



Influence of wood leachate industrial waste as a novel catalyst for the synthesis of UF resins and MDF bonded with them

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ABSTRACT

MDF (Medium Density Fiberboard) production processes produce a large amount of wood leachate as a hazardous waste. Wood leachate is a lignin-based waste material from the MDF production industry. It constitutes a potential environmental problem if discarded by penetrating into groundwater aquifers. Currently, there is no viable way for industrial MDF leachate waste to be transformed into environmentally friendly high value materials. The aim of this work was to present for the first time a novel approach which was successfully developed for the recovery of wood leachate industrial waste as a catalyst for the synthesis of UF adhesives for MDF panels. The leachates were examined by FTIR, ¹³C NMR, and DSC as well as by evaluating the properties of fiberboards bonded with liquid UF resins. In addition, the other aim of this work was to capture the free formaldehyde gas emitted by MDF panels. It was of interest to determine whether an MDF bonded panel prepared with a UF resin catalyzed by the wood leachate would exhibit lower formaldehyde emissions and the lowest thickness swelling, while still presenting a relatively good performance. The direct reuse of the fiberboard industrial leachate in the experiments demonstrated that the preparation method of the UF bonded fiberboard was environmentally friendly and sustainable. Therefore, this work arrived at some interesting conclusions that may be used as a base for future work on the recycling and reuse of MDF waste.

1. Introduction

Generally, hazardous wastes must be disposed of, or reused by a safe but separate process due to its detrimental and persistent environmental impact. Environmental pollution and the hazardous nature of this waste can be reduced by its reuse. The wood-based composites industry has developed rapidly during the last few decades and its continued development is expected. About 228 million cubic meter global production of particleboard and fiber-board was accounted for in 2015 [1,2]. This releases a huge amount of organic waste, from acid waste to aromatic leachates. In recent years, due to increasing global environmental

awareness, the need to decrease dependence on oil-based products and to new environmental regulations, great attention has been paid to the possibilities of synthesizing biodegradable polymers from bio-based, renewable agricultural waste [3–5]. Wood composites can be used in the production of furniture, in interior and exterior joinery and for buildings [6]. Formaldehyde-based synthetic resins such as industrial grade urea-formaldehyde (UF) adhesives [7,8], melamine-formaldehyde (MF) resins [9,10], urea-melamine-formaldehyde (UMF) [11,12] and phenol-formaldehyde (PF) [13] are extensively used in wood-based composites. Particleboard, plywood, dry process fiberboard (commonly known by Medium Density Fiberboard (MDF)) and other

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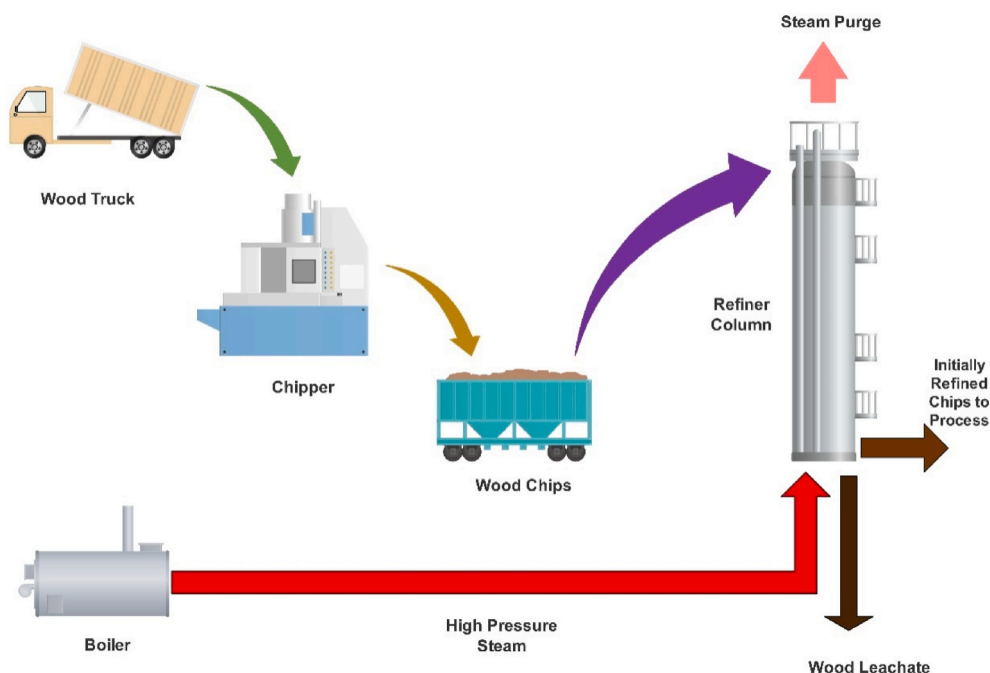


Fig. 1. Schematic of wood leachate production process.

composite wood products are the most common products that use formaldehyde-based binders [14,15]. More than 11 million metric tons of urea formaldehyde adhesive are produced yearly in the world and more than 80% of the wood products industry uses this type of adhesive for their production lines [16]. The good properties of UF adhesives (low cost, water solubility, good bond strength, adaptability to different curing conditions, thermal stability etc.) have attracted the industry to the use of this binder [17]. However, formaldehyde (HCHO) emission and poor water resistance are their main drawbacks [18]. Thus, toxic formaldehyde and volatile organic compound (VOC) emissions, potential health hazards, and non-biodegradability go together with the use of UF adhesives [19–21]. For instance, hazardous formaldehyde (HCHO) released from wood products in houses and furniture is carcinogenic and can potentially lead to sick building syndrome (SBS). This manifests itself by eye and nose irritation, upper respiratory problems, eczema, asthma even at low concentrations. It is the cause of health problems such as asthma and lung cancer at exposure levels of 10–20 ppm [22–25]. Therefore, it is beneficial to produce resins with increased water resistance and lower-toxicity from renewable resources.

A number of investigations have been carried out to decrease free formaldehyde and improve the stability of UF resins. Approaches such as decreasing the formaldehyde to urea molar ratio [26], and making use of formaldehyde scavengers [27–29] have been used. Younesi-Kordkheili et al. [30] worked on supplanting second urea addition by adjustment with glyoxalated soda bagasse lignin. However, all these approaches are either expensive, or lead to lower board mechanical performance, or manufacture becomes more complex. The attractive qualities (such as low cost and satisfactory bonding quality) of UF resins appears not to be maintained by using these approaches. One of the best approaches to prepare UF adhesives is the alkaline-acid-alkaline process which occurs in three steps; a) Reaction of urea and formaldehyde in an alkaline condition, b) condensation reaction at high temperature under acidic conditions, and c) reaction of residual formaldehyde with urea under alkaline conditions and neutralization [29]. The important factors which can affect the reaction of UF adhesive are the relative formaldehyde to urea molar ratio, the reaction temperature at each stage of the reaction and the pH of the condensation step [31]. The acid proton release rate during the condensation step controls the polymer chain

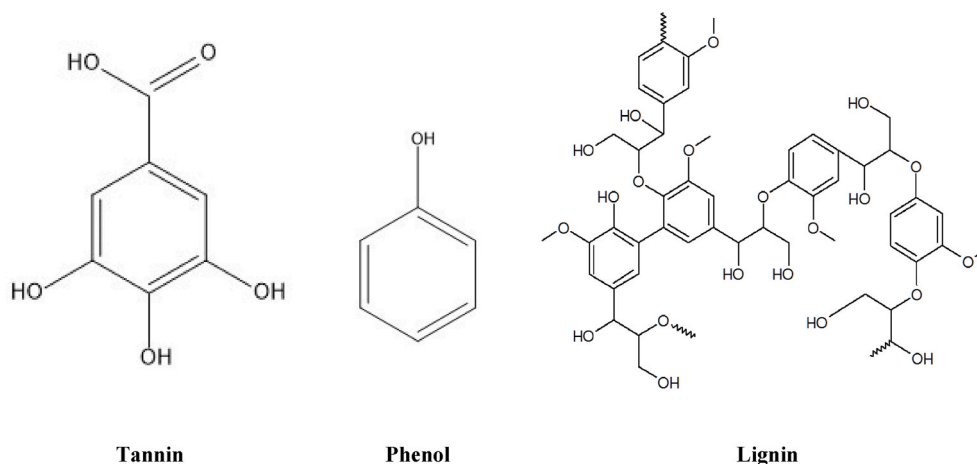


Fig. 2. Structure of the main components of the wood leachate.

