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LIQUEFACTION OF WOODY WASTE: A POTENTIAL AVENUE IN UTILIZATION OF WASTE WOOD

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ABSTRACT

Liquefaction of ligno-cellulosic biomass is one of the chemical conversion technologies for developing new materials, adhesives and resin systems. The process also provides an opportunity to utilize ligno-cellulosic wastes such as saw-dust, cut-off of unfinished wood based items (solid and composite wood) and furniture after service, woody wastes, branches and twigs, etc. for value added products. A large amount of saw dust and wood shaving and other types of wood waste are produced by wood based industries, which is generally incinerated. This paper presents the liquefaction of wood powder in different liquefying media to produce chemically active liquid which has potential to be used as a raw material for different products. Wood liquefaction was carried out at 120^{0}C, 140^{0}C and 160^{0}C temperatures with different liquefying agents. In all the cases, a viscous and sticky black liquid was obtained after the stipulated reaction time. The liquid was found to be soluble in organic solvents like methanol. Liquefaction efficiency of wood powder was found to depend on the type of liquefying reagent and quantity of liquefying agent. Liquefaction of up to 92% was achieved with phenol as the liquefying agent at 1:3 liquid ratio. Characteristics of liquefied wood and residues were also investigated. The liquefaction of wood opens up new avenues for utilization by recycling of wood waste for value added products.

Key words: Liquefaction, Lignocellulosic, Phenol, Wood.

Introduction

The wood based industries play a significant role in growth and development of global economy in general and national economy in particular. These industries are the main driving force for the sustenance of people directly or indirectly associated with forest and forest based activities. The liquefaction process is one of potential activities which can provide opportunities to utilize woody waste produced during primary processing of wood and the liquefied polyols can be used as raw material for development of biobased adhesive, energy, foam, polyester, preservatives, etc. The liquefaction process also provides an opportunity to utilize ligno-cellulosic wastes such saw dust, branches and twigs, agro-residues, etc., which is generally incinerated, for value added products.

The first liquefaction method was called phenolysis, involving phenol as the liquefying media with strong acids as a catalyst, which resulted in liquefaction products rich in combined phenolic compounds. Alternatively, liquefaction can also be achieved in existence of alcohols, especially polyhydric alcohols, and the resulting products can be used as polyols for the preparation of polyurethane and epoxy products (Hajime *et al.,* 2011; Niu *et al.,* 2011). It has been found that if polyhydric alcohols with appropriate molecular weights are used as reagents in the liquefaction of biomass, the resulting liquefied mixtures can be used directly as polyols to prepare polyurethane foams without any additional reaction (Wang *et al*., 2007). Chornet and Overend (1985) reported aqueous liquefaction of lignocellulosic materials which involves disaggregation of the wood ultra structure, partial depolymerization of the constitutive families (hemicelluloses, cellulose and lignin) followed by solubilization of the depolymerized material. Yao (1996), using Japanese birch as a wood sample, reported that the rapid liquefaction stage was mainly attributed to the components of lignin, hemicelluloses and some readily accessible cellulose, while the second stage, characterized by the slow decrease of residue amount, mainly depended upon the hard-to-access cellulose. In case of softwood samples, used in this experiment, wood constituents liquefied in the first stage may have affected the reaction rates of the subsequent stages.

Alma and co-workers (1995, 1996) 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^{0}C-180^{0}C or without catalysts at temperatures of 180^{0}C-250^{0}C. In their extensive studies, they used both strong acid such as sulphuric acid and, hydrochloric acid and weak acid such as phosphoric acid, oxalic acid as

The liquefaction of wood powder in different liquefying media to produce chemically active liquid which has potential to be used as a raw material for different products.

liquefaction catalyst. In presence of strong acid, the liquefaction reaction proceeded smoothly while in presence of weak acid liquefaction was slow and incomplete. However, the use of strong acid leads to many negative results, such as serious corrosion of metallic equipments and rapid hydrolysis of wood. On the other hands, although the biomass could be liquefied sufficiently without any catalyst, the viscosity of liquefied biomass is very high and very difficult to transfer from reactor.

