2. SUMMARY

The wood composites industry is one of the largest manufacturing sectors. Wood adhesives are essential components in wood composites. Formaldehyde-based adhesives such as phenol-formaldehyde, melamine-formaldehyde, and urea-formaldehyde are derived from petrochemicals, which release formaldehyde during hot pressing and during improper storage. Moreover, formaldehyde inhalation causes health problems and is suspected to carcinogen. Therefore, the wood composites would be benefit greatly by reducing the emission of free-formaldehyde. The present work aims to study the possibility to minimize emission of free-formaldehyde via several trials.

The first trial for reducing emission of free-formaldehyde was incorporating of some inorganic ammonium salts to conventional UF-adhesive system. It is clear that, the incorporated ammonium salts such as ammonium chloride, monoammonium phosphate, ammonium phosphate, ammonium sulfate and ammonium persulfate achieved improvement in reduction of free HCHO. The reduction in free-HCHO increases with increasing salt weight percent from 4 % to 20 % with respect to control sample (UF-adhesive). As can be seen that, salt of phosphate anion showed higher reduction percent in free-HCHO than salts of dihydrogen phosphate, sulfate, persulfate, and chloride anions, respectively compared to control sample. This is ascribed to the fact that, these salts reduced pH of the adhesive medium and caused acceleration of crosslinking of formaldehyde-based adhesive. Inorganic salt of sulfate anion resulted in high modulus of rupture (MOR) than other salts especially at 4-8 % incorporated weight percent. However, salt of persulfate anion only achieved higher modulus of elasticity (MOE) value than UF-bagasse composite. The strong adhesion of the UF-incorporated inorganic salt adhesive system may be due to the same reason

mentioned before. For the case of comparing the mechanical properties of UF-bagasse composites produced from incorporating optimum percentages (20 % /UF) inorganic salts for reducing free-HCHO adhesive system, UF-incorporated $(NH_4)_3PO_4$, UF, UF-NH_4Cl adhesive systems had relatively high MOR, MOE and I.B were about 15 MPa for MOR, and about 0.35 GPa for MOE and 0.43 MPa for internal bond strength (I.B) is satisfied load boards requirements.

For water resistance, ammonium salts of persulfate and dihydrogen phosphate anions showed best water resistance than other anions (chloride, phosphate, and sulfate). The lower water absorption percentages were about 33 % and 42 % at 4 % incorporated ammonium persulfate and soaking time of 2 hours and 24 hours, compared to 48 % and 54 % respectively for control composite. While, the lower thickness swelling percentages were 18 % and 26 % at 4 % incorporated monoammonium phosphate and soaking time 2 hours and 24 hours comparing to 36 % and 40 % for control UF-bagasse composite. For thermal behavior, there was significant increase in total activation energy ($\sum E_a = 350.5\text{-}426.1$ kJ / mole) due to incorporation of ammonium salts of sulfate, chloride, phosphate, and dihydrogen phosphate anions to urea-formaldehyde compared to composite from using urea-formaldehyde alone ($\sum E_a = 247.8$ kJ / mole). Salt of dihydrogen phosphate anion incorporation showed relatively high thermal stability ($\sum E_a = 426.1$ kJ / mole) than salts of other anions.

The second trial was incorporation of some shelf (available) organic compounds such as, starch, polyvinyl alcohol, polyacrylamide, urea, and melamine. As the case of inorganic salts, the improvement in free-HCHO reduction percent of adhesive systems increased gradually with increasing in weight percent of

% reduction in free-HCHO). However, UF-PVA achieved lower reduction percent of about 42 %. The observed reduction in free-HCHO content in adhesive system is probably ascribed to the formation of strong hydrogen and covalent bonds between free-HCHO and functional groups containing organic compounds, e.g. hydroxyl, amino, and amide groups. As the amount of incorporated organic compounds increased from 4 % to 16 % weight amount (based on weight of UF), the MOR increased then decreased by further incorporated amounts. The most common higher values were at 12 % weight percent. 16 % polyacrylamide gave higher MOR (~ 18 MPa). However, MOE behaved the reverse trend, where the MOE gradually decreased with increasing the amount of incorporating organic compounds. Polyvinyl alcohol achieved relatively high MOE than other compounds (~ 2.4 MPa). The improvement in MOR is due to formation of strong hydrogen as well as covalent bonds which plays an essential role in the strong adhesion. On comparing the static bending and internal bond of UF-composites produced from incorporating optimum percentages (20 %/UF) shelf organic compounds that gave optimum reduction of free-HCHO in adhesive system, UF-PAM and UF-PVA had higher MOR, MOE and I.B than those produced from UF-starch, UF-urea, and UF-melamine adhesive systems. For water resistance, incorporation shelf organic compounds to UF-adhesive reduced the water absorption and thickness swelling of composite produced. Increasing the percentage of PVA and PAM in adhesive system from 4 to 20 % led to gradually increasing the water resistance properties than using UF alone. While, for incorporating starch, urea, and melamine maximum improvement in water resistance was observed at 4 % weight percent. Incorporating 20 % of PAM to UF-adhesive system was the best compound for producing high water resistance composite. For thermal behavior, the incorporating organic compounds had the following improving sequence: urea > PVA > PAM > melamine > starch where, the

total activation energy ($\sum E_a$) due to incorporating shelf organic compounds in the range of (265-395.83 kJ / mole); which ($\sum E_a$) of UF-bagasse composite is 247.8 kJ / mole. As well as the maximum peak temperature of DTG curve was shifted to high temperature on incorporating organic compounds.