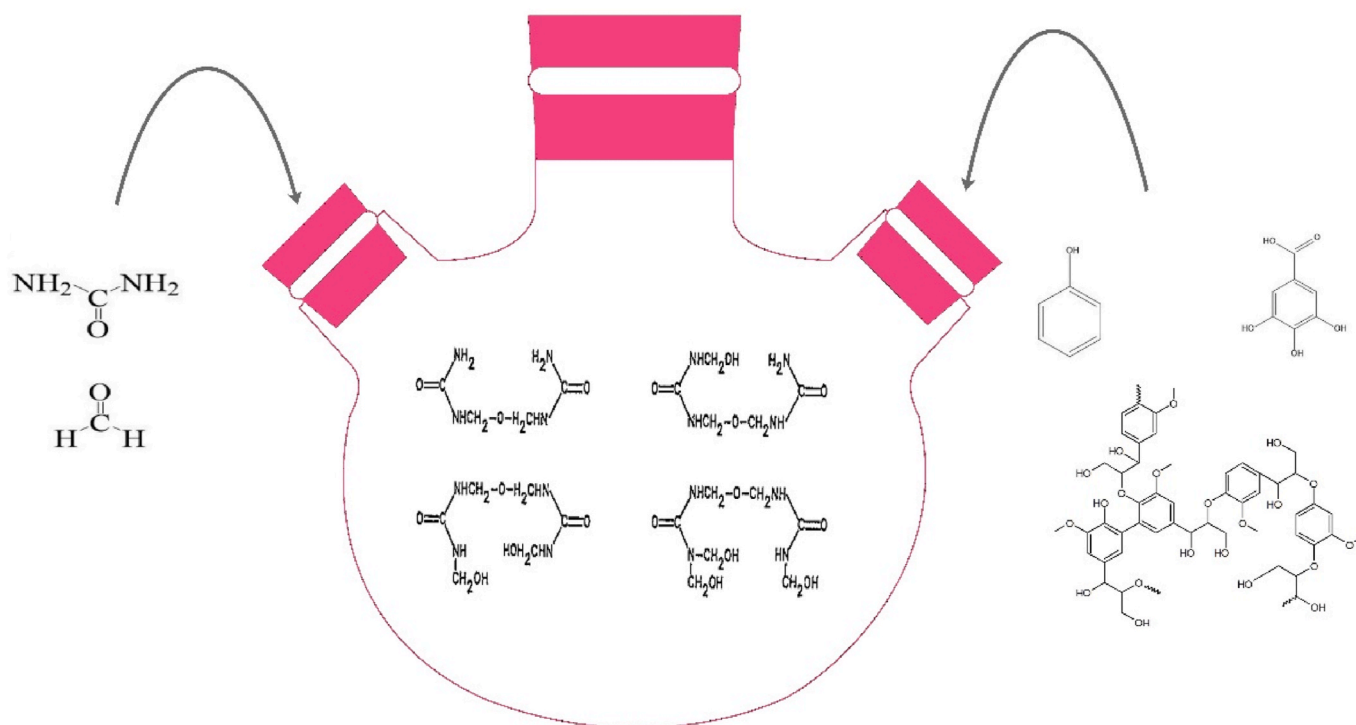


Fig. 3. Schematic of the UF resin synthesis reaction.

growth and drives the reaction to yield the desired products [32]. There are several works dealing with UF adhesives synthesized by the alkali-acid method. Some of the parameters like different pHs and temperatures [33], the various formaldehyde/urea (F/U) mole ratios [34,35], the effect of different additives [36], and using different acid catalyst types [32] have been investigated.

The MDF production factories usually use wood as the feedstock. After wood chipping, the chips are treated with high pressure steam which is necessary to separate the fibers by removing some lignin content from the wood structure. The process of production up to waste water release is as follows: in the first step wood was fed to a chipper to produce chips with approximately 5–25 mm thickness. The chips were then screened in order to obtain uniform size distribution and washed to remove contaminants before defibration. The washed chips were then fed into a digester where they were heated by high pressure steam at 600–1000 KPa at temperatures of 175–195 °C for 3–7 min. The high pressure steam softens the lignin and allows the fibers to be separated in the next step i.e. refining [37]. Some parts of the vapor condense in this process which contains lignin and wood leachates. The waste produced by this process is a dark brown liquid called leachate [38] which has a pH of around 4. It was reported that the production of wastewater in a single MDF manufacturing line is about 700 m³/day [39] of which about 400 m³/day is wood leachate. Fig. 1 shows the schematic process of wood leachate production.

This acid waste material can harm the environment and thus needs to be treated before discharge. For example, it has been shown that leached water from natural wood is even more hazardous than chromated copper arsenate (CCA)-treated wood [40]. Leachates may contain large quantities of organic pollutants such as, ammonia (NH₃), heavy metals, mineral salts, and phenol derivatives. Moreover, previous work has shown that this leachate can infiltrate and pollute the soil, and the surrounding water, creating an environmental problem that needs to be addressed [41,42].

Wood leachate has a complex composition. The literature mentions that the leachate is mostly composed of phenol, tannins, lignin and volatile fatty acids [38,43]. The structure of the majority of the

components present in the wood leachate are shown in Fig. 2.

In contrast to the huge amounts of wood leachate now discharged from wood manufacturing processes, it is instead convenient to implement recycling procedures. This particular waste is produced daily in the MDF manufacturing factory and is easy to access and use. Moreover, this acid waste catalyst is beneficial in cost and could remove the costs of the purchase of catalyst in a MDF production company. Thus, reusing wood leachate waste not only solves the waste management issue, but also has economic and environmental benefits. Nevertheless, in spite of some previous work on the wood leachate [44], there is no information in the literature on recycling and reusing it as a catalyst for UF adhesives and of the fiberboards (MDF) bonded with them. Mechanical strength, water resistance and chemical stability represent some of the desirable properties of UF resins for wood adhesives [19]. Reusing wood leachate as a catalyst, could be of interest in the synthesis of UF resins. Therefore, the purpose of the work presented here is to investigate the use of wood leachate as a catalyst in UF resin preparation and to better understand its influence on some MDF properties. The hypothesis is that phenolic compounds and lignin, as the major leachate components, might act as an absorbing substrate for formaldehyde. It has been assumed that all the processes could be carried out within the UF resin synthesis. Based on these assumptions, “greener” leachate-catalyzed UF resins for wood composites have been developed. Traditional acid catalysts like sulfuric acid and formic acid (HCOOH) are smaller molecular species, which might evaporate during UF preparation. Formic and sulfuric acid vapors can seriously affect the environment and human health during UF manufacturing [45,46]. Furthermore, HCOOH and other organic acids are markedly more expensive. Therefore, by replacing these materials with a less hazardous one presents potential benefits without compromising other properties. Thus, in the present work, the effects of wood leachate catalyst on resin synthesis, chemical structure, thermal behavior, non-volatile solid content, free formaldehyde (HCHO), and mechanical strength were studied. A novel and simple approach was thus successfully developed for the recovery of the wood leachate hazardous waste. As a result, formaldehyde emission and thickness swelling (TS) of fiberboard produced with WL-UF resins were improved.

Table 1

Properties of UF resins synthesized with different catalysts and initial F/U molar ratios.

Resin	Initial F/U	Final F/U	Catalyst
WL-2	2	1.12	Wood Leachate
WL-2.2	2.2	1.12	Wood Leachate
FA-2	2	1.12	HCOOH
FA-2.2	2.2	1.12	HCOOH

2. Experimental

2.1. Materials

The UFC-85 (Urea-formaldehyde concentrate-85) containing 60 wt % formaldehyde (HCHO) with a urea concentration of 25% with a methanol percentage below 0.1 wt % was supplied from Arian Jala Rang Incorporation (AJRI, Rasht, Iran) from Arian Saeed Industrial Group. A commercial solution of HCOOH (85% w/w) and sodium hydroxide solution (25 wt %) were employed to neutralize the pH value during the preparation. The raw wood leachate (with 3% solid content and a pH value of about 4; The pH and solid content of the catalyst are the most influential factors for UF resin synthesis, thus it should be measured before using the catalyst in each reaction.) and fiber used in this work was from Arian Maryam Incorporation factory (AMI, Rasht, Iran) from Arian Saeed Industrial Group.

2.2. Synthesis of UF resins

Four resins with different catalysts (HCOOH (30% w/w) and concentrated wood leachate (50% concentration by vaporization)) and different first step formaldehyde/urea mole ratios (2 and 2.2) were prepared with a constant final formaldehyde/urea mole ratio of 1.12/1 in the laboratory. There were three stages for each batch as follows:

- Reaction of urea and UFC in an alkaline condition
- Condensation reaction at high temperature under an acidic condition
- Reaction of residual formaldehyde with urea at an alkaline condition

A schematic of the UF resin synthesis reaction is shown in Fig. 3. A point by point portrayal of the synthesis method can be found in a previous research paper [26]. The UF resins catalyzed by two types of catalysts, HCOOH and wood leachate, in two diverse introductory F/U molar proportions were arranged with last F/U = 1.12 M proportion within the laboratory, as follows: 1500 g of UFC-85 solution (60% formaldehyde (HCHO), 29.96 mol and 25 wt % urea, 6.24 mol) was mixed with distilled water (500 g, 27.77 mol) and placed in a 3L jacketed reactor equipped with a condenser, hot and cold water circulation, thermometer and an overhead stirrer. The pH of the mixture was maintained at 8–9 by 40 wt % sodium hydroxide, and the temperature maintained at 45 °C. Accordingly, the initial urea (U₁) contents (525 g and 443 g, 8.7 mol and 7.37 mol) were added to the reactor. After dissolution of the urea, the temperature was increased to 88 ± 1 °C and mixed for 45 min with the pH of the mixture re-adjusted to 7.5. Subsequently, the pH was lowered to 4.5 ± 0.3 using two different catalysts (~5 ml of HCOOH and ~50 ml of wood leachate) and the condensation was performed at 100 ± 1 °C to obtain the target viscosity. A N° 3 Ford cup was used to measure viscosity at 60 °C at different time intervals during the reaction. Then, the reactor was cooled for 35 min. At a temperature of 55 °C the residual amount of urea (707 g and 789 g, 11.77 mol and 13.13 mol) was added to the mixture to obtain the final formaldehyde/urea mole ratio. The mixture was then cooled to 25 °C. Table 1 illustrates the batch descriptions in detail.

