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Review Article

The Removal of Cured Urea-Formaldehyde Adhesive towards Sustainable Medium Density Fiberboard Production: A Review

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ABSTRACT

Medium density fiberboard (MDF) is an engineered wood product that has density and specific gravity similar to solid wood, ranging from 600 to 800 kg/m^3 of density and 0.6 to 0.8 of specific gravity. This makes MDF suitable to partially replace solid wood, particularly for interior application. Approximately over than 100 million m^3 of MDF are produced in 2020, resulting in a large amount of waste MDF will be generated in the next 20 years. MDF is produced using urea-formaldehyde (UF) resins adhesive. UF resins adhesive is a poly-condensation product of urea and formaldehyde via an alkaline acid two-step reaction. Sustainable MDF production is required as the world is facing climate change and deforestation. Recycling is a way to support sustainable production in the engineered wood products manufacturing. Many attempts have been done to find ways to recycle waste MDF. The main problem is UF resins, which bond the MDF panel fibers. In order to re-manufacture the waste MDF into new recycled MDF, UF resins should be eliminated from the waste MDF before being used. The presence of UF resins in MDF can interfere with the utilization of the recycled fibers, whether it will be used as a raw material for new MDF or other composite products. This paper reviews the process of removal of cured UF resins from waste MDF panel by considering the hydrolytic stability of cured UF resins for MDF recycling, providing a comprehensive review of how cured UF resins can be removed from waste MDF and characterization of recycled fibers obtained from recycling prior to re-manufacturing of recycled MDF panel.

1. Introduction

Medium density fiberboard (MDF) is an engineered wood product formed by blending natural fibers with a mixture of resin and wax, and moulding the panels using hot-pressing at high temperature and pressure. In 1965, MDF was produced in accordance to the hardboard manufacturing in the United States. By the time, the dry-process MDF was developed as an alternative to the wet-process fiberboards, which generated huge amounts of polluted wastewater and must be treated before disposal (Ormondroyd and Stefanowski 2015; Suchsland and Woodson 1986). MDF is a relatively cheap building material with similar application to plywood. It has a more uniform density from 600 to 800 kg/m^3 and has tight edges compared to particleboard, resulting in an even and flat surface of MDF panel that can be assembled into complicated and curved shapes. This panel is widely used in many applications, such as decorative and interior applications, building components, and constructions. MDF is now versatile as solid wood because it can be nailed, glued, screwed, stapled, and attached with dowels (Antov and Savov 2019; Schulte and Frühwald 1996).

MDF has achieved great success as a superior product in the engineered wood product marketplace (Mantanis et al. 2018). A report by the Food and Agriculture Organization (FAO) in Forest Products Annual Market Review 2019 indicates that the global production of MDF is foreseen to reach 100 million m^3 in 2020 globally (FAO 2019). The upswing is attributed to the increase in the world population that makes a comeback of the housing construction and furniture industry. As presented in **Table 1**, around 69% of the world's MDF production is supplied from Asia which near to 70 million m^3 of MDF are produced annually, followed by traditional MDF powerhouses of America and Europe for around 10% and 17%, respectively (FAO 2019). In case of consumption trend, around 69% of total 99 million m^3 of MDF are utilized annually in Asia, mostly in China. Approximately 15% and 12% of total MDF are used in Europe and America, respectively. Less than 2.5% of MDF are utilized in Oceania and Africa regions. MDF panels are mainly used as furniture and other interior applications (Schulte and Frühwald 1996). Export and imports MDF activities are done to provide a balance supply chain of MDF panels. Europe becomes the largest MDF's exporter and importer, followed by Asia and America regions. In Indonesia, the average production of MDF panel is 500,000 m^3 per year. The MDF panels are used domestically for around 218,000 m^3, and the rest of panels are exported to Europe and America regions.

Table 1. Production, consumption, exports, and imports of MDF in 2019 (FAO 2019)

Region	**Production (1,000 m^3)**	**Consumption (1,000 m^3)**	**Exports (1,000 m^3)**	**Imports (1,000 m^3)**
Europe	17,764	15,278	9,792	7,306
America	10,518	12,129	2,203	3,822
Asia	69,385	69,145	6,520	6,113
Indonesia	500	218	402	120
Oceania	1,385	910	641	167
Africa	392	1,310	42	960
Total	99,944	98,990	19,600	18,488

MDF can be used roughly for 30 years in decorative and interior applications before disposal (Deak 2013). With nearly 10 million m^3 of MDF is produced every year globally, it can be estimated that around 20 million tons will become waste MDF in the next 30 years (FAO 2019; Kharazipour and Kues 2007; Morris 2017). These wastes are regularly disposed in landfills or burned (Morris 2017; Rivela et al. 2007). Nowadays, disposing or deploying in landfills is no longer considered a suitable solution for waste MDF due to it consumes a large land space. Furthermore, disposal of these wastes may be a source of formaldehyde emission due to the degradation of urea-formaldehyde (UF) resins by microorganisms (Pérez 2016). Moreover, the leached UF resins may influence the groundwater and form methane that has a hazardous greenhouse effect than carbon dioxide (Kharazipour and Kues 2007). On the other hand, burning or incineration does not give a solution as it releases dioxins and carbon dioxide (Morris 2017). As the main adhesives used in MDF manufacturing, UF resin is easy to hydrolyze in a humid environment. The hydrolysis reaction of UF resin is a reversible reaction of its synthesis reaction (Dutkiewicz 1983; Myers 1984, 1987). Therefore, recycling of waste MDF is a viable option to eliminate the disposing and burning of these wastes.

Waste MDF is traditionally placed of in landfills. According to European Regulation, waste containing more than 5% organic material cannot be deposited in landfills since 2005 (European commission 1997). This means to all wood waste, including decorative and interior appliances made from MDF. Therefore, deploying in landfills is not considered as a suitable solution for their handling because the degraded UF resins may affect the subsoil water (**Table 2**) (Kharazipour and Kues 2007; Rivela et al. 2007). In addition, around 72% of the waste produced from MDF manufacturing goes to incineration for energy recovery and 28% goes to landfills (Rivela et al. 2007). Therefore, growing attention has been given to the issue of recycling waste MDF panels. An understanding of the hydrolytic stability of cured UF resin can give a basic knowledge on how to eliminate the cured UF resin from the waste MDF panel. Furthermore, a method to recover the recycled fibers is needed to re-manufacture a new panel from the recycled fibers (Antov et al. 2020).

