

# Conversion of Corn stover and Wheat Straw Fermentation residue (FR) to valuable Resin

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Available online at: [www.isroset.org](http://www.isroset.org)

Received: 24/Jan/2020, Accepted: 14/Feb/2020, Online: 28/Feb/2020

**Abstract-**Conversion of stover/wheat straw fermentation residue(FR) to valuable resin is a big challenge for current fermentation process. Carbohydrates presents in residue strongly effects on the performance as well as physical properties of the lignin base resin. In this experimental work, we overcome this problem through simple and novel technique for the production of Fermentation residue base resin by the addition of cheapest catalyst sodium hydroxide and Sodium carbonate instead of using poison catalyst lead oxide. FR syntheses from two different residue of fermentation, investigated effects of lignin and carbohydrates on the physical and chemical properties of resin. Synthesized green resin from FR were utilized for the manufacturing of plywood with satisfactory bonding strength (1.09 MPa). Harmful organic compound (Formaldehyde) emission reduced to 97%. Synthesis Resin characterized by NMR, DSC, XRD for physical properties, chemical structure and curing behavior of the resin. This work developed a sustainable technology without any waste production.

**Keywords:** Fermentation Residue, cheapest catalyst, lignin, Resin

## I. INTRODUCTION

Ethanol is a good and environment friendly bio fuel and developing more rapidly in last four decades. According to World Ethanol and renewable energy sources, ethanol production reached to 28570 Million gallons in 2018[1]. Second generation of Biofuel as an alternative and environment friendly fuel production from waste feedstock such as animal waste, human being waste material, crops waste (baggas, wheat straw, rice straw, corncob, corn straw). Some of them are Lignocellulose waste producing material [2-4]. These material required some pretreatments or conditioning for fermentation process for the conversion of waste material to Biofuel and waste residue could be serve as alternative fuel sources or other linin base other valuable compounds [5-9]. if fermentation process residue can be converted into good quality compound then ethanol production industry can be adopting cleaner production by the utilization of its all waste generation resources. During the fermentation process carbohydrates converted in to bioethanol and remaining waste contain mainly lignin, protein, and unconverted cellulosic, hemicellulose material. Some time there was so much unnecessary compound produced during ethanol production due to feedstock fraction variation, environment condition changing, hidden errors in process parameters but most of them useless is lignin and there is valuable application of it [10]. It is a challenge for pretreatment and separation of lignin from other material then the conversion of lignin to valuable compounds/resin [11-13]. Resins are complex oil modified polyesters that serves as the film forming agent in some paints and clear coating<sup>[14]</sup>. Resin and emulsion both are two types of polymer. In recent year study it was investigated that conversion of lignin into resin, aromatic compounds, bio oil, carbon material and polymer matrixed [14-17]. Huge investment is required for the separation of different types of lignin such as Kraft lignin, organosolve lignin, steam exploded lignin and lignosulfonate so that's why it is cheapest solution to convert into valuable resin instead of separation / reaming in waste and added into pollution fraction[18-22]. In general fermentation process waste can be directly utilized for the conversion of biogas, animal feed, and bioplastic [23-24]. Lignin base resin is a valuable and green compound derived from different type resin of waste material. Lignin possess aromatic structure. It is possible to partially substitute lignin for phenol obtained from petroleum industries [25]. Resin is an important material for plywood [26]. according to food and agricultural organization annually plywood production  $415.9 \times 10^6 \text{m}^3$  in 2017 and biggest manufacturer is china producing  $204.7 \times 10^{10} \text{m}^3$ [27]. Phenol was used as an adhesive but lignin can be convert into resin for this applications. It will decrease the dependency on the phenol base resin [28]. Wheat flour is also using as a raw material for plywood material, 20-30% (w/w) wheat flour is usually added in the plywood material. [29]. Fermentation residue base resin(FRs) and Lignin base resins(LRs) that was further characterized by NMR, DSC, XRD. In this study we convert fermentation residue to resin without ant producing waste.

## II. MATERIALS AND METHODOLOGY

### *Materials*

fermentation residues (R) were obtained from industrial scale plants in Pakistan. R1 denotes the fermentation residue derived from acid-steam-exploded corn stover supplied by local former. R2 denotes the fermentation residue that resulted from the processing of neutral- steam-exploded wheat stover supplied by local former). Both R1 and R2 were directly used without further purification and modification. Phenol (97%), formaldehyde aqueous solution (36%), solid urea (99%), sodium hydroxide (98%), and sodium carbonate (99%) of analytical grade were used without further purification.