This paper emphasized on the liquefaction of wood waste powder in different liquefying media at different reaction conditions to produce chemically active liquid which has potential to be used as a raw material for development of different value added products. The liquefaction of wood opens up new avenues for utilization of wood waste for value added products.

Material and Methods

Material

The wood waste were collected, chipped into piece and pulverized to various mesh size as per BSS standard. Prior to the liquefaction process, the sawdust was dried in a laboratory oven (103^{0}C, 24 h). Glycerol (AR grade), Polyethylene Glycol (PEG-400) Laboratory Grade, Phenol (LR grade) supplied by The Industrial and Laboratories co. Mysore, India were used as the reaction reagents, and Hydrochloric acid (HCl) (LR. grade) was used as the catalyst.

Liquefaction of wood

The oven dry wood powder was used for the production of liquefied wood. The liquefaction reaction was carried out with three liquefying agents and at three temperatures. The liquid ratio between the sawdust and the various solvent such as phenol, glycerol and polyethylene glycol (PEG 400) kept in 1:2 and 1:3 ratio of wood powder were the different reaction conditions for liquefaction process. The liquefaction reaction was performed in a glass laboratory reactor, which was immersed in an oil bath that was preheated to the desired reaction temperature (120^{0}C, 140^{0}C and 160^{0}C). Wood powder was loaded in the reactor and the liquefying media was added to wood along - with the catalyst (on wt basis). After the liquefaction reaction process, the liquefied wood was diluted with excess methanol and filtered through glass filter paper under reduced pressure on G1 filtration apparatus. Methanol was recovered by distillation to obtain liquefied wood. The residual was dried in oven at 105^{0}C till it attained constant weight and was used to estimate liquefaction efficiency. The liquefaction efficiency (LE, %) was calculated from the initial weight of wood meal and residual weight using the following equation.

$$\text{Liquefaction efficiency LE (\%)} = \frac{m_0 - m_1}{m_0} \times 100$$

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

Estimation of acid number and hydroxyl values of polyols

The acid number of the biomass-based polyols was measured by titration method. A mixture of 1 g liquefied wood sample and 20 ml Dioxane – water solution (4:1 V/V) was titrated with 1 mol/L NaOH to pH 8.3 using a pH meter to indicate the end point. The number of milligrams of KOH required to neutralize the acid in one gram of sample was calculated as follows:

$$\text{Acid Value (mg KOH/9)} = \frac{56.1 \times V \times N}{W}$$

Where *V* is the consumed amount of sodium hydroxide solution at the neutralization point (ml); *N* is the equivalent concentration of potassium hydroxide solution used; and *W* is the weight of the sample (g).

The hydroxyl number of a liquefied mixture was measured as the number of milligram of potassium hydroxide equivalent to the Phthalic anhydride consumed in the phthalification of one gram of sample. Ten millilitre of Phthalic anhydride solution (dissolving 150g of Phthalic anhydride in 900 ml of 1-4 Dioxane and 100 ml of pyridine) and 1g of liquefied wood sample were added into a 150 ml beaker. The beaker was covered with aluminum foil and kept in a boiling water bath for 20 minutes. After cooling down, 20 ml of Dioxane –water solution (4:1V/V) and 5ml water were added to the beaker and then titrated with 1 mol/L NaOH to pH 8.3 using pH meter to indicate the end point. Blank titration was conducted using the same procedure. The hydroxyl number was calculated according to the following equation:

$$\text{Hydroxyl Number (mg KOH/9)} = \frac{(B-C) \times 56.1 \times N}{w} \times 100 + A$$

where *B* is the blank titration volume of the sodium hydroxide solution for the Pthalic anhydride-pyridine reagent (ml); *C* is the volume of the sodium hydroxide solution consumed in the back-titration of the sample (ml); *N* is the equivalent concentration of KOH solution; *W* is the weight of the sample (g); and *A* is the acid value of the sample (mg KOH/g).