Table 2. Effect of wood waste management to the environment (European Commission 1997)

Techniques	**Environmental effect**		
	Air	**Water**	**Soil**
Landfilling	Carbon dioxide and methane emission, and unpleasant smell	Releasing toxic compounds into subsoil water	Forming up of hazardous substances in soil
Incineration	Emits carbon dioxide, methane, sulfur oxide, nitrogen monoxide, and dioxin	Side effects of hazardous substances into water	Discharging of fly ashes and smoke residues
Recycling	No environmental effect		

Recently, four options are for the recovery of recycled fibers from MDF: ohmic heating process (Moezzipour et al. 2018), autoclaving process (Kharazipour and Kues 2007), microrelease and microwave technology (Elias and Bartlett 2018), and hydrothermal process (Lykidis and Grigoriou 2008). Much effort has been done to find ways for recycling waste MDF. Re-manufacturing of waste MDF into new MDF requires the removal of the cured resins. The simplest way to recycle waste MDF is by shredding and soaking it in a water solution. This method works well but utilizes huge amounts of water and energy. A new ohmic heating process has been developed by Moezzipour et al. (2018) specifically for MDF recycling. First, the MDF is mechanically shredded to form small particles. Furthermore, it is soaked in water, and an electric current is generated through it, resulting in expeditious heating and disintegrate the waste MDF into the fiber by using less water. The recycled fibers have quite a good grade to be re-manufactured into new MDF panel. Other alternative processes are micro-release and microwave (Elias and Bartlett 2018). The micro-release process consists of the following steps; shredding and separation of waste MDF, immersion in water at 98°C for 5 min, microwave release which causes swelling for fiber disintegration, separation of recycled fibers through mechanical screening, and drying process until the recycled fibers have 16% of moisture content. Finally, the recycled fibers can be used as raw material to replace a portion of virgin fiber to produce recycled MDF.

Another process that can be used to obtain recycled fibers from waste MDF is autoclaving (Kharazipour and Kues 2007). This process combines a vacuum and pressurized steam with mechanical agitation at temperatures of up to 160°C. Pressures in the process are relatively low at 2 bar. Also, there is no addition of chemicals, so the process does not damage the fibers. The advantages of this process are it produces good quality fibers, very little effluent produced, less adhesive retain on the fibers, and coatings such as melamine can be removed due to a combination of vacuum and pressurized steam at high temperatures. However, it possesses several disadvantages such as, it is still a laboratory scale, limited end uses for the fiber, seen predominantly as a pre-processing step. The last process to recover the recycled fiber from waste MDF is the thermohydraulic process (Lykidis and Grigoriou 2008). It is particularly used to separate the UF resin from the wood fibers in waste MDF by hydrolysis in a pressurized saturated steam environment. It is an integrally capital and energy-intensive process, predominantly due to the use of pressurized saturated steam up to 5 bar and temperatures of up to 120°C. This process is a combination of the autoclaving process. In general, the thermohydraulic process uses the same basic set up. It includes a chipper, an impregnation solution of urea and water, an autoclave, a dryer, and a drum screen. It can be operated with large scale capacities. The recycled fibers then display less resin content, which eventually possess less formaldehyde emission than other processes (Roffael and Hüster 2012).

2. Synthesis of UF Resins

Urea-formaldehyde (UF) resins adhesive is most widely used in the manufacture of wood-based panels due to their low cost, high reactivity, good performance, and easy to use (Dunky 1998; Gonçalves et al. 2018). UF resins adhesive is generally prepared via an alkaline-acid (addition-condensation) two-step reaction (Gonçalves et al. 2019; Kim 1999). The addition (or hydroxymethylation) reaction usually occurs at alkaline condition, while the condensation reaction occurs at acid pH (Kim 1999, 2000, 2001). As depicted in **Fig. 1**, formaldehyde is hydrated to form methylene glycol ($CH_2(OH)_2$) and the urea forms its anion ($-H_2N-CO-NH-$) at the initial reaction (Smythe 1951, 1952). A certain amount of $CH_2(OH)_2$ is then reacted reversibly with $-H_2N-CO-NH-$ to form mono-hydroxymethyl urea ($H_2N-CO-NH-CH_2OH$). Further reaction leads to the formation of di-hydroxymethyl urea ($HOH_2C-H_2N-CO-NH-CH_2-OH$) or tri-hydroxymethyl urea ($HOH_2C-H_2N-CO-NH-(CH_2OH)_2$) during the addition reaction. The formation of mono-, di-, and tri-hydroxymethyl ureas are counted for around 25%, 63%, and 12%, respectively, at the addition reaction (Gonçalves et al. 2019; Wang et al. 2018). The formation of hydroxymethyl groups depends on the F/U mole ratio. A higher F/U mole ratio increases the formation of highly hydroxymethylated species. It is also shown that the addition reaction kinetics followed the second-order and is proportional to the initial F/U molar ratio, showing that less formaldehyde has been reacted at a lower initial F/U molar ratio and resulting in poor performance of UF resins (Lubis and Park 2020a; Wibowo et al. 2020). The condensation reaction of UF resins takes place at acidic condition, at pH of 4 to 6. As displayed in **Fig. 2**, condensation reaction allows mono-, di-, and tri-hydroxymethyl ureas to react with each other and with urea, leading to the formation of UF oligomers such as methylene diurea and hydroxymethyl-methylene diurea (Kibrik et al. 2014; Steinhof et al. 2014).

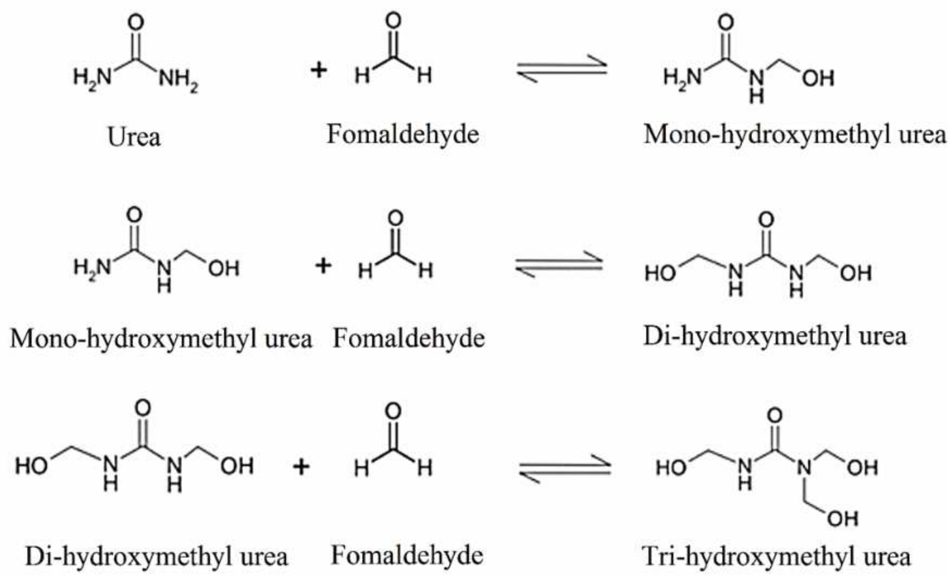


Fig. 1. Addition reaction of UF resins at alkaline condition.