### *Syntheses of fermentation residue based resin*

Resinification was carried out to partially replace phenol with resins in the production of FRs. The synthesis of FRs was carried out in a round bottom flask three necks equipped with temperature sensor as well as heat exchanger/condenser for the condensation of Polycondensation water vapors and equipped with 15RPM automatic mechanical stirrer. The substitution rate of lignin to phenol was set at 50% (w/w). The lignin content was calculated based on the chemical composition of the fermentation residues. Urea, formaldehyde, and phenol were prepared in the laboratory with a molar proportion of 1.0: 4.0: 1.0 via two-step reactions. The Resinification was catalyzed by sodium hydroxide and sodium carbonate. In the first step, urea and half of the formaldehyde were placed in the reaction flask, and the temperature was gradually increased to 110 °C. The system was maintained at 110 °C for 50 minutes, and the pH was maintained at 9.5. During the second step, the remaining formaldehyde, phenol, fermentation residues, sodium hydroxide solution, and carbonate were added to the mixture. The system was maintained at 110 °C for 50 minutes, and then, the temperature was reduced to 95 °C for 40 minutes. The temperature was then decreased to 65 °C, and 6.2 g of urea and 30 g of sodium hydroxide solution were added and reacted 40 minutes. The obtained resins were rapidly cooled and stored at room temperature before further uses. LR, FR separated by centrifuging. The Fermentation residue were characterized by XRD to examine the structural feature.

## III. RESULTS AND DISCUSSION

### *Structure and curing behavior characterization of the prepared resins*

The solution-state  $^{13}\text{C}$  NMR and solid-state CP-MAS  $^{13}\text{C}$  NMR spectra were acquired on a Bruker AV-III 400 MHz spectrometer (Germany). The cured resins were prepared by treating the uncured resins at 135 °C for 3 hours in an air convection oven [30-34]. The DSC analysis of the uncured freeze-dried resins was performed on a Shimadzu DSC-60A (Japan) under a nitrogen atmosphere with a flow rate of 60 mL min<sup>-1</sup>. Scans were run at heating rates of 5 °C min<sup>-1</sup>, 10 °C min<sup>-1</sup>, and 15 °C min<sup>-1</sup>. The scanning temperature ranged from 30 °C to 200 °C.

### *Properties of the prepared resin adhesives and plywood testing*

The viscosity, PH, solid content of the LR and FR adhesives were determined in accordance with the Chinese National Standard (GB/T 14074-2017). The performance of the LR and FRs was tested by preparing plywood and evaluating the formaldehyde emission and bonding strength according to the Chinese National Standard (GB/T 17657-1999). Duplicate three-layer laboratory plywood panels (330 mm × 330 mm × 6.1 mm) were prepared using LR and FR adhesives and poplar veneers without any curing agent. The FR adhesives were mixed with 20% (w/w, based on the solid resin and water) wheat flour as filler. The LR was firstly adjusted so that the solid content would be the same as that of the FRs. The LR was then mixed with 30% (w/w, based on resin) wheat flour as filler. The glue spread was 325 g m<sup>-2</sup> and consisted of a single glue line. The plywood was hot-pressed at 125 °C under 1.5 MPa for 340 s (80 s mm<sup>-1</sup>). Hot pressing, the plywood was stored in an ambient environment for 18 hours before further testing. The glue lines in the plywood bonded with FR and LR adhesives were tested by fluorescence microscopy (FM) according to a previous study [41-45].

### *Chemical composition of Fermentation residue*

The chemical composition of the fermentation residues was investigated according to the standard laboratory analytical procedure developed by national renewable energy Laboratory (NEREL/TP-510-42618)[35]. Chemical composition of two fermentation residue is listed in the table 1. And comparison of two sample was carried out on the bases of its constituents and lignin is a important element which was converted into resin. In this process polycondensation reaction was occurred between lignin, urea, phenol, formaldehyde As shown in Table 1, both R<sub>1</sub> and R<sub>2</sub> consisted of a portion of the protein that originated from the enzyme and yeast. Protein is also a feedstock that can be used to produce bio- based resins, which can partially replace petroleum-based wood resin adhesives.[36-40].