FTIR analysis of the liquefied biomass-based polyols

The changes of components of the liquefied biomass based polyols during the liquefaction were analyzed by using Bruker make Fourier transform infrared

(FTIR) spectrometer (Tensor 27 model). The spectra were recorded for wood meal, liquefied wood, 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. The KBr was previously oven-dried at 105°C to reduce the interference of water.

Result and Discussion

The effect of various liquefying agents such as phenol, glycerol and polyethylene Glycol (PEG-400) on the liquefaction reaction and liquefaction efficiency under conventional bath heating is given in Table 1.

The results indicated that liquefaction efficiency varied from 76% to 92% in these solvents under different reaction conditions. It was observed that the liquefaction efficiency increased with increase of liquid ratio and temperature in all the solvent systems. The liquefaction efficiency was highest in phenol based liquefaction followed by PEG -400 and glycerol. The liquefaction in phenol increased from 76.26% to 86.75% at 1:2 liquid ratio when the temperature was increased from 120°C to 160°C. Similarly, at 1:3 liquid ratio, the increase in liquefaction efficiency was found to be 81.06% to 91.66%. The liquefaction reaction with glycerol as liquefying agents comparatively low and was ranging from 58.69% - 78.36 % under different reaction conditions. The liquefaction reaction with polyethylene glycol (PEG-400) indicates liquefaction efficiency from 62.23% to 82.93%.

It was observed that the difference in liquefaction efficiency in phenol between temperature 140°C and 160°C was not remarkably higher in both 1:2 and 1:3 liquid ratio. Thus 140°C temperature was found to be the optimum reaction temperature.

The acid value and hydroxyl values are estimates of chemical reactivity of polyols which needs to be understood in order to develop value added products from polyols. The acid value of polyols indicates the number of free H^+ ions and hydroxyl value represents the number of OH^- ions available for further reaction. The acid values and hydroxyl values of liquefied wood in phenol are shown in Table 2. The acid value of liquefied wood varied from 16.78 to 19.74 mg KOH/g and hydroxyl value varied from 163 -181 mg KOH/g.

The acid values and hydroxyl values for wood liquefied in glycerol and PEG-400 are given in table 3 and 4 respectively. The acid value of wood powder polyols after liquefaction in glycerol varied from 4.67 to 6.89 mg KOH/g and hydroxyl value varied from 221-238 mg KOH/g (Table 3). The acid value of wood powder liquefied in PEG -400 varies from 10.91 to 15.94 and hydroxyl value of wood powder after liquefaction varies from 185-210 mg KOH/g.

Table 1: Liquefaction efficiency of wood powder in phenol, glycerol and PEG-400 liquefying media.

Temperature ↓ / Liquid ratio →	Liquefaction efficiency (%) in phenol		Liquefaction efficiency (%) in Glycerol		Liquefaction efficiency (%) in PEG-400	
	1:2	1:3	1:2	1:3	1:2	1:3
120°C	76.26	81.06	58.69	63.06	62.23	67.95
140°C	83.35	88.57	65.76	74.05	70.24	76.23
160°C	86.75	91.66	73.83	78.36	78.27	82.93

Table 2: Acid value and hydroxyl value of wood liquefied in phenol.

Temperature ↓ / Liquid ratio →	Acid Value (mg KOH/g)		Hydroxyl value (mg KOH/g)	
	1:2	1:3	1:2	1:3
120°C	18.03	19.74	174	163
140°C	17.13	18.93	179	176
160°C	16.78	17.33	181	178

Table 3: Acid value and hydroxyl value of wood liquefied in glycerol.

Temperature ↓ / Liquid ratio →	Acid Value (mg KOH/g)		Hydroxyl value (mg KOH/g)	
	1:2	1:3	1:2	1:3
120°C	5.46	6.89	227	221
140°C	5.19	6.25	229	226
160°C	4.67	5.65	236	238

Table 4: Acid value and hydroxyl value of wood liquefied in PEG-400.

