromatic skeletal vibration and 1220 cm^{-1} is assigned to guaiacyl ring breathing with carbonyl stretching (Pandey and Vuorinen 2008, Poletto *et al.* 2012).

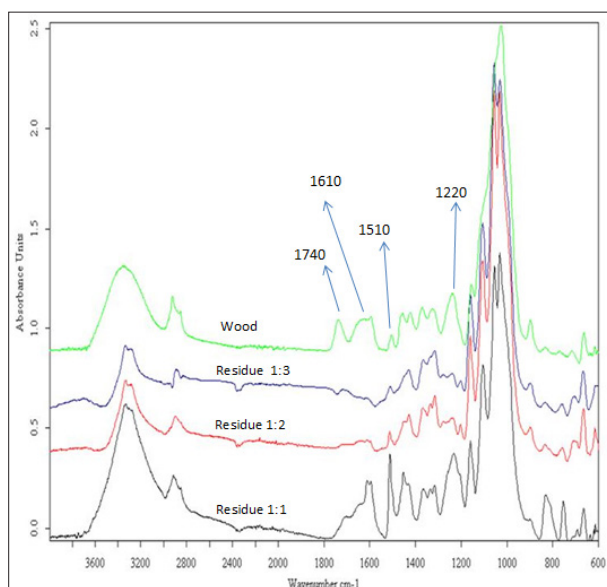


Figure 1. FTIR spectra of wood and residues obtained on liquefaction at 1:1, 1:2 and 1:3 liquid ratio.

In case of residues, the carbonyl peak intensity at 1740 cm^{-1} has almost disappeared indicating the dissolution of hemicellulose component of wood. The characteristic peaks associated with lignin (1510 cm^{-1} , 1610 cm^{-1} , 1460 cm^{-1} and 1220 cm^{-1}) have also shown marked reduction in the wood residues particularly obtained with 1:2 and 1:3 liquid ratios. Pan *et al.* (2007) has also reported disappearance of peak at 1735 cm^{-1} , attributed to the ester carbonyl group in xylan, in the FTIR spectra of the residues from liquefied wood. They observed reduction in the Klason lignin content and increase holocellulose and α -cellulose contents as the phenol to wood ratio (P/W) increased. At 1:1 liquid ratio, peak corresponding to aromatic vibration stretching are visible and this may be attributed to incomplete liquefaction of lignin components and also presence of phenol in the wood residues.

The spectra of wood polyols at different liquid ratio (Figure 2) differ significantly from the spectra of wood residues and wood (Figure 1) and shows that almost all peaks gradually become stronger with increase in liquid ratio i.e. from 1:1 to 1:2 and 1:3.

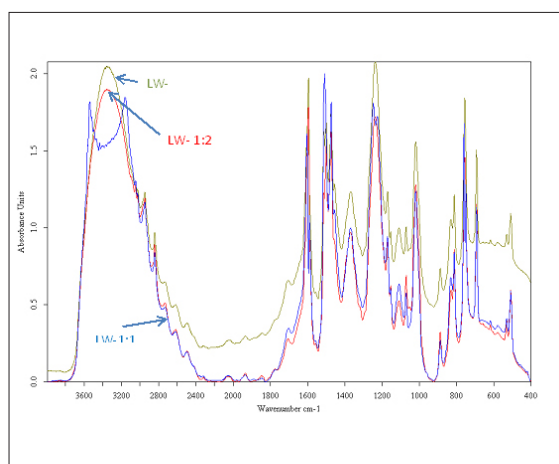


Figure 2. FTIR spectra of the liquefied wood at different liquid ratio.

The spectra at 1:1 and 1:2 were nearly overlapping in the fingerprint region. The liquefied wood had peaks associated with both carbohydrate (1740 cm^{-1} , 1375 cm^{-1}) and lignin components (1610 cm^{-1} , 1510 cm^{-1} , 1220 cm^{-1}) and therefore is an indicative of liquefaction of all the components of wood. The spectral analysis clearly indicates that almost all the component of wood converted into liquefied wood polyols.

CONCLUSIONS

The study revealed that wood meal from different hardwood species can effectively be liquefied in phenol using HCl as a catalyst with liquefaction efficiency ranging from 69% to 93% under similar reaction. With increasing phenol content, liquefaction efficiency increased but the liquefied wood was more acidic in nature. Extractive content had an adverse impact on liquefaction efficiency. Viscosity and pH value will help in deciding further processing for developing products from liquefied wood. Although wood density was correlated negatively with liquefaction efficiency but the range is relatively narrow. FTIR spectra suggest complete dissolution of lignin and hemicelluloses and the residuals are mainly the crystalline cellulose. It is desirable to have high liquefaction efficiency at a low liquid ratio to make liquefied wood economical and 1:2 liquid ratios appears to be effective in achieving satisfactory liquefaction. The liquefied wood polyols having huge potential as a raw material for development of value added products adhesive, energy, preservative and materials.

ACKNOWLEDGEMENTS

Authors express sincere gratitude to the Director and Group Coordinator Research, Institute of Wood Science and Technology, Bengaluru and the Head, Wood Processing Division for their support and encouragement in carrying out this study. The authors are also thankful to the Indian Council of Forestry Research and Education, Dehradun for the financial support to this research.

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