Due to the limitations of high viscosity, short durability, and poor water resistance, protein-based resins are unsuitable for wide applications.<sup>25,26</sup> According to the reported research, alkaline treatment results in the unfolding of the globular structure of protein to allow entry of hydrophilic and hydrophobic groups and exposure so that they can make contact with each other, which can improve the bonding strength.<sup>27,28</sup> In this work, the pH value of the prepared resins was approximately 12. This ambient alkaline environment properly reduced the viscosity and increased the water tolerance of resins, which was proved by the

viscosity and bonding strength, as shown in Table 2. The above results indicated that adding carbohydrates to the lignin-based resin adhesive would significantly improve the performance of wood resin adhesive *via* this simple and novel process, and this overcame the adverse effect of carbohydrates and protein on the resin adhesive [46-48]. The excellent performance of the fermentation residue resin adhesive was investigated in detail *via* properties, structural characterizations, and formation mechanism of FRs in the following sections, especially the synergistic effect of lignin and carbohydrates.

**Table 1:** chemical composition of fermentation residue samples

Composition	R1	R2
Total Lignin	73.7	60.7
Kalson lignin	65.98	38.9
Acid soluble lignin	2.7	4.8
Carbohydrates	11.06	15.06
Golucose	10.9	13.9
Xylose	0.8	0.9
Protein	10.8	12.8
other	4.0	2.0

### **Properties and performance of prepared resin adhesives**

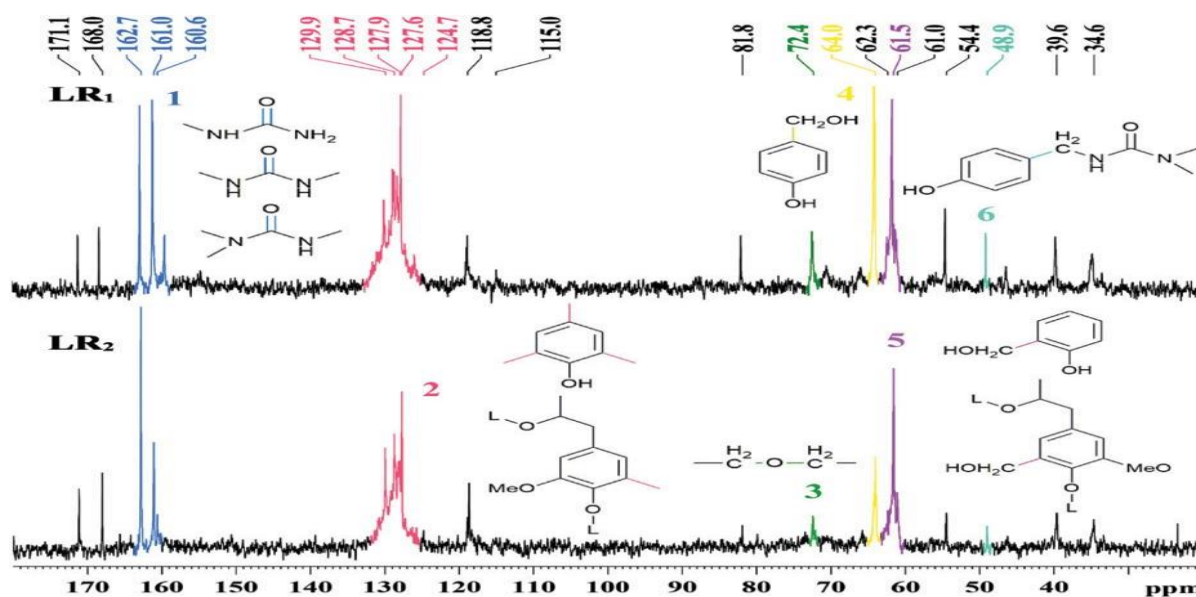
The physical properties of FR and LR adhesives were tested according to the Chinese National Standard (GB/T 14074- 2017), and the results are listed in Table 2. The solid content of LRs was lower than that of FRs because the SRs separated from the FRs. In addition, the viscosity of FRs was higher than that of LRs, which implied that the viscosity was also markedly influenced by the SRs. This indicated that the SRs in FRs could perform the same function as that of wheat flour to adjust the viscosity of the adhesive to an optimum condition. The pH values of the FRs and LRs were constant, and all reached the Chinese National Standard [49]. The adhesion strength of the FRs and LRs was tested for their ability to bond pieces of plywood. The solid content of LRs was firstly adjusted so that they contained the same net resins as those in FRs, which would ensure that an equal quantity of adhesives was used to glue each piece of plywood. The bonding strength and formaldehyde emission of plywood were tested according to the Chinese National Standard (GB/T 17657-1999), and the results are shown in Table 2. The bonding strength of the plywood bonded with FRs reached the requirements of exterior-grade panels (first grade,  $\geq 0.7$  MPa). The bonding strength of the plywood bonded with FR<sub>1</sub> and LR<sub>1</sub> was distinctly higher than that bonded with FR<sub>2</sub> and LR<sub>2</sub>, and this was due to the carbohydrates in the fermentation residues that hindered the condensation reaction. Formaldehyde pollution of the indoor environment mainly comes from wood panel products.