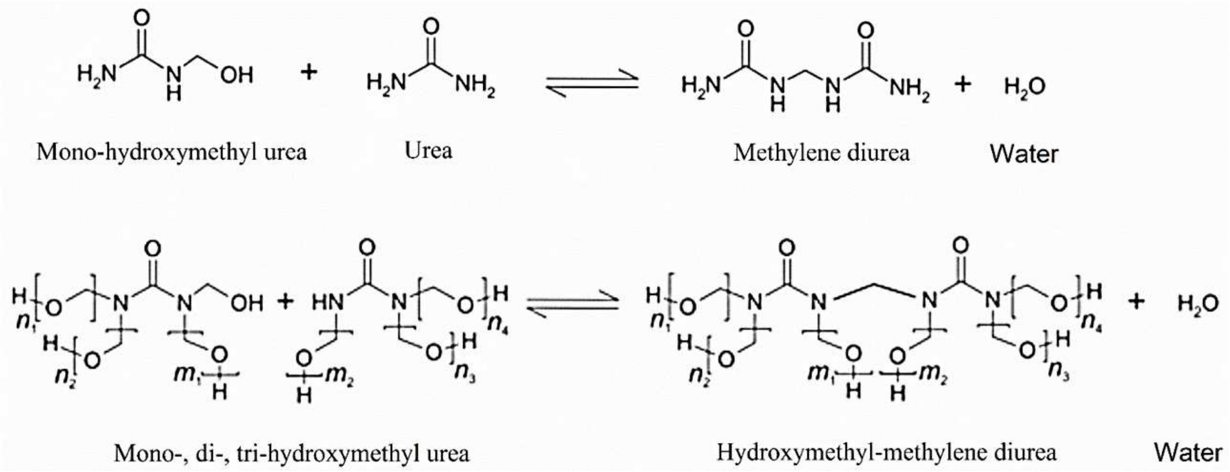


Fig. 2. Condensation reaction of UF resins at acidic condition.

Properties of UF resins can be tailored by adjusting their F/U mole ratios. **Table 3** compiles several reports on how F/U mole ratio affects the properties of UF resins. Initial and final F/U mole ratio play a significant role on the formation of UF polymer and properties of final UF resins. Increasing the final F/U mole ratio from 1.0 to 1.6 significantly improves the reactivity of the resins, indicating by shorter gelation time. However, it comes with a greater amount of free formaldehyde in the resins, which leads to high formaldehyde emission from UF-bonded panels. By contrast, lower F/U mole ratios UF resins, such as 1.0, show less free formaldehyde and longer gelation time, regardless of their initial F/U mole ratios used for the synthesis. This will lead to different hydrolytic degradation behavior of UF resins.

Table 3. Synthesis method and properties of UF resins

No.	F/U mole ratio		Properties				References
	Initial	Final	Solids content (%)	Viscosity (mPa.s)	Gelation time (s)	Free formaldehyde (%)	
1	2.0	1.6	53–55	250–300	50–70	0.6–0.8	(Myers 1984; Park et al. 2006; Park and Kim 2008; Yadav et al. 2020)
2	2.0	1.4	54–56	240–280	70–90	0.5–0.7	
3	2.0	1.2	55–58	230–260	100–120	0.4–0.6	
4	2.0	1.0	58–60	210–250	130–140	0.3–0.4	
5	3.0	1.0	60–61	190–230	150–160	0.2–0.3	(Chuang and Gary 1992; Lubis and Park 2020a; b)
6	4.0	1.0	61–62	190–220	170–180	0.2–0.3	

3. Hydrolysis of Cured UF Adhesive

As the main adhesive in MDF manufacture, UF resins adhesive is known as highly cross-linked thermosetting, rigid, and crystalline-like polymers (Chiavarini et al. 1978; Jada 1988). This adhesive is noted for its reactivity, inexpensive, low curing temperature, good mold resistance, superior thermal properties, and colorlessness (Conner 1996; Dunky 1998). Owing to its advantages, UF resins adhesive has been widely used as an adhesive in the engineered wood products manufacturing, such as MDF, particleboard, and plywood. However, this resin possesses two critical disadvantages namely, formaldehyde emission and low water resistance (Myers 1984, 1987). The possible structure of cured UF resins is shown in **Fig. 3** (Kibrik et al. 2014; Steinhof et al. 2014). UF resins are connected via methylene and ether linkages to form cross-linked thermosetting cured adhesive. Low stability of cured UF resins against hydrolysis under acidic and humid conditions causes formaldehyde release from engineered wood products bonded with UF resins (Abdullah and Park 2009; Lubis et al. 2018b; Park and Jeong 2011b). The brittleness of the cured UF resins causes cracking and allows the moisture to penetrate the UF-bonded products, resulting in cured UF resins susceptible towards hydrolysis. This eventually leads to splitting down the amino bonds within the cured resin (Dutkiewicz 1983; Lubis and Park 2018).

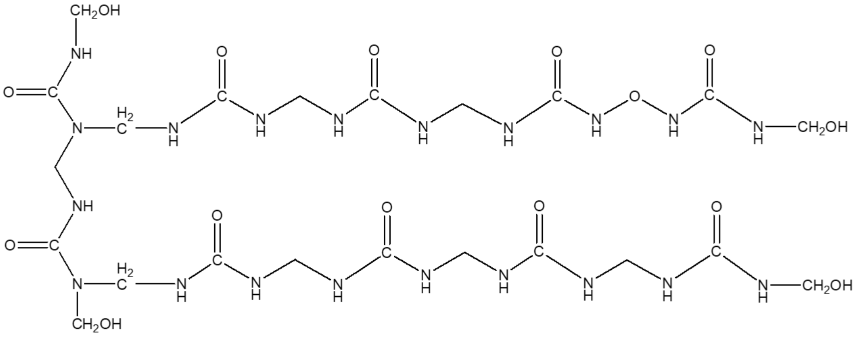
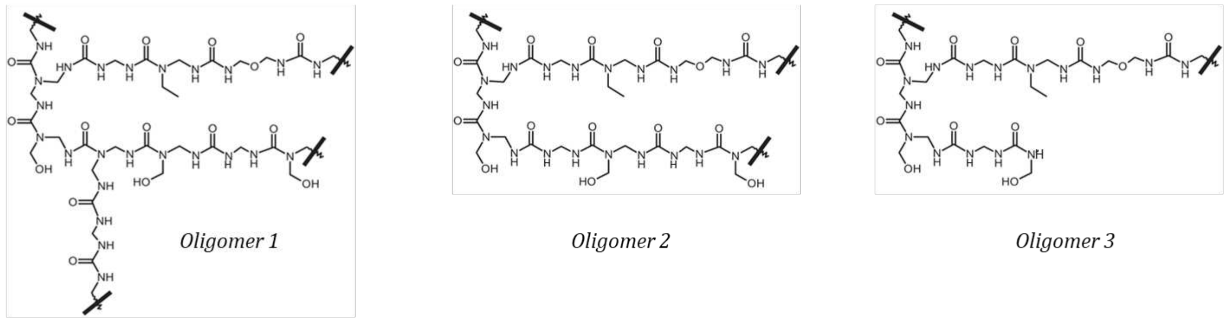


Fig. 3. Possible structure of cured UF resins.