2.3. Resin properties determination

The curing time, viscosity, pH, nonvolatile content, specific gravity (SPG) and unreacted formaldehyde proportion were measured. The viscosity of resins was measured at 20 °C by a Ford cup (Number 4). The pH value of resins was measured using a Metrohm 827 pH-meter. The solid content of the resins was determined by weighing 1.5 g of adhesive, placing in an aluminum dish and monitoring the exact weight before and after drying in a convection oven for 2 h at 120 °C. For measuring the curing time of the resins, 5 g of resin was placed in a glass tube and reacted and turned into a high viscosity gel at 100 °C. 5 g of 20 wt % NH₄Cl aqueous solution was used for 5 g adhesive as curing catalyst. The SPG of resin was obtained by glassy hydrometer. An incubator oven at 30 °C was employed for investigating the storage stability of the resins by placing the resins in an oven and daily tracking of the viscosity changes for 40 days. To determine the free formaldehyde (HCHO) of the samples, a modified sodium sulfite (Na₂SO₃) procedure was used in this study [32].

2.4. Structural properties

The transmittance mode of FTIR spectroscopy was employed for the identification of functional groups present in the urea formaldehyde adhesives. A drop of the liquid resin was blended with KBr pellets (sandwich) prior to characterization [47]. Spectra of the resins were obtained in the spectral region 4000–400 cm⁻¹, with a resolution of 16 cm⁻¹ and 200 scans.

2.5. ¹³C NMR spectroscopy

The ¹³C NMR spectra were obtained using a Bruker AVANCE 400–500 MHz instrument; deuterated dimethyl sulfoxide (DMSO-*d*₆) was used as the solvent. 40 mg of liquid resin was blended with 10 mL of dimethyl sulfoxide (DMSO-*d*₆) for the analysis. Each spectrum was accomplished with about 400–500 scans. Tetramethylsilane (TMS) was used as the spectra standard for the determination of chemical shift. The detected chemical structures were assigned following the literature [48–52]. The relative amounts (%) of methylene carbons were calculated using equation (1):

$$\text{Molar\%} = \frac{A_i}{\sum A_i} \times 100\% \quad (1)$$

where A_i is the area under the peak for a methylene carbon, and $\sum A_i$ is the summation of peak areas for all methylene carbons. The relative amounts of different carbon atoms of carbonyl groups were calculated using the same method.

2.6. Adhesive curing behavior

Adhesive curing behavior was assessed using DSC (TA METTLER TGA/STTA 851, Switzerland). Samples (3–5 mg) were placed in a hermetic pan. The calorimetry analysis was carried out over a temp ramp of 25–160 °C at 10 °C/min, with nitrogen at a pressure of 4 MPa used as the flushing gas. As a hardener catalyst, 2 wt% NH₄Cl was added to the liquid UF adhesive just before the analysis.

2.7. Preparation of medium density fiberboards (MDF)

Synthesized UF resins were mixed with water to achieve a solids content of 55 wt%. Approximately 2% of total liquid UF adhesive solids of an oven dry mass (NH₄)₂SO₄ as curing agent was added to the mixture. The prepared adhesive mixtures were mixed with fiber (10:90 w/w resin solid content: dried fiber). MDF panels with dimensions of 300mm × 300mm × 11 mm (length × width × thickness) were prepared under the following conditions: panels were hot-pressed for 5 min at

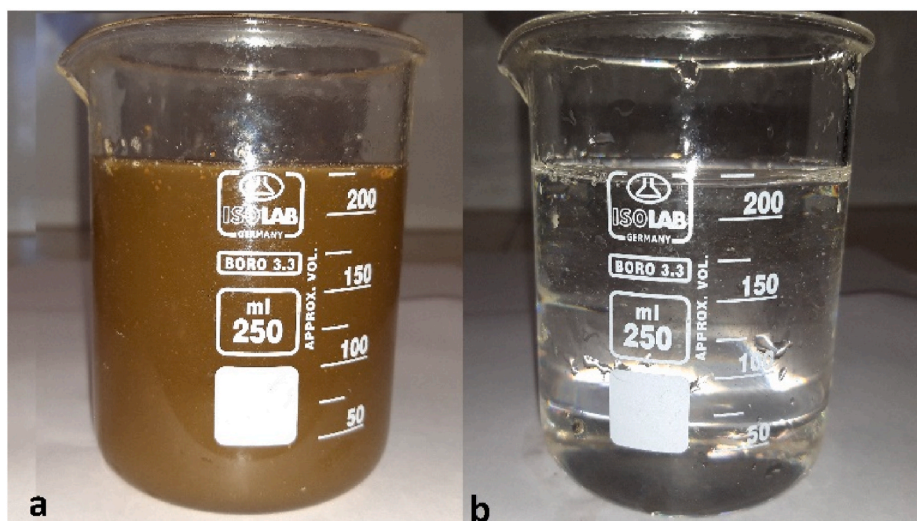


Fig. 4. Appearance of the UF adhesives synthesized by a) wood leachate as catalyst and b) HCOOH.

Table 2
Properties of UF resins synthesized with different catalysts and initial F/U molar ratios.

Resin	Free Formaldehyde (%)	Solid content (%)	Endpoint (min)	Viscosity (mPa.s)	Curing time (s)	Density (g/cm ³)	pH
WL-2	0.2	63.6	36	180.9	61	1.266	8.2
WL-2.2	0.35	63.4	58	154.7	56	1.265	8.1
FA-2	0.4	65.1	27	202.8	55	1.273	8.3
FA-2.2	0.62	64.7	45	184.5	51	1.271	8.4

180 °C using a press unit with a maximum pressure of 3.5 MPa over the selected area (the effective pressure to obtain the thickness was about 2.5 MPa). A density of 700 kg/m³ was considered for the MDF panels. Following fabrication the boards were stored at a temperature of 20 ± 2 °C at a relative humidity of 65 ± 5% [53].

The mechanical specifications of the composite panels were determined by modulus of elasticity (MOE) and modulus of rupture (MOR) measurements following EN 310: 1993 using sample of dimensions of 50 mm × 250 mm [53]. The EN 319:1993 standard method was used for measuring the internal bond (IB) strength of the fabricated composite panels. The extent of thickness swelling (TS) was determined by soaking panels in cold water for 24 h; the process explained in EN 317:1993 was employed for this goal. The formaldehyde (HCHO) emission of the MDF composite boards was surveyed following the EN ISO 12460–5 procedure. An IMAL (IB600) universal testing instrument was used for mechanical property measurements. At least 3 measurements were carried out for each sample.

3. Results and discussion

3.1. Adhesive properties

The color of the adhesives prepared using the wood leachate changed from transparent solution (no color) to a dark brown during its synthesis. This is caused by the color of the wood leachate. The appearance of the samples is shown in Fig. 4. Table 2 shows the physico-chemical properties of the industrial grade liquid UF adhesives prepared with different catalysts and different initial formaldehyde/urea molar ratios. The free formaldehyde (HCHO) proportion in the liquid UF adhesive is directly affected by the initial molar ratio in the resin synthesis. Formaldehyde concentration of the resin samples was measured by titration and it is shown in Table 2. It can be seen that the higher formaldehyde concentration in FA-2.2 and WL-2.2 compared to FA-2 and WL-2 respectively is caused by a higher initial molar ratio in the resin synthesis. By increasing the initial urea content in the reaction, the free

formaldehyde reacts with it reducing the proportion of free formaldehyde in the final resin [26]. Conversely, the catalyst type could play a key role in the free formaldehyde content [54]. The lignin content in the structure of the wood leachate could have the role of formaldehyde scavenger by reacting with the unreacted residual formaldehyde [55–58].

One of the most effective parameters in UF resin synthesis is resin viscosity which is used as an indicator of the polymerization end point. This can affect the adhesive penetration, curing and crosslinking ability and the final strength of the wood board bonded with it [59–62]. Poor resin penetration is a result of high viscosity, while a low viscosity adhesive can cause starved bond-lines because of excessive penetration [26,63–66].

The wood leachate has a weak acid behavior and tends to slow down the polymerization. As shown in Table 2, the end points of the condensation reaction step for FA-2 and FA-2.2 are at about 27 min and 45 min respectively, but increased to 36 min and 58 min for WL-2 and WL-2.2. It should also be noted that the reaction with the same catalyst but with different first formaldehyde/urea molar ratio yields different viscosities. The rate of condensation increased at the lower initial formaldehyde/urea molar ratio. It increases up to the point to yield a partly gelled mass.

The larger proportion of water in the wood leachate tends to slow down the reaction rate when compared to a HCOOH catalyzed reaction. Viscosities between 180 cP to 190 cP and a condensation time up to 58 min were considered for the reaction. The polymerization was quicker for the synthesis with a lower initial formaldehyde/urea molar ratio. As can be seen from Table 2, the end point of the reaction occurred in a shorter time for the F/U = 2 reactions than for those at F/U = 2.2. This occurs since there are more urea amide groups available for reaction with formaldehyde (HCHO). The excessive amount of urea during the first reaction step for the lower molar ratio resins is the reason for this difference.