<sup>29</sup> The formaldehyde emission of plywood bonded with FRs met the  $E_0$  grade ( $\leq 0.5$  mg L<sup>-1</sup>) as specified by the Chinese National Standard (GB/T 9846.3-2004), and that with FR<sub>2</sub> was extremely low (0.03 mg L<sup>-1</sup>). The low amount of released formaldehyde is beneficial for the environment. If wood-based panels are produced using these green FRs, the formaldehyde content will be reduced by a maximum of 94%, as compared with  $E_0$  grade. As compared with the traditional lignin-phenol-formaldehyde (LPF) resin adhesives (substitution rate of lignin to phenol was 50% w/w), the bonding strength of FR<sub>1</sub> was approximately equal to that of LPF resins. The formaldehyde emission of FR<sub>2</sub> was markedly lower than that of LPF resins.<sup>30-32</sup> It was noteworthy that the traditional LPF resin adhesives were synthesized with high-purity lignin as the feedstock. Moreover, modification was usually conducted to increase the reactive sites of lignin.<sup>33-35</sup> In addition, a more optimal comprehensive performance of plywood using FR<sub>2</sub> adhesive (solid content 41.0%) was obtained than that of plywood using other ethanol biorefinery residue-based adhesives (solid content 50.0%).<sup>18,36</sup> Both bonding strengths met the requirements of the Chinese National Standard, but the formaldehyde emission of the plywood using FR<sub>2</sub> adhesive (0.03 mg L<sup>-1</sup>) was significantly lower than that of the plywood in previous works (0.23 mg L<sup>-1</sup>). The wood failure of the plywood bonded with FRs and LRs is shown in Fig. 1. The wood failure of the plywood bonded with FR<sub>1</sub> was markedly higher than that with others, which was consistent with the results of the bonding strength tests. To investigate the functions of each component in the fermentation residue, the lignins derived from fermentation residues were also used to produce resins LR<sub>3</sub> and LR<sub>4</sub>, which were compared, and the properties are listed in Table S2.† The bonding strength of LR<sub>3</sub> and LR<sub>4</sub> was lower than that of the FRs. The formaldehyde emission of LR<sub>3</sub> and LR<sub>4</sub> was extremely higher than that of the FRs and even  $E_0$  grade. These results indicated that lignin can react with urea, phenol, and formaldehyde to form lignin-based resin adhesive, while the carbohydrate and protein increased the viscosity of the resin adhesive to increase the bond strength and suppress the amount of formaldehyde released. Based on the process described above, the fermentation residues from the bioethanol process could be directly used to prepare high quality co-condensed FRs. More importantly, these satisfying results indicated that the addition of carbohydrate could greatly improve the performance of the resin adhesives. Additionally, the direct transformation of the fermentation residues into bulk and high-value products can contribute to the sustainability and cost-effectiveness of both bioethanol production and wood manufacturing.