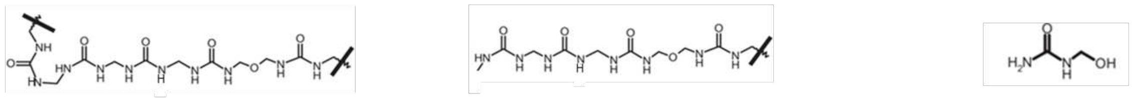
Hydrolysis is a chemical reaction that breaking down a chemical compound by the water molecule. In organic chemistry, hydrolysis can be considered as the reverse reaction of condensation. Based on the ^{13}C-CP-MAS-NMR analysis, dimethylene ether linkage groups attached next to amides are more sensitive to hydrolysis than linear and branched methylene linkages (Chuang and Maciel 1994). Tri-hydroxymethyl urea is more susceptible to hydrolysis than that of di-hydroxymethyl uron. The decomposition of the cured resin depends on its formaldehyde to urea (F/U) mole ratio, chemical structure, and cross-linking density. **Fig. 4** displays the chemical compounds of UF resins after hydrolysis. Initial hydrolysis results in UF oligomer 1, 2, and 3 are composed of linear and branched structures which connected through methylene and ether linkages. The hydrolyzed compounds have a molecular weight (MW) of around 600 g/mole to 1,000 g/mole, depending on the oligomers. Further hydrolysis forms smaller molecules such as trimer, dimer, and possibly monomer. These compounds consist of mono-, di-, tri-hydroxymethyl ureas, methylene diurea, and methoxymethylene diurea (Kibrik et al. 2014; Steinhof et al. 2014).

1. Molecular weight : 900 - 1000 2. Molecular weight : 800 - 900 3. Molecular weight : 600 - 700



Oligomer 1 *Oligomer 2* *Oligomer 3*

4. Molecular weight : 400 - 500 5. Molecular weight : 200 - 300 6. Molecular weight : 60 - 100



Trimer (monomethylol urea + methylene diurea + methoxymethylene diurea) *Dimer (methylene diurea + methoxymethylene diurea)* *Monomer (urea, monomethylol urea)*

Fig. 4. Possible chemical compounds from hydrolysis of UF resins (adapted from Dutkiewicz 1983; Lubis and Park 2018; Steinhof et al. 2014).

The cured resins are more susceptible to hydrolysis in humid and acidic conditions than in neutral and basic conditions (Dutkiewicz 1983; Lubis and Park 2018). Several approaches have been attempted to estimate the stability of UF resin against hydrolysis by assessing the formaldehyde liberation and structural stability (Myers and Koutsky 1990; Nuryawan and Park 2016; Park and Jeong 2011a; Ringena et al. 2006). Formaldehyde liberation is an important indicator for the degree of hydrolysis of the resin. This approach quantifies the amount of dissolved formaldehyde in the hydrolyzed filtrate or extracts solution. The determination of the dissolved formaldehyde is according to the acetylacetone method (EN 1992) or the sulfite method (TAPPI 2001). Structural stability determines the mass loss of the resin due to decomposition by hydrolysis. The general procedure for hydrolysis of UF resin is shown in **Fig. 5**.

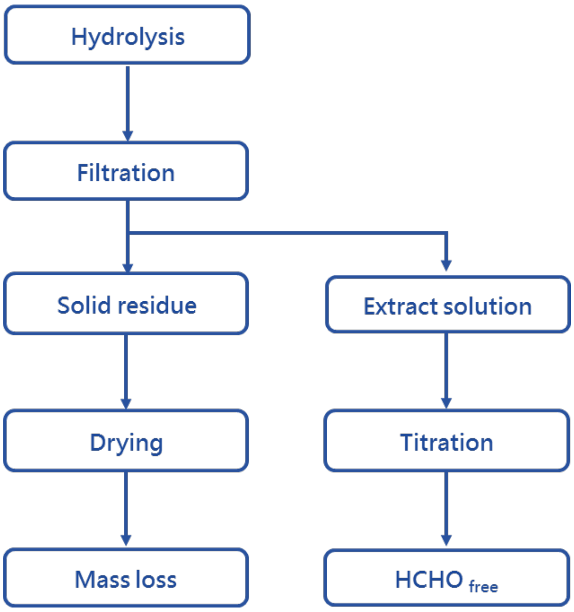


Fig. 5. Flow diagram of general hydrolysis of UF resin (Park and Jeong 2011a; Ringena et al. 2006).

Regarding the stability of cured UF resin against hydrolysis, the crystalline regions in the cured resin influence the hydrolytic stability of the cured resin (Levendis et al. 1992; Nuryawan et al. 2017; Park and Causin 2013; Singh et al. 2014). Furthermore, the X-ray diffractogram reveals that the crystalline regions are presented in UF resin with lower F/U mole ratios, while amorphous regions appear in UF resin with higher F/U mole ratios. The crystal formation in UF resin with lower F/U mole ratios contributes to the improvement of stability of the cured resins towards hydrolysis (Park and Causin 2013). Park and Jeong (2011a) proved that two areas were obtained in cured UF resin by the atomic force microscopy, namely the hard phase and soft phase area. The hard phase area belonged to the crystalline structure that was more resistant to hydrolysis than the soft phase area. This indicates that low molar ratio UF resins have greater stability towards hydrolysis than those of high molar ratio UF resins.

The durability of cured UF resins adhesive joint facing environmental force is important for the long-term performance of an engineered wood product (Ringena et al. 2006). Several causes are responsible for this phenomenon. First is the disruption of adhesion between wood and adhesive due to replacing the reactive groups of the adhesive by water (Pizzi and Valenzuela 1994). Second is the disruption of cohesion at the glue line due to the water inducement, which changes the dimensional of wood (River et al. 1994). The last is the degradation of the cured resins by hydrolysis that splitting the linkages within the adhesive network (Myers 1984, 1987). However, less information regarding the removal of cured UF resin from an engineered wood product, particularly MDF panel, because of hydrolysis. Herein, a method is proposed to allow us to calculate the quantity of cured UF resin that has been degraded by hydrolysis from the waste MDF. The detailed method will be explained in the next part.

4. Hydrolysis of MDF for Removal of Cured UF Adhesive

MDF performance is obtained by combining the adhesion and cohesion strength resulted from UF resin as a bonding agent, wax as a hydrophobic agent, and their interaction with natural fibers (Grigsby et al. 2012). It was shown that both wax and UF resin are mobile on the fiber during MDF manufacturing, and the distribution of the resin highly depends on the fiber drying and pressing (Grigsby and Thumm 2012; Loxton et al. 2003). Several works have been attempted to determine the distribution and coverage of cured UF resin in the MDF panel by applying confocal laser scanning microscopy (CLSM). The rhodamine as the fluorescent dye was incorporated into UF resin at a loading of 0.19% (w/w oven-dry solid) for fabricating the MDF panel (Loxton et al. 2003). Approximately 3 MDF cubes (10 mm x 10 mm) were cut from the MDF panel between the below surface and the core of the panel. Subsequently, the cubes were immersed in a glycerol/water mixture (70:30) and then analyzed using a Leica TCS/NT confocal microscope with a 20 x 0.5 of the dry lens. Filters were used to separate the fluorescence of fiber and resin label components into green and red light. CLSM image distinguished the fiber as green and cured resin as red, which indicates that the MDF fiber is covered by resin. The measurement obtained a calculated resin coverage between 42 and 94%.