As expected, the use of the wood leachate catalyst tends to lower the non-volatiles content because of its high proportion of water. The

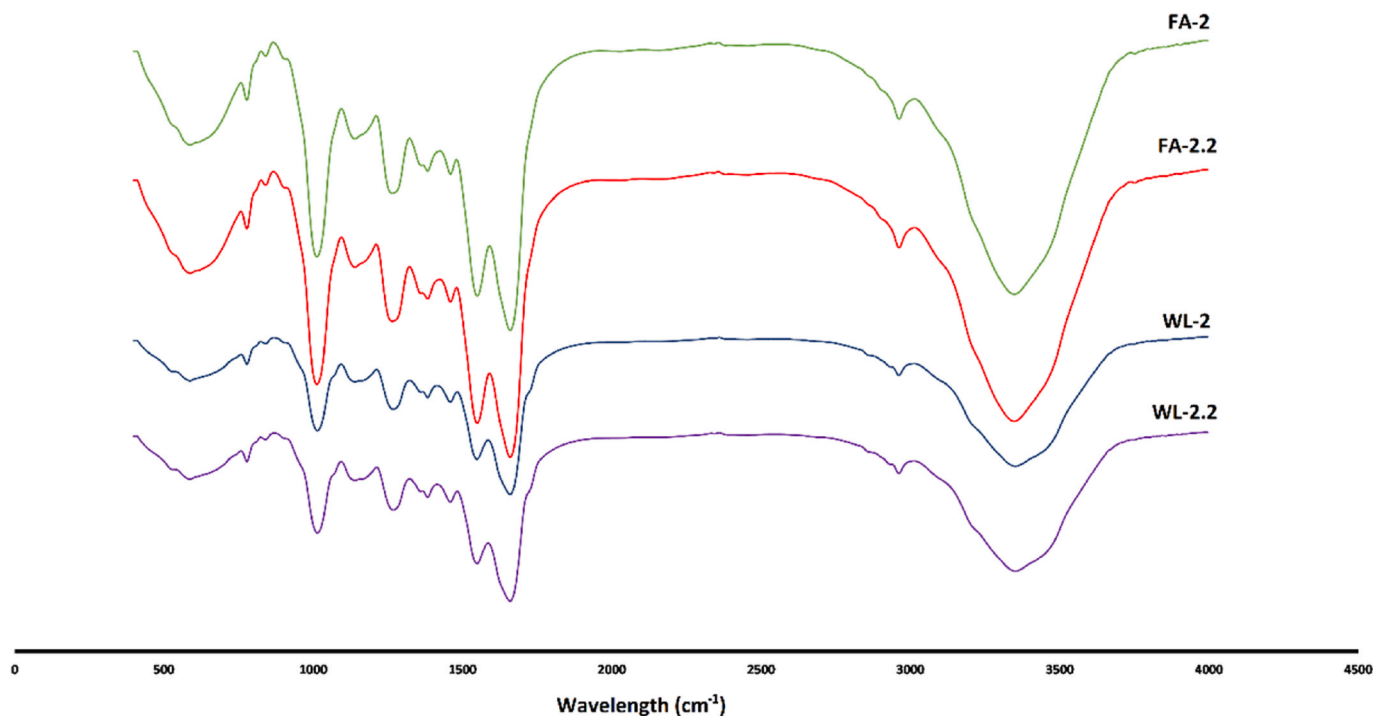


Fig. 5. FTIR spectra of the synthesized UF adhesives with different catalysts and initial molar ratio.

Table 3

Absorption band assignment of FT-IR spectra of WL-2, WL-2.2, FA-2 and FA-2.2

Range Absorption Band (cm ⁻¹)	Chemical structure assignment	Observed band (cm ⁻¹)			
		WL-2	WL-2.2	FA-2	FA-2.2
3340–3355	NH stretching of primary aliphatic amines	3349	3352	3348	3355
2930–2970	-CH ₂ -	2962	2963	2963	2966
1646–1664	C=O stretching of primary amide	1660	1661	1658	1655
1545–1560	C–N stretching of secondary amines	1549	1550	1548	1552
1440–1465	C–H bending in NCH ₂ N, CH ₂ O, OCH ₃	1460	1460	1459	1457
1380–1400	C–H mode in CH ₂ and CH ₃	1384	1384	1386	1388
1330–1380	CON stretching of CH ₂ ON	1346	1351	1354	1356
1300–1320	=C–N or =CH–N of tertiary cyclic amides	–	–	–	–
1250–1270	C–N and N–H stretching of tertiary amides	1269	1267	1265	1266
1130–1150	C–O stretching of aliphatic ether	1140	1139	1141	1141
1010–1020	C–N or NCN stretching of methylene bridges (NCH ₂ N)	–	–	–	–
1000–1020	COO stretching of hydroxymethylol group	1015	1013	1016	1015
650–900	N–H bending of primary aliphatic amines	779	779	777	773

specific gravity of the adhesives is also in direct relation with the resin solids content and decreases with the decrease of the solid content in WL-2 and WL-2.2. Furthermore, a longer curing time was observed for the resins catalyzed with the wood leachate. Usually, ammonium salts ((NH₄)₂SO₄, NH₄Cl and NH₄NO₃) are used as UF adhesive hardeners (as latent catalysts) and consume formaldehyde, causing a slower gel time but nonetheless essential because UF adhesives need an acid environment to cure [15]. The low free formaldehyde content in these samples leads to longer resin gel times. In this case, there is a very limited level of free formaldehyde (HCHO).

Table 4

The relative content of the methylene and carbonyl carbons (%) and chemical shift of UF resins samples by ¹³C NMR.

Structures	Chemical shifts/ppm	FA-2	WL-2	FA-2.2	WL-2.2
–NH–CH ₂ –NH– (I)	46–49	11.65	12.60	9.78	9.74
–NH–CH ₂ –N= (II)	53–55	11.20	11.80	7.92	10.06
=N–CH ₂ –N= (III)	60–61	–	–	–	–
Methylenes, Σ	Total	22.85	24.40	17.7	19.8
–NH–CH ₂ OCH ₂ –NH– (I)	68–70	16.71	17.63	12.92	14.92
–NH–CH ₂ OCH ₂ OH	–	–	–	–	–
–NH–CH ₂ OCH ₂ N= (II)	75–77	3.54	3.01	3.8	2.69
=N–CH ₂ OCH ₂ N= (III)	78–80	1.3	2.01	2.93	2.43
Uron-type ether	Total	21.55	22.65	19.03	20.04
Dimethylene ethers groups, Σ	Total	21.55	22.65	19.03	20.04
–NH–CH ₂ OH (I)	64–66	55.30	52.35	63.10	59.68
HO–CH ₂ –OH	82–84	0.3	0.6	0.17	0.3
HOCH ₂ –O–CH ₂ –OCH ₂ OH	86–88	–	–	–	0.18
Hydroxymethyls, Σ	Total	55.6	52.95	63.27	60.16
Carbonyl region	Total	27.04	17	26.92	19.10
NH ₂ –CO–NH–	161–163	27.04	17	26.92	19.10
–NH–CO–NH–	159–161	36.30	36.30	38.94	38.50
–NH–CO–N=	157–159	36.66	46	33.54	41.06
Uron	154–157	–	0.7	0.6	1.34

3.2. FT-IR spectra

Fig. 5 shows the FTIR spectra of the synthesized samples using HCOOH and the wood leachate catalysts. The spectra for the four UF resin samples appear to be very similar. The broad and strong absorption peak at 3200–3600 cm⁻¹ that is assigned to the –OH stretching vibration appears in UF resins [47]. It means that the –OH surrounding chemical environment is complex and diverse. Besides, the stretching vibrations of the –NH₂ and –NH groups do not seem to be present.

The carbonyl group (C=O) stretching of primary amides was the most dominant absorption band of the infrared spectra of the UF adhesives, occurring at 1660 cm⁻¹. Similar variations occurred for the 1265–1270 cm⁻¹ bands, assigned to the C–O–C stretching vibration of