Table 2: Adhesive Properties and Plywood Performance of the FR and LR adhesive

Adhesive	Adhesive properties			Plywood performance	
	Solid content (%)	pH (25 °C)	Viscosity (22 °C, mPas)	Bonding strength (MPa)	Formaldehyde emission (mg L <sup>-1</sup> )
FR <sub>1</sub>	44.4	12.2	3191.0	1.07	0.17
LR <sub>1</sub>	38.6	12.1	37.8	0.88	0.11
FR <sub>2</sub>	41.0	12.0	3503.0	0.78	0.03
LR <sub>2</sub>	34.3	12.1	16.8	0.60	0.02
GB/T 14074-2017	≥35.0	≥7.0	≥60.0	≥0.70 <sup>a</sup>	≤0.50

### Solution-state <sup>13</sup>C NMR of the uncured lignin-based resins

The performance of the resins correlates with their chemical structures. To avoid the disturbance of carbohydrates, the chemical structures of the LRs were investigated by obtaining solution-state <sup>13</sup>C NMR spectra. Fig. 2 shows the <sup>13</sup>C NMR spectra of the freeze-dried uncured LRs, while the <sup>13</sup>C NMR spectra of the lignin separated from residues are also displayed. The signals were assigned according to previous studies[50]. There were some significant differences between the spectra of LR<sub>1</sub> and LR<sub>2</sub>. The series of peaks from 160.6 to 162.7 ppm were attributed to the carbonyl peaks of urea, indicating that the urea was mainly substituted. There are signals from the carbonyl groups of mono substituted (162.7 ppm), di substituted (161.0 ppm), and tri substituted (160.6 ppm) urea in LRs.<sup>38,39</sup> The di- substituted and trisubstituted urea of LR<sub>1</sub> was markedly higher than that of LR<sub>2</sub>, which indicated that there were more co-condensed linkages among urea, phenol, formaldehyde, and lignin. The series of peaks from 124.7 to 129.9 ppm represents the reacted sites of the aromatic nucleus (C-C) in the phenol and lignin. The chemical shift of substituted *ortho* carbon sites on the aromatic ring in LR<sub>1</sub> (127.6 ppm) was obviously stronger than that in LR<sub>2</sub>. Unsubstituted *para* and *ortho* carbons were present at 118.8 ppm and 115.0 ppm, respectively.<sup>30,39</sup> There were more unsubstituted *para* carbon sites on the aromatic ring in LR<sub>2</sub> as compared to those in LR<sub>1</sub>. These results indicated that more *ortho* and *para* sites in R<sub>1</sub> reacted with formaldehyde and urea than those in R<sub>2</sub>. In addition, the unsubstituted *ortho* carbon sites were scarce both in LR<sub>1</sub> and LR<sub>2</sub>. This was due to the fact that the catalyst Na<sub>2</sub>CO<sub>3</sub> hydrolyzed and formed bicarbonate ions during the synthesis process. The bicarbonate ions accelerated the condensation reaction of formaldehyde or methylol groups towards the *ortho* positions of benzene rings.<sup>40-42</sup> The signals around 81.8 ppm belong to methylene glycol (HO-CH<sub>2</sub>OH, free formaldehyde), especially in LR<sub>1</sub>.<sup>31,36</sup> This accounted for the higher formaldehyde emission of the plywood bonded by LR<sub>1</sub> than that by LR<sub>2</sub>. The signals at 72.4 ppm were assigned to the methylene ether linkages formed during the condensation process of phenolic resins.<sup>40</sup> The intensity of the methylene ether peaks of LR<sub>1</sub> was markedly stronger than that of LR<sub>2</sub>. The intensity of the peak at 64.0 ppm (*p*-Ph-CH<sub>2</sub>OH) and 61.5 ppm (*o*-Ph-CH<sub>2</sub>OH) of LR<sub>1</sub> was higher than that of LR<sub>2</sub>.<sup>40</sup> The *para* position of the phenolic -OH was provided by the phenol, and the *para* position in phenol was more active as compared to the *ortho* position. This implied that the carbohydrates in the fermentation residues formed steric hindrance to impede the condensation reaction of the *para* position of phenol. The signals at 54.4 ppm are attributed to the methylene group between urea (-NH-CH<sub>2</sub>-N(CH<sub>2</sub>-)-).<sup>37</sup> The strong signals at 48.9 are assigned to the *para* co-condensed methylene group (Ph-CH<sub>2</sub>-N(CH<sub>2</sub>-)CO-).<sup>40</sup> The intensity of the co-condensed peaks of LR<sub>1</sub> was obviously higher than those of LR<sub>2</sub>. In addition, this also indicated that the *para* position of phenol was more active than the *ortho* position, and the lignin was extremely less active than the phenol. The signals at 39.6 and 34.6 ppm are attributed to *p,p* Ph-CH<sub>2</sub>-Ph and *o,p* Ph-CH<sub>2</sub>-Ph, respectively, and the intensity of these peaks of LRs was nearly the same.<sup>39</sup> According to the results of solution-state <sup>13</sup>C NMR, the schematic of the main synthetic route of FRs is shown in Fig. S4.†