Another work also tried to determine the cured UF resin distribution and coverage in MDF panel using CLSM (Grigsby et al. 2005). This work did not use rhodamine as a fluorescent dye, but it used acrifavine (3,6-diamino-10-methyl-acridinium chloride). Furthermore, they did not mix the fluorescent dye with the resin prior to MDF manufacturing. Approximately 1 g of unresinated and resinated fiber obtained from the MDF mill was immersed in 20 mL of staining solution. The staining solution consisted of 0.5% (w/w) acriflavine solution, 50% HCl, and water. The solution was gently agitated for 3 min. Then the suspension was filtered and cleaned with 500 mL of water. Subsequently, fiber was air-dried. They called this as original staining method. Furthermore, they tried to compare the CLSM images obtained from the original staining method and adapted it. In the adapted staining method, after the suspension was filtered, the fiber was immediately immersed in 20 mL of 20% formalin solution for 2 min. Then, the suspension was filtered again and washed with 500 mL of water. The same Leica TCS/NT confocal microscope was used to determine the UF resin distribution and coverage in the MDF panel. Both fiber and resin appear as yellow-green to red color. However, with the adapted staining method, the fiber and resin can be distinguished by CLSM. The introduction of formalin as a washing solution for stained fibers created a greater contrast between the resin component and the fiber. This indicates the cured resin is well distributed in MDF fiber. However, as the main adhesives used in MDF manufacturing, UF resins adhesive is easy to hydrolyze under acid and humid environments (Lubis et al. 2018b; Lubis and Park 2018).

To investigate the curing of UF resins in MDF panels, several works have been accomplished by hydrolyzing the MDF panel in different hydrolysis chemicals at different temperatures and times (Grigsby et al. 2014, 2015; Lubis et al. 2018b). They prepared MDF panel, cured UF resin alone, cured UF resin on fiber, and a combination of wood flour with UF resin. The MDF was first ground by a hammer mill to obtain the sample with 12 mesh of size. Furthermore, the sample goes to hydrolysis and analysis, as shown in **Fig. 6**. The sample was then filtrated to separate the solid residue and extract the solution. The nitrogen (N) content in the MDF panel prior to hydrolysis treatment was determined by the Kjeldahl method. Furthermore, the N content in solid residue and extract solution was measured by the Kjeldahl method. It is well known that UF resin is composed of an amide bond, which is consists of a C−N−H bond (Dunky 1998). Therefore, measurement of N content in the MDF before and after hydrolysis can be used in calculating how many cured UF resin has been removed from the panel. The Kjeldahl method was first introduced by Johan Kjeldahl in 1883. This method determines the N content in organic and inorganic materials. The N content of the MDF panel before and after hydrolysis can be determined according to T418 cm 97 (TAPPI 1997).

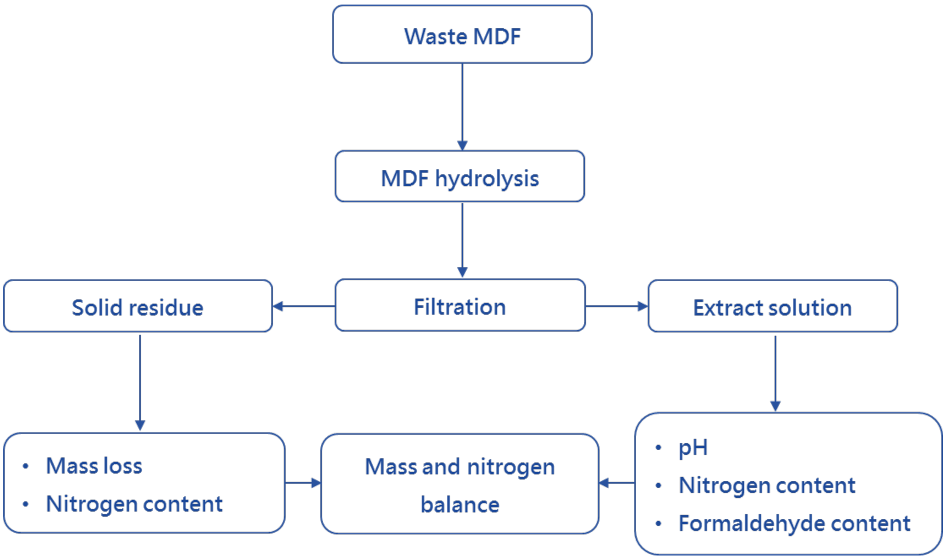


Fig. 6. Flow diagram of waste MDF hydrolysis (Grigsby et al. 2014, 2015; Lubis et al. 2018b).

1. Digestion

Approximately 2 g of MDF powder is weighed using an analytical balance. The sample is then put into 500 ml of Kjeldahl flask. Furthermore, 15 g of potassium sulfate (K_2SO_4) and 0.7 g of mercuric oxide (HgO) are added into the flask. Subsequently, 25 ml of concentrated sulfuric acid (H_2SO_4) is carefully added into the flask. The sample is agitated slowly in the fume hood until all MDF powder is wetted by the acid. Then, the sample is heated cautiously with an electric heater in the fume hood. The digestion process is finished until the solution becomes colorless. A scheme reaction for the digestion of an organic sample is presented below:

$$\text{Sample} + H_2SO_4 \longrightarrow (NH_4)_2SO_4 + H_2O + CO_2 + SO_2$$

2. Distillation

After digestion, the solution is cooled to room temperature. Some liquid should remain after cooling. Furthermore, 300 ml of ammonia-free water is added cautiously into the flask, followed by 25 ml of sodium thiosulfate ($Na_2S_2O_3$) to precipitate the mercury. The digestion solution is then allowed to stand and occasionally agitated for 10 min. After that, 50 ml of the boric acid (H_3BO_3) indicator solution is prepared in a 500 ml Erlenmeyer flask receiver to capture the free ammonia. Finally, 55 ml of 50% sodium hydroxide and boiling stone are added into the digestion solution. The distillation process is done in the fume hood using a distillation unit. The distillation process is finished until 150 ml of solution in the receiver. A general reaction for the distillation is shown below:

$$(NH_4)_2SO_4 + 2NaOH \longrightarrow Na_2SO_4 + 2H_2O + 2NH_3$$
$$NH_3 + H_3BO_3 \longrightarrow NH_4^+ : H_2BO_3^-$$

3. Titration

Titration is done to measure the ammonia concentration in the sample. It is generally accepted that ammonia concentration is proportional to nitrogen content in the sample (Taheri et al. 2016). Before titration, the distillate solution is diluted to about 250 ml with ammonia-free water. Furthermore, the distillate solution (green color) was titrated directly with 0.1 N of hydrochloric acid (HCl). During the titration, the color will change from green to gray and finally to purple (pH about 4.9). About 1 g of dextrose is prepared in the Kjeldahl flask for blank determination through the entire procedure. A scheme reaction for the titration step is shown below:

$$2NH_4^+H_2BO_3^- + 2HCl \longrightarrow 2NH_4Cl + 2H_3BO_3$$

4. Calculation

The N content (%) in the sample is counted by using equation 1 (TAPPI 1997):

$$N\,(\%) = (1.4 \times V \times N)/W \times 100\% \qquad (1)$$

where: V = amount of hydrochloric acid required to titrate the distillate (ml)
N = concentration of hydrochloric acid (N)
W = mass of sample (g)
1.4 = equivalent mass of nitrogen (g)

The resin removal (%) from the waste MDF is counted by using equation 2 (Grigsby et al. 2014):

$$Resin\ removal\ (\%) = (Resin\ mass\ loss)/(Resin\ content) \times 100\% \qquad (2)$$

where: *Resin mass loss = MDF panel mass loss - Fiber mass loss*

Kjeldahl method and elemental analysis are often used for the measurement of N content. Increment of the N content in the MDF panel was detected at different recycled MDF panels (**Fig. 7**). Further studies showed that around 60% of N had been extracted by hydrolysis at different conditions (**Fig. 8**). Depending on the hydrolysis chemicals and conditions, acidic and elevated temperatures extracted more N from waste MDF than those of neutral and basic conditions. Similar trend is showed that the removal of cured UF resins from waste MDF panels increased at acidic and elevated temperatures (**Fig. 9**). Increasing the resin content provides a greater chance for the resin component to be fully cured by reacting to each other, leading to a lower removal of cured UF resin from the panel with increasing the resin content.