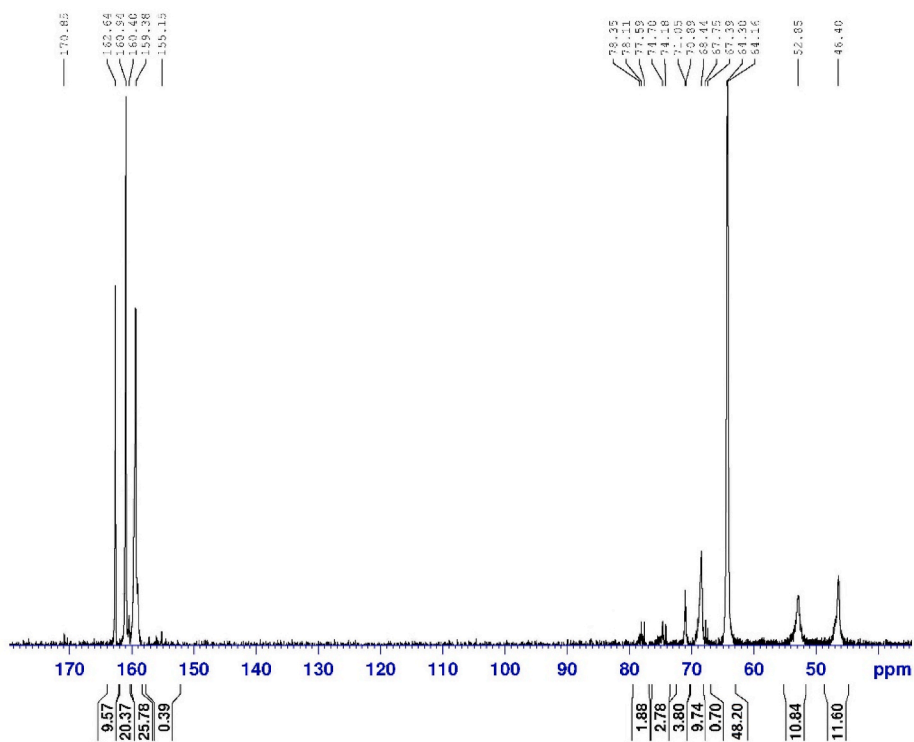


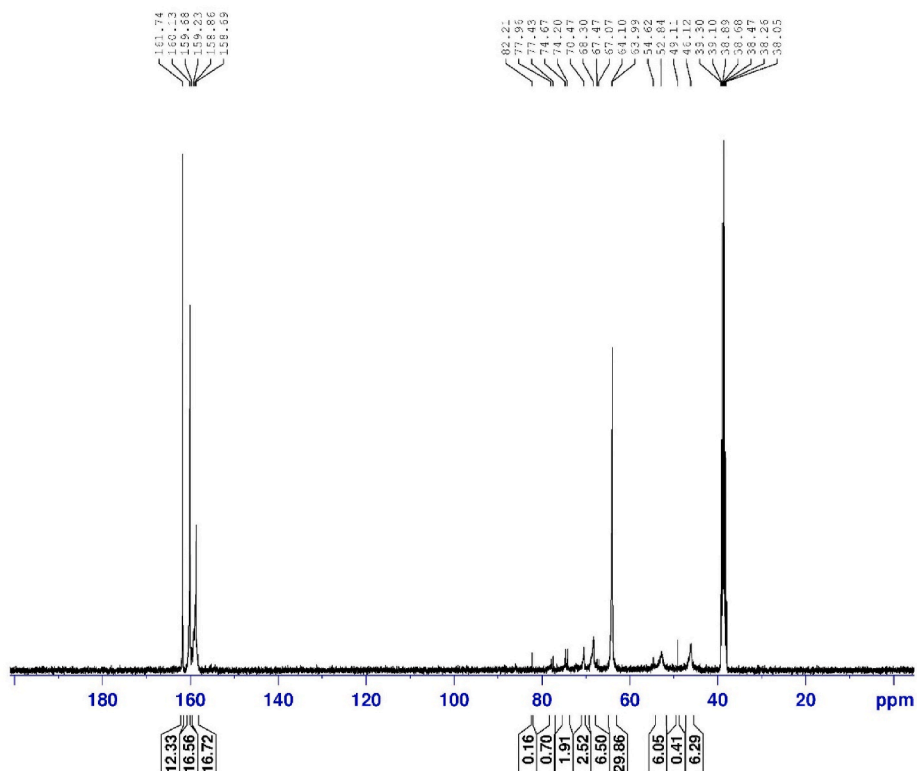
Fig. 6. ¹³C NMR spectra of the wood leachate catalyzed UF resin with initial F/U molar ratio of 2 (WL-2).

methylene ether bridges, and at 1010–1020 cm⁻¹, reflecting the stretching and vibration mode of the C–O and N–H bonds in the (CH₂OH) group. The vibration band from 1010 to 1020 cm⁻¹ could be assigned to C–N stretching from C–N or C–N₂, of amides in the adhesives. The peak at 2950 cm⁻¹ belongs to antisymmetric stretching

vibration of –CH₂– in the resin, Table 3.

3.3. ¹³C NMR spectra

The quantitative ¹³C NMR results for the samples are shown in



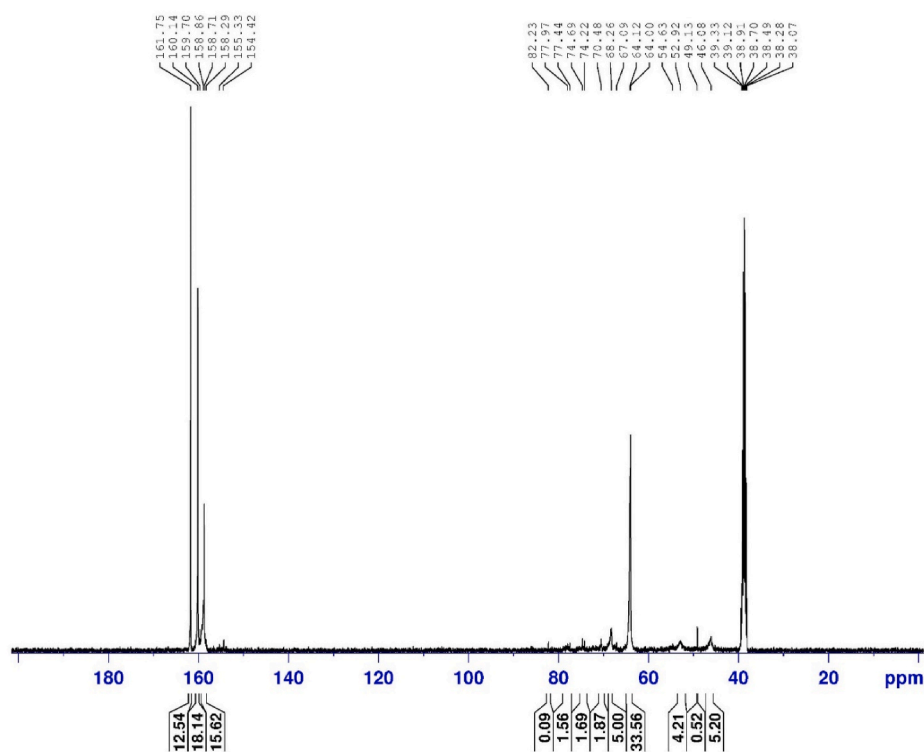


Fig. 8. ^{13}C NMR spectra of the HCOOH catalyzed UF resin with initial F/U molar ratio of 2.2 (FA-2.2).

Table 4. The chemical structures and peaks of synthesized resins were assigned according to published literature based on their ^{13}C NMR spectrum [67–70]. The most important groups of peaks were detected in the spectra; the first group of peaks refers to methylene carbons containing functional groups in the range of 45–95 ppm and were assigned into three sections, each of which is explained in detail later. The carbons of the methylene linkage peaks appeared at 47, 53, and 60 ppm. The chemical shift at 64–66 ppm, belongs to the hydroxymethyl groups

of the type $-\text{NH}-\text{CH}_2\text{OH}$. Methylene ether linkage ($-\text{CH}_2\text{OCH}_2-$) shifts appeared at 68, 75, and 78 ppm. The formation of methylene ether and methylene linkages often occurs concurrently during the UF resins synthesis. The second peaks range belongs to the carbonyl functional group appearing between 150 and 170 ppm, the assignment differs depending on the urea substitution. The peaks at 153–157 ppm belong to cyclic intramolecular urea methylene ether structures known as urons. Peaks at 50 and 39 ppm are assigned to methanol and deuterated

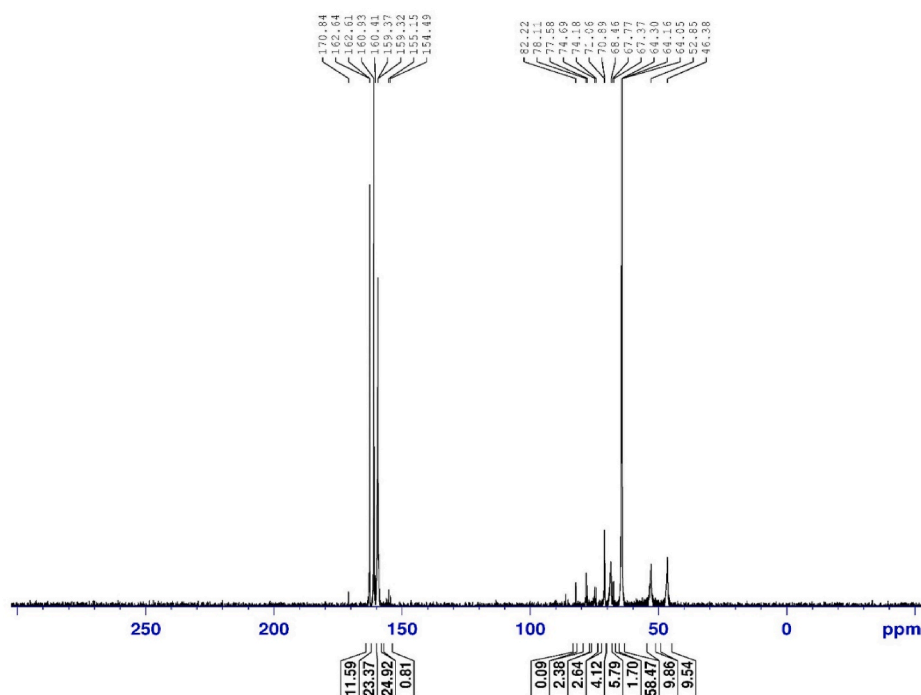


Fig. 9. ^{13}C NMR spectra of the wood leachate catalyzed UF resin with initial F/U molar ratio of 2.2 (WL-2.2).