Figure 1: Solution State <sup>13</sup>C NMR spectra of the LRs



**Solid-state CP-MAS  $^{13}\text{C}$  NMR of the uncured and cured resins**

The solid-state CP-MAS  $^{13}\text{C}$  NMR technique was chosen to study the curing behavior of FRs and LRs. The spectra of cured as well as uncured FRs and LRs are shown in Fig. 3. The spinning side bands present in the range of 78.5 ppm and 180.8 ppm. The signals of aromatic carbons of methylene ether bridges is 161.3 ppm bridges, some of which was broken during the curing process. The signals around 152.7 ppm and 129.8 ppm are attributed to the phenolic hydroxyl and the substituted aromatic carbons, respectively [18,40]. The peaks around 103.9, 88.0, 78.5, 70.3, and 62.6 ppm were assigned to carbohydrates, and the intensity of these signals were the strongest for FR<sub>2</sub> because of its higher carbohydrate content[50]. These carbohydrate signals exist in superposition with the signals of co-condensed resins. The peaks around 70.3 ppm decreased as the aliphatic carbons of methylene ether bridges cracked during the curing process. The decrease in the signals around 62.6 was accompanied by an obvious increase at 31.1–38.6 ppm. This indicated that the main reaction was that of condensation between methylol groups and remaining unsubstituted *para* and *ortho* positions of benzene rings during the curing process. In general, the spectra of the cured FRs were broadly similar in signals. This signified that the FRs could be directly used to produce phenolic resin adhesives that had stable chemical structures. According to the statistics of the report on China Wood-based Panels Industry 2018, the phenolic resin consumption was reached to 1.43 million tons in the Chinese wood panel industry in 2017[51]. If fermentation residues are used to substitute 50% of the phenol when producing adhesives, the consumption of phenol will be reduced by over  $100 \times 10^3$  tons/year in China, and the cost of wood manufacture will also decrease

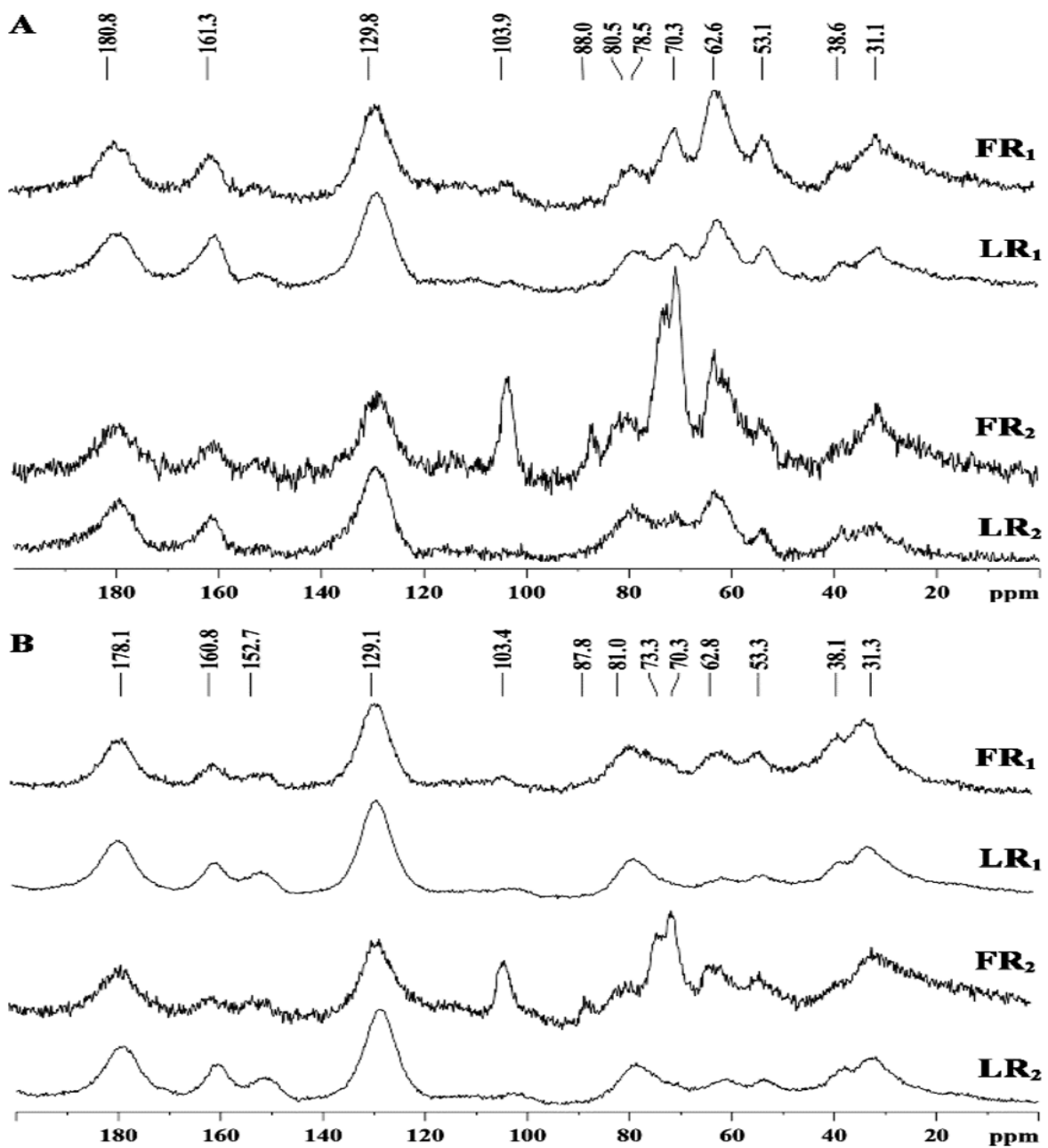


Figure 2: Solid State CP-MAS  $^{13}\text{C}$  NMR spectra of the (A) uncured and (B) cured FRs and LRs