Temperature ↓ / Liquid ratio →	Acid Value (mg KOH/g)		Hydroxyl value (mg KOH/g)	
	1:2	1:3	1:2	1:3
120°C	13.78	15.94	193	185
140°C	12.16	14.61	196	192
160°C	10.91	13.30	210	194

The results indicated that the acid value of polyols is lowest in wood liquefied in glycerol and correspondingly have highest hydroxyl value. The high acid value of phenol base liquefied wood may be attributed to highly acidic nature of phenol, which also would have been the major reason for high liquefaction efficiency of wood in phenol as compared to both PEG and glycerol.

The insoluble residues from the liquefaction process as well as liquefied wood were analyzed by FTIR spectroscopy. Spectra of residue differ significantly from the spectrum of wood. Absorption bands at 1719 cm^{-1} and 1286 cm-1 have almost disappeared while the intensity of the band at 1506 cm^{-1} and 1600 cm^{-1} has reduced considerably in residue (Fig. 1). These changes in the band intensity of residues and in liquefied wood indicate complete dissolution of hemicelluloses and lignin as the strong band at 1719 cm^{-1} in wood is indicative of carbohydrate specifically xylan which dominates hemicelluloses in hardwood while the band at 1600 cm^{-1} and 1506 cm^{-1} are indicative of benzene ring breathing in lignin. The band at 1286 cm^{-1} is due to C–O stretching vibration in lignin. The strong band at 3386 cm^{-1} is due to o-H strong stretching vibration in phenolic component dissolved and appears in liquefied wood. The FTIR spectroscopic analysis of the residuals indicated complete dissolution of lignin and partial dissolution of cellulose.

Developments of adhesives from liquefied wood

Adhesive was synthesized from the liquefied wood

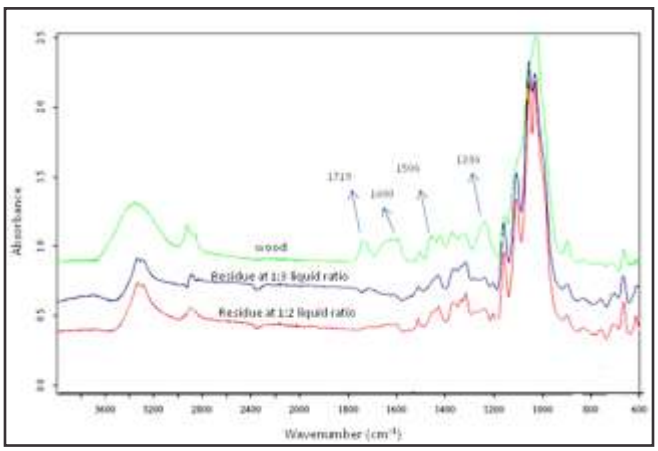

Fig. 1: FTIR analysis of wood residues at different liquid ratio.

replacing phenol, which is conventionally used in phenolic resin. Phenol liquefied wood was reacted with formaldehyde in proportion of 1:1.5-1.8. The reaction was carried out in a three neck resin kettle. The phenol based liquefied wood was reacted with formaldehyde in presence of catalyst. The reaction was continued with stirring for exothermic reaction initiated. Then reaction continued for 120 min at 90°C until bubbles stops. The water tolerance and pH value were checked regularly and finally maintained at 8.7. Then prepared resin was kept overnight for further process and some amount kept in oven for calculation of solid content of resin. The desired traits of adhesive shows better quality than phenol formaldehyde resin and may be a suitable substitute for phenol in PF based adhesives.

Plywood with 3 plies of 1 foot by 1 foot dimensions were prepared by using liquefied wood polyols. The liquefied wood polyols based adhesive was applied on the both surface of core veneer by brushing and kept for 45minutes for drying. The face veneers were placed on top and bottom of the core veneer, with grain direction of core veneer was perpendicular to the face veneers. Then assembled boards were pressed under hot press machine. The platens were pre-heated to 155°C temperature and a pressure of 15.5 kg/cm^2 was applied for 10 minutes. After the stipulated time under hot-press, the board was removed from press, sponged with water to avoid the excessive drying of face veneers and conditioned for overnight at room temperature. The specimens were cut from the prepared boards for glue adhesion test as per IS specification IS: 848:1983. The initial results indicated that the plywood made from the liquefied wood based adhesives meet the requirement for warm water resistant and boiling water resistant grade.