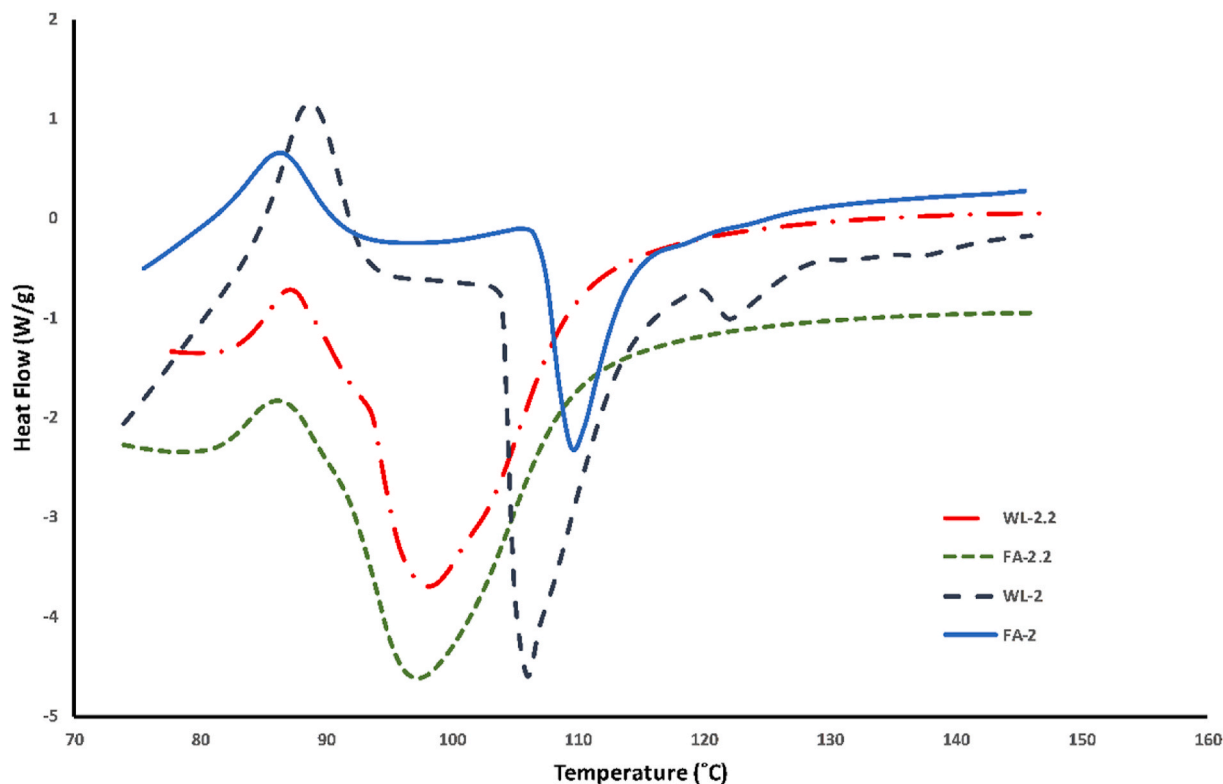


Fig. 10. DSC curves for the curing reaction with various catalysts and initial F/U molar ratios of UF resins at a heating rate of 10 °C/min.

DMSO- d_6 solvent. Weak peaks are present in the range of 80–90 ppm, these chemical shifts belonging to unreacted formaldehyde (HCHO) present in the liquid UF adhesive.

As listed in Table 4, the WL-2 reaction yields the highest proportion of methylene linkages ($-\text{NH}-\text{CH}_2-\text{NH}-$), linear methylene ether linkages and tri-substituted ureas ($-\text{NH}-\text{CO}-\text{N}=\text{N}-$) but the lowest proportion of hydroxymethyl groups, and monosubstituted ureas than the other resins. The decrease in methylene ether signals ($-\text{NH}-\text{CH}_2\text{OCH}_2-\text{NH}-$ (I) or $-\text{NH}-\text{CH}_2\text{OCH}_2\text{OH}$) at 68–70 ppm and the formation of a lower proportion of methylene ethers ($-\text{CH}_2-\text{O}-\text{CH}_2-$) was observed for the WL-2 resin. The ^{13}C NMR peaks of the WL-2 resin are also shown in Fig. 6.

Table 4 shows that in the FA-2 resin the total proportion of methylene bridges is 22.85%. The methylene bridges are usually absent at the end of the initial alkaline step in the conventional industrial process of synthesis of a liquid UF adhesive. The FA-2 resin possesses a higher proportion of hydroxymethyls, mainly the $-\text{NH}-\text{CH}_2\text{OH}$ group, and mono substituted ureas, than the WL-2 sample, and no uron derivatives. Fig. 7 also shows the ^{13}C NMR peaks for the FA-2 resin.

The spectrum of the FA-2.2 resin is shown in Fig. 8 and the relative quantitative results are shown in Table 4. The adhesive synthesis by HCOOH with an initial formaldehyde/urea molar ratio of 2.2 (FA-2.2) yields the highest proportion of hydroxymethyl groups (mostly $-\text{NH}-\text{CH}_2\text{OH}$) than the WL-2.2, FA-2, and WL-2 resins. The increase in the methylol ($-\text{NH}-\text{CH}_2\text{OH}$) groups in the adhesive can result from the free formaldehyde (HCHO) reaction with the second urea, that causes the formation of the lowest proportion of methylene linkages.

WL-2.2 yields the highest proportion of tri-substituted ureas (157–159 ppm) and methylene linkages but the least linear methylene ether linkages, hydroxymethyl and mono-substituted ureas than the FA-2.2 resin. As shown in Table 4, the uron carbonyls are 1.34% of the whole carbonyls of urea, observed in the resin synthesis with wood leachate at the F/U initial molar ratio of 2.2 (WL-2.2). This is higher than for WL-2 (0.7%) and FA-2.2 (0.6%), respectively. Fig. 9 shows the ^{13}C NMR spectrum of WL-2.2.

It can be seen from the integrals of the ^{13}C NMR spectra that the

wood leachate as an acid catalyst yielded a slightly more marked decrease in methylene ether linkages than HCOOH. This was due to a rearrangement of some unstable structure of the UF adhesive and the relative content of the phenolic rings of lignin which could react with more formaldehyde. Thus, the wood leachate reacting to yield a lower viscosity has resulted in a decrease in the proportion of methylene ether linkages. As a result, the lower content of hydroxymethyl groups in resins catalyzed by the wood leachate compared to those catalyzed by HCOOH, confirms and explains the longer gel time in the resin synthesis induced by the wood leachate. The chemical shift at 46–49 ppm belongs to the increased proportion of methylene bridges for resins catalyzed by the wood leachate, showing that the molecular mobility of the UF resin decreases as a consequence of the leachate catalyst used during its synthesis [71,72]. As a matter of fact, the chains of the UF resin are locked together by mean of methylene bridge cross-links [73–75]. The small proportion of uron-type structures observed in the resins is due to the uron ring structures being generally in a rather minor proportion when the formaldehyde/urea mole ratio is in the 2–2.2 range. The cyclic uron-type structures form and subsist under strong acid and strong alkaline conditions [76,77]. As shown in Table 2, the resin catalyzed by the leachate resulted in a considerably lower free formaldehyde content than the other common resins. According to the small proportion of catalyst used in the UF resin synthesis, the amount of phenolic compounds of the wood leachate in the adhesive is very low. In this regard, the peaks of phenolic compounds in the ^{13}C NMR are not even present or noticeable.