### Thermal behavior of the lignin-based resins

The curing process during the manufacturing of resin is a critical and required high attention, and it has a major impact on plywood and play vital role of the performance. The curing kinetic analyses of LR<sub>s</sub> were performed using dynamic scanning calorimetry (DSC) at different heating rates. The DSC kinetic analysis began by obtaining the kinetic parameters from the first exothermal peak temperatures of the DSC scanning curves at various heating rates. The activation energy data were calculated according to the method of Kissinger (1) and Flynn–Wall–Ozawa (2): Fermentation residue can be used for the manufacturing of lignin base high quality resin and having low cost as compared to adhesive/phenolic base resin. Now we present a new technology which produced high quality lignin base resin with producing wastages as well as no need of further purifications. Herein, we developed a simple and novel strategy to successfully overcome this drawback by using bioethanol fermentation residues (lignin-rich substrates) to produce green and high-quality resins without any purification and modification. The eco-friendly FR<sub>s</sub> can substantially reduce the usage of phenol and the emission of formaldehyde. The co-condensed linkages among urea, formaldehyde, phenol, and lignin were sufficiently abundant so that a firm structure of the resins could be built. The solid residues (carbohydrate-rich substrate) could be satisfactorily used instead of wheat flour to adjust the viscosity, prevent excessive osmosis, and distinctly increase the bonding strength of the resins. Under the synergistic effect of lignin and carbo- hydrates, the fermentation residue-based resins could be utilized to prepare plywood with satisfactory performance. The high-efficiency application of the fermentation residues can realize green production with zero waste, as well as increase the revenue and stimulate the sustainable development of bioethanol manufacturing. This work bridges bioethanol fer- mentation residues and petroleum-based products, affording a green and sustainable strategy that is of great importance for the full valorization of lignocellulose, and will decrease chemi- cal dependence on fossil-based resources

### X-ray diffraction (XRD) analyses of solid residues in fermentation residue-based resins

The cellulose crystal structure is a significant property that may result in variation and influence the scarification kinetics during the bioethanol production process [50-51]. XRD characterized the structure of the fermentation residues (RS) and solid residues (SR<sub>s</sub>) base resin. The XRD images are shown in Fig. 4, and the crystallinity index (CrIs) values of the R<sub>s</sub> and SR<sub>s</sub> were cal- culated according to the XRD. The peak of amorphous cellulose 17.7° (R<sub>1</sub> and SR<sub>1</sub>) and 18.1 (R<sub>2</sub> and SR<sub>2</sub>), and the peaks at 16.5° and 22.2° are crystalline cellulose. All these types of cellulose exhibited the typical diffraction patterns of cellulose I. The original CrIs of fermentation residues were distinct from the different feedstock and bioethanol processes. The intensity of the signal band around 16.5° of R<sub>1</sub> was weaker than that of R<sub>2</sub> due to the fact that the feedstock of R<sub>1</sub> was pretreated with an acid stream explosion [52]. As we can see, a marked decrease in the CrI was found between R<sub>1</sub> and SR<sub>1</sub>. The main signal around 16.5° and 22.2° was weakened, and no peak appeared at 12.1°. These results confirmed that the cellulose in R<sub>1</sub> was in a transition state from cellulose I to cellulose II, and the expansion of the cellulose I lattice occurred under an alkaline environment[48]. In contrast, the CrI of SR<sub>2</sub> was nearly the same as that of R<sub>2</sub>.