Conclusion

Liquefaction efficiency of wood powder was found to depend on the type of liquefying reagent, liquid ratio and temperature. Liquefaction of up to 92 % was achieved with phenol as the liquefying agent at 1:3 liquid ratio which was the highest as compared to other solvents like Glycerol and Polyethylene Glycol (PEG-400). The wood liquefied with phenol was used for preparation of adhesive and plywood panels were prepared using the

adhesive. The adhesives appeared to be a promising replacement of conventional PF resin. However further studies need to be carried out on viscosity, shelf-life and flow time for industrial scale applicability. The liquefaction of wood opens up new avenues for utilization by recycling of wood waste for value added products.

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काष्ठ अपशिष्ठ का द्रवीकरण : अपशिष्ठ काष्ठ के उपयोग में एक सक्षम मार्ग

अनिल कुमार, ए.के. सेठी और शक्ति चौहान

सारांश

लिग्नों–सेल्यूलोसिक जैवमात्रा के द्रवीकरण नए पदार्थों, आसंजकों एवं राल प्रणालियों का विकास करने के लिए रासायनिक रूपान्तरण प्रौद्योगिकी में से एक है। प्रक्रिया उपयोगिता परिवर्धित उत्पादों के लिए लिग्नों–सेल्यूलोसिक अपशिष्टों यथा–बुरादा, अपरिष्कृत काष्ठ आधारित मदों (ठोस एवं संग्रथित काष्ठ) के टुकड़े, और सेवा के बाद फर्नीचर, काष्ठीय अपशिष्टों, शाखाओं एवं टहनियों का उपयोग करने का सुअवसर भी उपलब्ध कराती है। काष्ठाधारित उद्योगों द्वारा बड़ी मात्रा में बुरादे तथा काष्ठ बचत और अन्य प्रकार के काष्ठ अपशिष्टों का उत्पादन होता है, जिसे सामान्यत: भस्म कर दिया जाता है। यह शोधपत्र रासायनिक रूप से सक्रिय द्रव उत्पादित करने के लिए विभिन्न द्रवीकरण मीडिया में काष्ठ पाउडर का द्रवीकरण प्रस्तुत करता है, जिसमें विभिन्न उत्पाद के लिए एक कच्चे पदार्थ के रूप में उपयोग की क्षमता है। विभिन्न द्रवीकरण एजेन्टों के साथ 120 डि.से., 140 डि.से., और 160 डि.से. तापमानों पर काष्ठ द्रवीकरण किया गया। सभी मामलों में एक अनुबद्ध अभिक्रिया समय के बाद एक श्यान एवं चिपचिपा काला द्रव प्राप्त हुआ। द्रव आर्गेनिक विलायकों जैसे मीथेनॉल में विलेय पाया गया। काष्ठ पाउडर की द्रवीकरण क्षमता द्रवीकरण अभिकर्मक, द्रवीकरण एजेन्ट की मात्रा, काष्ठ की नमी मात्रा, अभिक्रिया समय एवं तापमान की किस्म पर निर्भर पाई गई। 3:1 द्रव अनुपात पर द्रवीकरण एजेन्ट के रूप में फीनॉल के साथ 92 प्रतिशत तक द्रवीकरण हासिल किया गया। द्रवीकृत काष्ठ और अपशिष्टों के लक्षणों की भी जांच की गई। उपयोगिता परिवर्धित उत्पादों के लिए काष्ठ अपशिष्ट के पुनरचक्रण द्वारा उपयोग हेतु काष्ठ के द्रवीकरण नए मार्गों को खोलते हैं।

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