3.4. DSC analysis

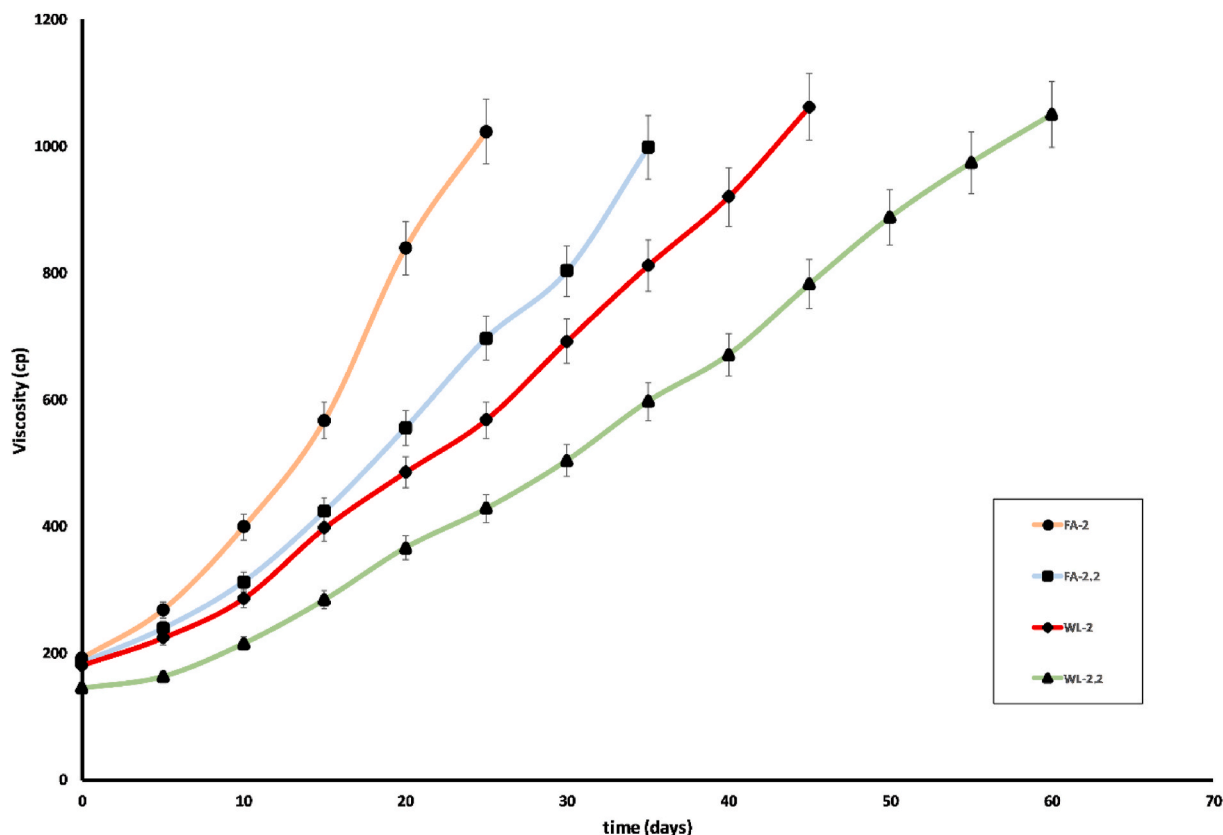
DSC thermograms of the curing of the synthesized urea formaldehyde resins are shown in Fig. 10. The heating rate was 10 °C/min and the calorimetry temperature range was 70–150 °C. Exotherm peak and endotherm peak temperatures, onset temperature and total heat of reaction are the data derived by a dynamic DSC scanning of the UF resins.

The results of the DSC thermograms for the curing of the UF resins

Table 5

Peak data for the curing reaction with various catalysts and initial F/U molar ratios of UF resins.

Resin	Exothermic Peak °C	Exothermic ΔH (J/g)	Endothermic Peak °C	Endothermic ΔH (J/g)	Peak temperature span
WL-2	88.96	211.6	105.96	115.5	17
FA-2	86.49	126.4	109.49	62.96	23
WL-2.2	86.82	22.4	96.82	226.4	10
FA-2.2	85.95	21.3	97.95	231.3	12

**Fig. 11.** Storage stability curve (viscosity as a function of storage time) for synthesized UF resins with different catalysts (FA and WL) at two different initial molar ratios.

synthesized with two different catalysts (wood leachate and HCOOH) are summarized in Table 5. The detected exotherm peak below 100 °C is related to the condensation reaction of the unreacted urea amide groups and methylol groups (-CH₂OH). A wide endothermic peak has appeared in the 90 °C–140 °C range belonging to condensed water evaporation, decomposition of the methylene-ether linkages and free formaldehyde evaporation [78–80]. The curing transition peak area is related to the curing reaction enthalpy (ΔH_{curing}). This presents the total liberated heat from the curing reaction. The results indicate that there are exotherm peaks at 88.96 °C, 86.49 °C, 86.82 °C and 85.95 °C and endothermic peaks at 105.96 °C, 109.49 °C, 96.82 °C and 97.95 °C for resins with an initial molar ratio of F/U = 2 catalyzed by the wood leachate and HCOOH; and resins with an initial molar ratio of F/U = 2.2 catalyzed by the wood leachate and HCOOH respectively. The peak temperature span is the difference between the exothermic and endothermic peak temperatures.

From the results of the DSC thermograms (Fig. 10) the highest temperature for the exothermic peak belonged to WL-2, a resin prepared by wood leachate catalysis at an initial U/F molar ratio of 2. The lower initial molar ratio tends to yield higher amounts of unreacted urea resulting in a higher reaction temperature. Conversely, the WL is a natural wastewater with an acidic pH and has lower catalytic activity in comparison with pure formic acid, thus it is clear that the unreacted urea

should be in a higher proportion in this case. This is confirmed by the lower viscosity and longer reaction time. The lowest exothermic peak temperature belongs to the HCOOH catalyzed resin which had the initial F/U ratio of 2.2. When the proportion of unreacted urea in a resin sample is high, the heat released by the exothermic curing reaction is also higher [26]. The heat of curing (ΔH_{curing}) of synthesized samples proves the relation between unreacted urea and reaction heat. The endothermic reaction temperature had the highest value for the FA-2 sample which was catalyzed by HCOOH and had the initial molar ratio of 2. The solid content of the resin could affect the DSC endothermic reaction of the resin curing. The lowest solid content belonged to the WL-2.2 resin which has the lowest endothermic peak temperature. This is due to the fact that the excessive water slows down the collision frequency at the molecular level, hence the resin with the lower solids content presents a lower curing rate during the early stages of reaction in comparison with resins with higher solid contents [81]. Due to the presence of high molecular weight lignin, the endothermic reaction in the DSC analysis presents a higher energy in the wood leachate catalyzed resin samples than in the samples catalyzed by HCOOH at an identical initial F/U molar ratio. The lignin role as filler, locks the UF resin chains and prevents formaldehyde and water evaporation [61,62,75,82], therefore, a higher energy input is needed for evaporation.

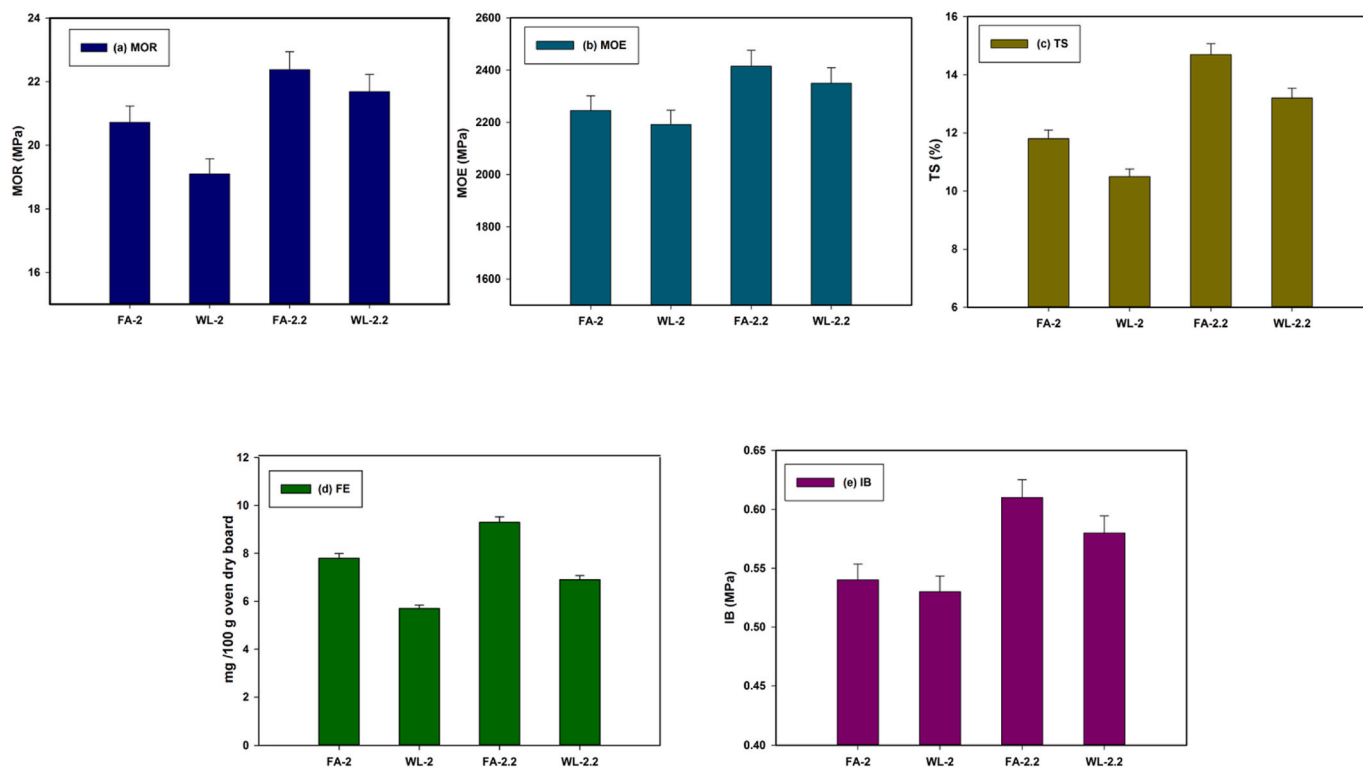


Fig. 12. Physical and mechanical properties of the fabricated MDF panels.