The disintegration of cured UF resin from waste MDF panel indicates that a remarkable amount of UF resins adhesive may not fully cross-link to form an integral matrix in MDF (Grigsby et al. 2014; Lubis et al. 2018b). Around 40-90% of cured resin has been removed by hydrolysis is predicted to be UF oligomers. Based on the gel permeation chromatography (GPC) analysis, the extract solution of the MDF panel contained both wood fiber extracts and UF resin components. The latter dominated the molecular weight (MW) profiles of extract solution. The GPC analysis also showed that the extract solutions obtained from MDF with different resin content were mainly low-MW oligomers species. There were no high-MW oligomers present in the extract solution (Grigsby et al. 2015). These low-MW oligomers are probably susceptible to hydrolysis and emit formaldehyde from the panel.

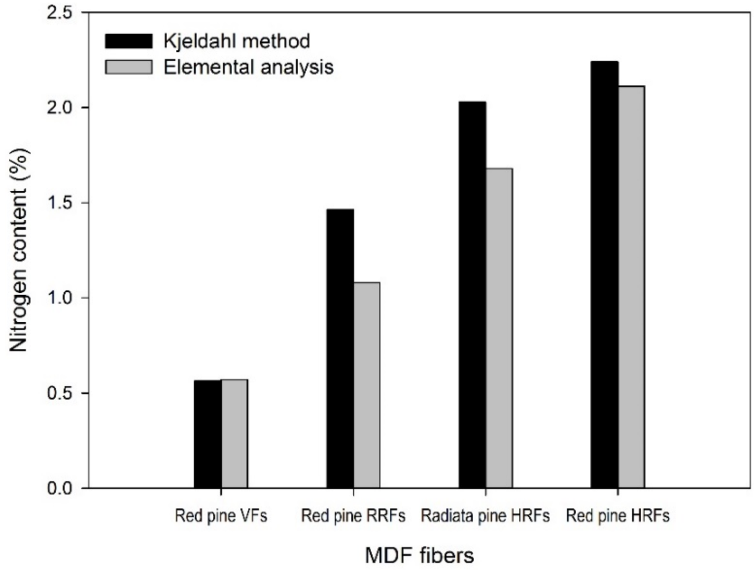


Fig. 7. Nitrogen content of different types of MDF panels.

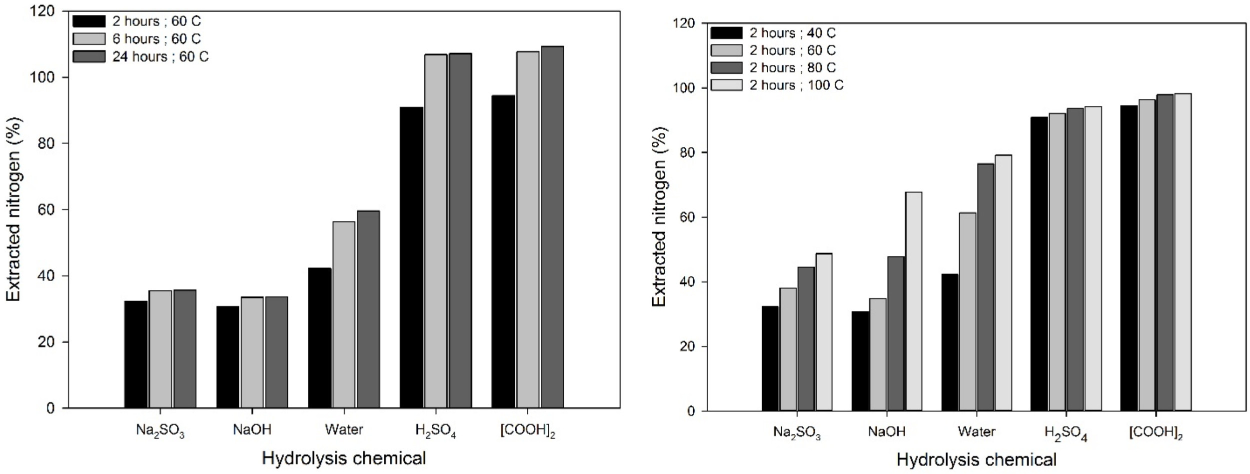


Fig. 8. A comparison of extracted nitrogen from MDF panels at different hydrolysis conditions.

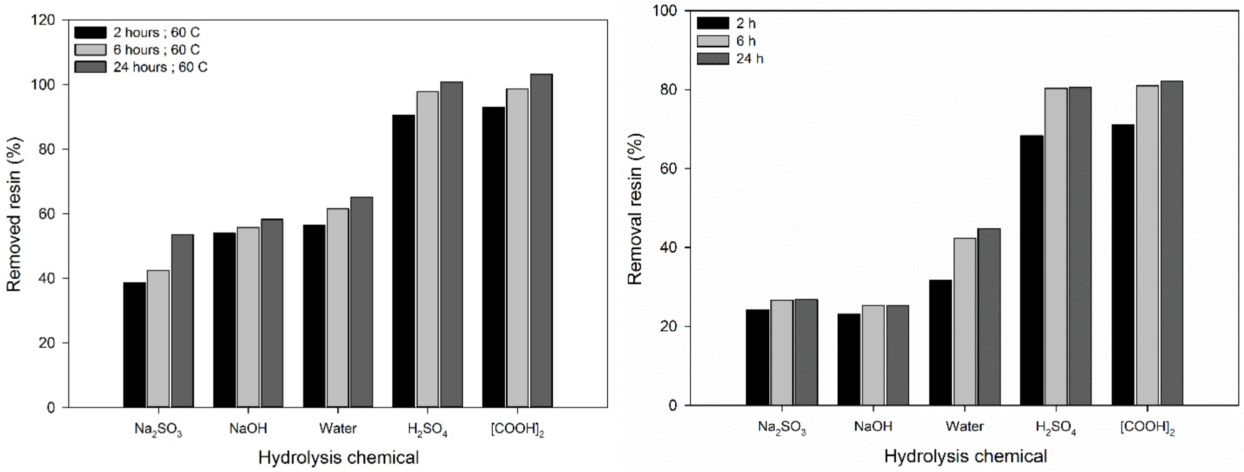


Fig. 9. A comparison of resin removal from MDF panels at different hydrolysis conditions.