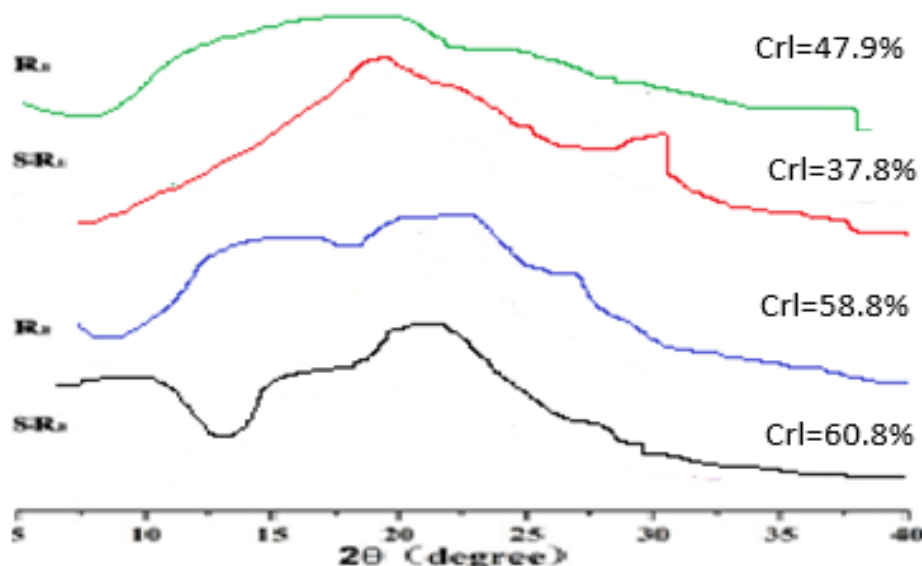


Figure 3: X-ray diffraction (XRD) analyses of solid residues in fermentation residue-based resins

### The influence of carbohydrate on the performance of resins

lignin-based resins are syntheses with high-purity technical lignin. Insufficient attached carbohydrates can reduce the feasibility of lignin usage and impede the condensation reaction due to steric hindrance when synthesizing resins. Furthermore, the carbohydrates would decrease the adhesive power of the cured resins, especially under wet conditions[51]. As shown in Fig. 2, the *para* position of the phenolic–OH was provided by the phenol, and the *para* position in phenol was more active than the *ortho* position. These implied that steric hindrance would result from the carbohydrates in the fermentation residues to impede the condensation. The cellulose could swell under alkaline circumstances, which would result in the amplification of the steric

hindrance effect. Moreover, the addition of carbohydrates markedly increased the viscosity of the reaction system and hindered the condensation reaction, which could bring about a heterogeneous reaction and adversely affect the strength of the final resins. However, in this study, the existence of the carbohydrates significantly improved the performance of resins. To evaluate the positive effect of carbohydrates, wheat flour was substituted for the SRs and blended with LR to prepare plywood. The results indicated that the strength of the plywood bonded with FRs was markedly higher than that with LR, which confirmed that the SRs in the fermentation residues enhanced the bonding strength and were satisfactory substitutes for wheat flour as filler. The satisfactory adhesion strength of FRs also favored water resistance. The glue lines in the plywood using FR and LR adhesives were tested by FM, and the images are shown in Fig. 1. The bonding strength and wood failure correlated with the osmosis of the adhesive. There was a markedly greater amount of osmosis of LR than that of FR. This result indicated that the SRs in fermentation residues acted as a filler to prevent the excessive osmosis of resin adhesives. The continuous and steady glue line could favor the bonding strength and wood failure. In general, this is the first time that the effect of solid fermentation residues has been thoroughly investigated. The carbohydrates in fermentation residues may have an adverse effect on the condensation reaction. However, by using SRs as substitutes for wheat flour, not only is the excessive osmosis of adhesives prevented, but also, the decreased use of wheat flour for this purpose will allow more of this resource to be directly used as a food source, thus increasing wheat availability and reserves. Based on these results, the fermentation residues from the bioethanol generation process can be directly used to produce high-performance resins. The synergistic effect of lignin and carbohydrates imparts new possibilities for the utilization of fermentation residues.

#### IV. CONCLUSION

Fermentation residue lignin base resin can be used for the manufacturing of plywood with high performance which decrease uses of phenolic resin to produce green resin without further purification required. Hence we investigated new, novel, applicable, easy to control technology for lignin base resin manufacturing. The eco-friendly FRs can substantially reduce the usage of phenol and the emission of formaldehyde. High quality resin is developed by co-condensed linkages among urea, formaldehyde, phenol, and lignin. We can increase viscosity of the resin by using solid fermentation residue instead of wheat flour to prevent more osmosis. The high-efficiency of lignin base resin can realize green production without waste, as well as increase the revenue. This work bridges bioethanol fermentation residues and petroleum-based products, affording a green and sustainable strategy that is of great importance for the full valorization of lignocellulose, and will decrease chemical dependence on fossil-based resources

#### Conflict of interest

Author have not conflict of interest.

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