3.5. Storage stability

One of the important parameters in the adhesive production industry is the resins storage stability. Fig. 11 shows the storage stability of the resins synthesized in this work. The results presented were obtained by measuring the viscosity at 5-day intervals until it reached 1000 cP [15]. Samples were stored at room temperature ($\sim 25^\circ\text{C}$) and each sample was tested at least three times. Adhesives with an initial mole ratio of 2 have a shorter shelf life than those having an initial formaldehyde/urea ratio of 2.2. The resins with the lower initial molar ratio have a lower proportion of cross-linked chains as well as a higher proportion of unreacted amide groups ($-\text{NH}_2$). A lower proportion of crosslinked chains tends to yield a lower adhesive storage stability and under these conditions there are more sites able to react resulting in a faster growing polymer network resulting in a shorter adhesive shelf life. Furthermore, the leachate catalyzed resins present a lower viscosity increase. UV degradation and oxidation are also mostly linked, generally because UV radiation generates free radicals by breaking bonds [83]. The peroxide radicals then produced by reaction between free radicals and oxygen cause further damage, often in a chain reaction. There are many effective anti-oxidants and in this respect wood is one due its content of several types of phenolic groups. The wood leachate is a rich source of anti-oxidants. It is well known that many phenolic and polyphenolic compounds show concentration-dependent anti-oxidant activity in biological systems [84]. The free radical scavenging activity of the wood leachate is due to its phenolic OH groups. The wood leachate (WL) shows a very marked anti-oxidant activity at different concentrations; the main mechanism for the WL anti-oxidant activity being the proton H-transfer from the phenolic group to the active radicals. Moreover, owing to the stability of the resulting phenoxyl radical, the anti-oxidant capability of the WL is further enhanced. The lignin and phenolic compounds which are present in the structure of the wood leachate partly inhibit the resin polymer chain growth and result in a lower viscosity increment rate [85,86].

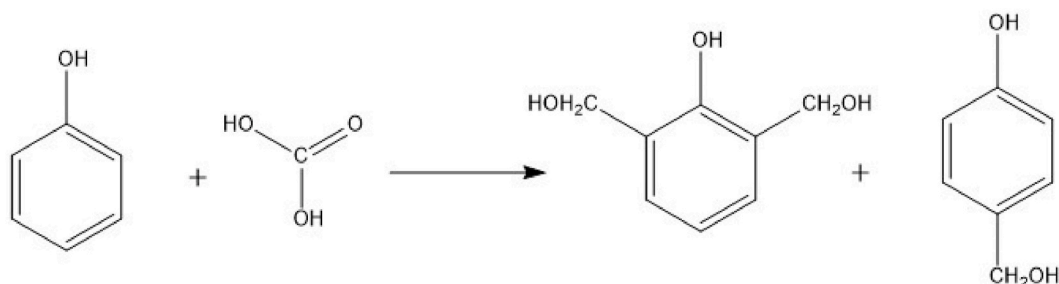
3.6. Physical and mechanical properties of MDF

Average physical and mechanical properties as well as formaldehyde (HCHO) emitted from the fabricated MDF panels are shown in the bar chart in Fig. 12.

The results of modulus of rupture (MOR) and modulus of elasticity (MOE) of the panels prepared are shown in Fig. 12. Although there was no significant difference for MOR and MOE between different resin compositions, the lowest MOE (2192) and MOR (19.10) values were however measured for MDF bonded with resins of initial F/U = 2 catalyzed by the wood leachate. Moreover, the highest MOE (2415) and MOR (22.38) values were determined for panels type FA-2.2, including resin catalyzed by HCOOH with initial F/U = 2.2. These results show that the MOR and MOE of MDF decrease by using the wood leachate as a resin recycled catalyst. From the results, the MOR and MOE values were higher than the requirements of the EN6-225 standard for all of the samples prepared, except for WL-2 [87].

One of the major problems for using MDF is its stability in terms of thickness swelling (TS) as these products are for building applications and to be used under wet conditions. Thus, panel stability needs to be proved under wet condition [88]. Fig. 12 (c) shows the effect of resin type on TS of MDF. TS of the MDF for all types of resins were almost the same and comparable for all liquid UF resins. However, the lowest and highest TS were that of the MDF panels bonded with WL-2 (10.5%) and FA-2.2 (14.8%), respectively. The result obtained for TS confirmed that the wood leachate as a catalyst replacement for HCOOH not only did not have any negative effect but also tended to lower the TS value for the MDF panel. The MDF bonded with UF resins catalyzed by the leachate produced the lowest thickness swelling compared to HCOOH catalyzed resins. As a result, the MDF composites bonded with the WL-2 resin includes the highest amount of branched-type methylene bridges (i. e.24.40. Table 4) to give a good resistance to water. The TS measurements showed that samples with an initial molar ratio of 2.2 resulted in MDF panels which met the requirements of the EN6-225 standard [87].

The effect of different resin compositions on the formaldehyde



Scheme 1. Mechanism of formaldehyde catching by phenol.

emission (FE) level for MDF is shown in Fig. 12 (d). The results show that the foremost impact of the leachate-catalyzed resin was its lowest formaldehyde emission. These results may be related to the lower free formaldehyde (HCHO) and hydroxyl methyl groups. The formaldehyde emission has diverse sources: unreacted free formaldehyde (HCHO), rearrangement of methylene-ether linkages and hydrolysis of methylene bridges. When utilizing the leachate catalyst during resin synthesis, its phenolic sites reacts with formaldehyde.

The minimum value of formaldehyde (HCHO) gas emission was measured for MDF bonded with WL-2. Thus, MDF bonded with UF resins catalyzed by wood leachate with initial F/U = 2 M ratio had the lowest formaldehyde (HCHO) emission with 5.7 mg/100 g (27% less than FA-2). They were followed by MDF bonded with F/U = 2.2 M ratio (6.9 mg/100 g) and finally MDF produced with FA-2.2 (9.3 mg/100 g). By diminishing the initial F/U molar ratio, the formaldehyde content of the liquid UF adhesive so prepared will be lower. This leads to a decrease of the relative proportion of hydroxymethyl groups, particularly of the -NH-CH₂OH one. The results show that the free formaldehyde (HCHO) emission of the MDF types WL-2, WL-2.2 and FA-2 met the requirement of a maximum limit of 8 mg/100 g for the E1 emission class. The decrease in formaldehyde emission of the MDF where HCOOH was replaced by the wood leachate in the UF resin synthesis can be attributed to the amount of phenolic derivatives, especially lignin and tannin in the wood leachate. Environmentally friendly tannin-formaldehyde adhesives are known to be among the cheapest binders and present low-formaldehyde emission. The results obtained for formaldehyde emission have important practical implications so that the wood leachate could be applied as an excellent formaldehyde catcher for UF-bonded MDF. This is due to the reactions between unreacted formaldehyde and unsubstituted para or ortho aromatic sites in the wood leachate constituents, i.e. phenol, tannin and lignin (Scheme 1).

Fig. 12 (e) shows the internal bond (IB) strengths for the MDF panels bonded with the industrial grade liquid UF adhesives synthesized in this work. The IB values of the experimental MDF panels ranged from 0.53 to 0.61 MPa. Although there was no significant difference between different adhesive compositions, MDF panels manufactured with FA-2.2 (0.61 MPa) had the highest internal bond, while the lowest internal bond was obtained for MDF manufactured with WL-2, i.e. 0.53 MPa. The IB values at the same initial molar ratio decreased when the HCOOH was replaced by the wood leachate. According to the results, the IB strengths of the panels prepared are near to the requirements of the EN6-225 standard which is of 6 MPa and it met its requirements for the FA-2.2 sample [87].

By comparing the results of the MOR, MOE, IB and TS with the FE values, it can be concluded that the samples that were bonded with the adhesive with the higher initial molar ratio resulted in better physico-mechanical properties. This is related to the higher formaldehyde content of the resin which reacts with the still unreacted urea during the hot-pressing process leading to better bonding [26].

Wood leachate as a biomass derived catalyst can be a remarkable innovation. The key is to coordinate synthetic chemistry, natural catalyst and process improvement beneath the umbrella of green chemistry

standards. Results from this work provide justification for future process scale-up and wood leachate performance evaluation. Apart from wood leachate performance, bio-based resins can offer other commercially relevant advantages. The most important one is pricing. Broadly, the “wood leachate” approach can be applied to other resins, catalyst chemistries, and acid applications to accelerate the development and adoption of renewable materials.

4. Conclusions

Intrinsic renewability of bio-based components can ease the process of recycling, and better environmental compatibility can save costs and efforts in terms of health and safety. The work presented here reports that a hazardous wood leachate waste can be used as a renewable catalyst for industrial grade liquid UF resins and for MDF bonded with them. Such an approach has not been investigated before. Thus, a novel and simple approach has been developed for the recovery of a hazardous waste as a catalyst to synthesize UF resins for MDF panels. Addition of wood leachate as a recycled catalyst into UF resins significantly reduces the formaldehyde emission of the MDF bonded with them, of considerable interest for indoor furniture manufacture. Besides, using resins catalyzed by wood leachate improves MDF thickness swelling but there does not appear to significantly influence the mechanical properties compared to UF HCOOH catalyzed MDF. Developing high value-added use from these waste-waters would prevent environmental concerns and add economic returns to the wood-based composite industry. Thus, wood leachate as a recycled catalyst in MDF and resin production has the potential to markedly lower manufacturing cost, and to reduce the burden of wood waste as a result of the biodegradability of the final environment-friendlier products. Further optimization to the process described here can be envisaged (e.g. addition of wood leachate as UF resin hardener and formaldehyde scavenger) to further improve production efficiency, or wood panel properties.

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