Low water resistance and formaldehyde emission of UF resins are considered due to the hydrolytic degradation (Chuang and Maciel 1994; Dutkiewicz 1983; Lubis and Park 2018). The degree of hydrolysis of the cured resin can be determined by measuring the acidity and formaldehyde content of the hydrolyzed extract solutions. At least two hydrolysis reactions occur in the hydrolysis of wood composite. The first is the hydrolysis of wood components, and the second is the hydrolysis of cured UF resin (Wan et al. 2014). The hydrolysis of wood components will decrease the pH of the extract solution because it releases acid, such as acetic and formic acid, into the solution. Otherwise, the hydrolysis of cured UF resin will increase the pH of the extract solution due to the conversion of urea to ammonia, which eventually produces the ammonium hydroxide (NH_4OH) in the solution. This NH_4OH is a very strong alkaline substance that increases the pH of the extract solution (Lubis et al. 2018b; Roffael and Hüster 2012). Another important parameter to determine the degree of hydrolysis of the resin is the formaldehyde content in the extract solution. The method to determine the formaldehyde content is according to the sulfite method (TAPPI 2001). The higher formaldehyde content in the extract solution indicates the higher degree of hydrolysis of the resin (Lubis and Park 2018; Park and Jeong 2011a). This means more cured UF resin has been removed by hydrolysis from the MDF panel. The estimation of removal of cured resin in MDF by hydrolysis, including analysis of the pH of hydrolyzed extract solution and the formaldehyde content in extract solution was also reported previously (Lubis et al. 2020). Therefore, full analysis of MDF hydrolysis-like explained in **Fig. 6** is important to understand the removal of cured UF resin for MDF recycling.

5. Properties of Recycled Fibers

The utilization of recycled fibers in the manufacture of engineered wood products is very common to expand the sources of raw materials. New work has recently been done to examine the characteristics of the recycled fibers obtained from waste MDF and particleboard. It revealed that a combination of steam explosion, chemical impregnation, and hammer milling process could be applied to isolate the recycled fibers (Wan et al. 2014). However, the recycled fibers still contain cured UF resin and release a high formaldehyde emission from the re-manufactured panel (Roffael et al. 2016). Moreover, it has been reported that replacement virgin fibers by recycled fibers over 20% reduced the internal bond strength of the MDF panel (Lubis et al. 2018a). Therefore, it is essential to characterize the recycled fibers to better understand how it can be used as a raw material for MDF recycling.

Several methods have been established regarding the recovery of recycled materials, such as chips and fibers, from wood-based composite waste (Conroy et al. 2006; Hamad et al. 2013; Hong et al. 2020; Kharazipour and Kues 2007; Lubis et al. 2018a; Mantanis et al. 2004; Zeng et al. 2018). **Table 4** briefly shows four different methods that can be applied to recover the recycled fibers from waste MDFs, namely mechanical, hydrolysis, hydrothermal, and chemical-hydrolytic. Typically, the structure of recycled fibers obtained from mechanical disintegration is highly damaged. A lot of fines chips are generated during the disintegration process. Moreover, the recycled chips still contain the residues of the cured resin and exhibit a high formaldehyde emission from the re-manufactured panel (Roffael et al. 2016). A combination of mechanical and hydrothermal disintegration can reduce the amount of cured resin in the recycled chips. The wood-based composites' wastes were subjected to saturated steam in an autoclave at temperatures between 120-180°C and a pressure of 2-11 bar for 2-5 min after initially broken down into chips. However, this process also produces damaged chips because of the combination of elevated temperature and pressure with initial mechanical disintegration. Moreover, the equipment to operate this process is expensive (Deak 2013; Rivela et al. 2007). Chemical treatment of recycled materials with Na_2SO_3 and NaOH has been reported to reactivate the cured UF resin, leading to a low resin content applied in the manufacture of recycled MDF (Mantanis et al. 2004). The waste MDF was mechanically disintegrated into chips. Subsequently, it soaked in the water together with virgin chips at a ratio of 1:1. The mixture was then treated with steam and a combination of an aqueous solution of sodium sulfite (Na_2SO_3) and sodium hydroxide (NaOH) at 170°C for 3 min.

Table 4. Various recycling Process of waste MDF

Recycling process	Reagent	Condition	References
Mechanical	-	Disintegration using refiner at 1000 rpm, and hammer mill at 1500 rpm	(Conroy et al. 2006; Hamad et al. 2013; Hong et al. 2020; Kharazipour and Kues 2007; Lubis et al. 2018a; Mantanis et al. 2004; Zeng et al. 2018)
Hydrolysis	Water	Hydrolysis on a hot-plate with continuous stirring of 200 rpm at 40, 60, and 80, and 100°C for 2, 6, and 24 h	
Hydrothermal	Water	Autoclave at a temperature between 120–180°C and a pressure of 2–11 bar for 2–5 min	
Chemical-hydrolytic	NaOH, Na_2SO_3, $(COOH)_2$, H_2SO_4	Chemical-hydrolysis using acid and alkaline reagents under continuous stirring of 200 rpm at 170°C for 3 min	

Physical characteristics such as fiber length is one of the main characteristics of recycled fiber. The application of elevated temperature steam and pressure is the main reason for the production of relatively short fibers for thermo-mechanical processes such as refining. Therefore, a greater amount of fine fibers are produced and automatically reduce the average fiber length (Benthien et al. 2016). A study reported that the average fiber length of recycled MDF fiber was 30% shorter than the average of the virgin MDF fiber from the same mill. The average fiber length of recycled fibers obtained from particleboard was longer than the recycled fibers from waste MDF but much shorter than that of virgin MDF fibers (Wan et al. 2014). This indicates that the recycling process reduces the average fiber length of recycled fibers (**Table 5**). The refining process produces shorter and more fines recycled fibers than those of the hammer milling process. Furthermore, utilization of fines fiber in recycled MDF manufacturing can consume a large amount of UF resin to meet the minimum standard. Moreover, MDF made from recycled fibers is difficult to compress but easier to spring back. Thus will contribute to the variations in panel density of recycled MDF (Dazmiri et al. 2018; Hong et al. 2020).

Table 5. Characteristics of recycled fibers from waste MDF after recycling

Type of fiber	Fiber length (mm)	Fines content (%)	pH	Buffering capacity (meq/100 g OD fiber)		N content (%)	References
				Acid	Alkaline		
Virgin fiber	1.2–1.5	15–25	5.0–6.0	2.6–2.8	5.5–6.2	0.1–0.5	(Bütün et al. 2018; Hong et al. 2020; Hwang et al. 2005; Lubis et al. 2018a; Lykidis and Grigoriou 2008)
Refining recycled	1.1–1.4	15–20	6.2–6.3	1.5–1.6	9.0–10.2	1.0–1.5	
Hammer milling recycled	1.7–1.9	10–15	6.5–7.1	1.8–1.9	14.0–19.0	1.5–2.5	
Hydro-thermal recycled	1.2–1.3	15–30	6.2–6.5	1.4–1.5	6.5–8.5	1.5–2.0	

The other important characteristic is the acidity and buffering capacity of recycled fibers. It is well known that MDF bonded with UF resin is composed by an amide bond, which is consists of a C−N−H bond. This indicates the recycled fibers still contain a small amount of nitrogen from the resin, as shown in **Table 5**. The acid and alkaline buffering capacity of MDF fibers can be assessed by following a combined method of the T 435 om-02 method (TAPPI 2002) and Xing et al. (2004). A calculated amount of fibers is weighed and poured into a flask. Subsequently, distilled water is added into the flask. Furthermore, the mixture is heated at 100°C for 60 min. The extract solution is filtered by a vacuum filter system and Whatman filter paper No.1 (Ø: 90 mm) afterward. The solution is stored in an Erlenmeyer flask overnight prior to analysis. Around 100 ml of extract solution are pipetted into beaker glass for pH and buffering capacity measurement. In addition, relative acid buffering capacity can be used by divided the acid and alkaline buffering capacity through equations 3, 4, and 5 (Xing et al. 2004). The acidity of recycled fibers, including pH and buffering capacity, can retard the curing of UF resins adhesive in MDF panels.

$$\text{Acid buffering capacity} = (V_1 \times N \text{ of base} \times V_2 \times 100)/(V_3 \times W) \text{ (meq/100g OD fiber)} \quad (3)$$

$$\text{Alkaline buffering capacity} = (V_1 \times N \text{ of acid} \times V_2 \times 100)/(V_3 \times W) \text{ (meq/100g OD fiber)} \quad (4)$$

$$\text{Relative acid buffering capacity} = (\text{Acid buffering capacity})/(\text{Alkaline buffering capacity}) \quad (5)$$

where:

V_1 = amount of the titrant (acid or base) required to titrate the sample (ml)
V_2 = volume of the flask (ml)
V_3 = amount of the titrated sample (ml)
N = concentration of the acid or base
W = oven-dried weight of the sample (g)

A work reported that the acidity of both recycled fibers isolated from waste particleboard and MDF were greater than the virgin fiber (Wan et al. 2014). The work explained that the hydrolysis of UF resins had occurred during the process. Hydrolysis has possibly broken down the cured UF resins into ammonia and reacted with water to form ammonium hydroxide (NH_4OH), resulting in an increase in pH value and N content of the recycled fibers (**Table 5**). Owing to recycled fibers still contain a small amount of N from UF resin, the alkaline buffering capacity of the fiber probably will higher than the virgin fiber (**Table 5**). It means the recycled fibers have high interference for bonding with UF resin in MDF manufacturing. It has been reported that the utilization of recycled fibers over 20% reduced the internal bond strength of the MDF panel (Lubis et al. 2018a; Roffael et al. 2016). However, further treatment of recycled fibers with chemical treatment using a combination of the aqueous solution of Na_2SO_3 and NaOH could increase the internal bonding strength by 16% (Mantanis et al. 2004). In addition, Xing et al. (2004) explained that relative acid buffering capacity expressed the final hydrogen ion (H^+) in the solution, meaning that recycled fibers with low relative acid buffering capacity are not suitable for UF resins.

The chemical characteristics of recycled fibers also play an important role in MDF manufacturing. The main characteristic is nitrogen (N) content in the recycled fiber. As already explained before, the MDF bonded with UF resin is composed by an amide bond which is consists of a C−N−H bond (Pizzi and Mittal 2003). This indicates that the recycled fibers still contain a small amount of nitrogen from the resin. Measurement of N content can be accomplished by following T418 cm 97 (TAPPI 1997). The N content in recycled fibers depends on the degree of removal of cured UF resin during recycling. Other characteristics are N distribution across recycled fiber and chemical elements in recycled fibers, which can be determined using Microscopy and Spectroscopy techniques. This technique is relatively new in the characterization of recycled fibers. Penetration of UF resins into radiata pine (*Pinus radiata*) tracheid walls was assessed using Transmission Electron Microscopy (TEM) combined with an Energy Dispersive X-ray Spectroscopy (EDS). Singh et al. (2015) revealed that the lumen and cell walls were filled with N originated from UF resins. This means that UF resins could penetrate through the cell wall. It proved that the TEM-EDS technique could be applied to analyze the UF resin penetration (Singh et al. 2015). Interaction of UF resins with the cell walls comprises of physical and chemical reactions. Mechanical interlocking takes place via penetration of UF resins into cell wall cracks. The covalent and hydrogen bonds are formed via intermolecular spaces within the cell walls (Singh et al. 2015). Fourier transform infrared (FTIR) spectroscopy showed that reaction occurs between the $-NH-CH_2OH$ groups of a UF resin with wood carbonyl (C=O) and hydroxyl (−OH) groups (Kamke and Lee 2007; Paris and Kamke 2015). Thus, the penetration of UF resins into the cell walls can further enhance the bonding with wood via a chemical reaction with cell wall polymers (Singh et al. 2015). Based on those reports, a combination of microscopy and spectroscopy techniques can be used to measure the N-containing UF resin components present in the recycled fibers.

The morphology of recycled fibers is the last important characteristic. Owing to the recycling process, the fibers probably receive a lot of damage and produce both internal and external fibrillation (Bajpai 2014; Ibrahim et al. 2013). A comparison of SEM micrographs of unrefined fibers and refined fibers of loblolly pine (*Pinus taeda*) obtained from different refining conditions showed that the unrefined fibers have a relatively clean and uncontaminated surface (Groom et al. 2005). The defects are natural, such as pits, or induced, such as microcompressions that resulted from mechanical stirring during SEM sample preparation. Otherwise, refined fibers have a distinct appearance from the unresinated fiber. The refined fibers show an extensive interwall and intrawall delamination damage on the surface. The damage increased as the refining pressure increased to 18 bar. This means the recycling process has a high chance to produce recycled fibers with much damage on it. An understanding of this characteristic can provide some information regarding the recycling of MDF panels and the utilization of recycled fiber as raw material for MDF recycling.

6. Conclusions

Much effort has been done to find ways for recycling of waste MDF. The main problem is the UF resins which hold the fibers together to form MDF panel. Re-manufacturing newly MDF from recycled fibers requires the removal of cured UF resins. Depending on the hydrolysis condition, several works have shown that around 40-90% of cured UF resins can be removed by hydrolysis. Low MW UF oligomers are the main compounds that have been extracted. There are no high MW UF resin components detected in the hydrolyzed extract solution. Application of water extraction system at low temperature for hydrolysis probably only removes a small amount of cured resins that are mechanically bonded with wood fiber components. Applying high temperatures and the addition of acidic chemicals during hydrolysis extracts more cured resin from the waste MDF. This treatment also will affect the properties of the recycled MDF made from those recycled fibers. Recycling MDF is a way to minimize the impact of wood waste on the environment and expand the source of raw materials in MDF manufacturing. Characterization of recycled fibers is important in the production of recycled MDF with standard properties. The physical, chemical, and morphology of recycled fibers are the main characteristics of the recycled fibers. Thus, a full hydrolysis method for measuring the disintegration of cured UF resins from waste MDF and characterization of recycled fibers obtained from recycling must be done prior to the manufacturing of recycled MDF.

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