In third trial, the lab prepared nitrogen containing starch derivatives (polyacrylamide-based starch and polacrylonitrile-based starch derivatives) were incorporated to UF-adhesive systems. The reduction in free-HCHO, mechanical, and water resistance properties of the composites produced were found to be dependent on both the nitrogen content and amount percent of incorporated nitrogen containing organic polymer. Generally, increasing the nitrogen content and amount percent of incorporated polymer resulted in an increase in the reduction of free-HCHO in adhesive systems. The properties of the agro-based composites showed that, the prepared composites from UF-incorporated polymer and bagasse had static bending and internal bond significantly higher than EN and ANSI Standards requirements for conventional particleboard and this may be due to formation of hydrogen and covalent bonds between the incorporated nitrogen containing starch derivatives and excess HCHO. The results were processed in a computer programmer to obtain regression equation, 3D-surface response and the predicted properties. Carbamoylethylated starch (CmE-starch) and hydrolyzed Polyacrylonitrile-grafted starch (HPAN-g-starch) gave the higher reduction in free-HCHO than other incorporated organic polymer. Carbamoylethylated starch (CmE-starch) amount is greatly affected on increasing the reduction percent. While, nitrogen content had no significant effect in the case of relatively high incorporated amount (16-20 %). Higher reduction in free-HCHO (~ 100 %) with relatively low amount percent (12 %) is noticed at 2.5 % nitrogen content of CmE-starch. HPAN-g-starch, at nitrogen content 9.29 % and amount percent 16-20 %, higher reduction in free-HCHO to about 100 % is observed. On isolation of homopolymer from PAM-g-starch showed that PAM-g-starch has less effect on reducing the free-HCHO of UF-adhesive than crude grafted starch. AmO-starch behaved as HPAN-g-starch gave the same reduction percent (~100 %) at higher weight amount (16-20 %). PAM polymer gave (68.31 %) reduction in free-HCHO were at 20.98 % nitrogen content and 20 % amount percent respectively. Cm-starch gave 26.338 % reduction in HCHO were at 6.65 % and 16 % respectively.

The data of free-HCHO content in mg /100 g board showed that, HPAN-g-starch reduces free-HCHO content to give (~ 4.2), AmO- starch gave (~ 8.1), CmE-starch gave (~16), HCE-starch gave (~ 18.5), and CE-starch gave (~ 18.8) compared to control, UF-adhesive (21.8 mg /100 g board).

Greater improvement in static bending is achieved on incorporating CmE-starch, MOR was at 2.5 % nitrogen content and 16 % weight amount to give value ~ 37 MPa, while optimum nitrogen content and amount percent that achieved the higher MOE were at 1.8 % and 16 % respectively to give value of about 4.2 GPa.16 %. On studying the effect of purification of the prepared crude starch from homopolymer showed that, incorporating PAM-g-starch to UF-adhesive produced bagasse composites with relatively low static bending strength than those produced from incorporating crude PAM-g-starch to UF-adhesive.

For the water resistance property, where, the relatively low amount percent of incorporated grafted starch (4 % / UF) achieved best water resistance properties than higher amount (8-20 %). Increasing the nitrogen content of the grafted starch accompanied by increase in water resistance of composite produced. PAM composite showed the better water resistance than other incorporated organic polymer composites especially water absorption giving 23.4 % water absorption and 12.4 % thickness swelling at 21 % nitrogen content and 4 % weight amount while PAM-g-starch composite gave better thickness swelling 25 % water absorption and 8 % thickness swelling at 9.5 % nitrogen content and 4 % weight amount. Thermogravimetric measurements of investigated composites on using organic compounds showed that, incorporating HPAN-g-starch achieved relatively high improvement in thermal stability than urea and conventional hardener bagasse composite was 483.25 kJ / mole while ($\sum E_a$) of UF-bagasse composite was 247.8 kJ / mole.

In fourth trial, bagasse composites were surface-treated by using aqueous solution contains 20 % of PAM, PAM-g-starch, and carbamoylethylated starch based on the dry weight of UF-adhesive. It was found that, this surface treatment showed improvements in both mechanical and water resistance. However, incorporation treatment with the same compounds gave better results than surface one.

Finally, the resistance of the prepared composites to aging conditions was studied. The boards were treated with HPAN-g-starch and CmE-starch were exposed to 93 %, 65 % relative humidities respectively compared with conventional UF-hardener composites for different periods from one day to seven days at 26 ^{0}C. It was noticed that, increasing exposure to relative high humidity with time produced a progressive increase in emission of HCHO of board. When boards were exposed to 93 % relative humidity (RH) showed higher increase of emission percent in free HCHO than when exposed to 65 % RH. The conventional hardened particleboard was the most influenced than CmE-starch and HPAN-g-starch treated particleboards respectively. This may be

discussed based on moisture caused hydrolysis of the resin decreasing its molecular weight. It was noticed that, 93 % RH showed higher loss in mechanical properties than 65 % RH. The greater resistance in mechanical strength to aging conditions (MOR, MOE, and I.B) in both relative humidities order was as following: in case of MOR, MOE, and IB: HPAN-g starch treated board > CE-starch treated board > conventional UF-hardener composite.

-Results of the UF-agro-composites from different raw materials such as, rice straw, reed, and cotton stalks in addition to sugar-cane bagasse as lignocellulosic fibers were treated with highly effective organic polymer (HPAN-g-starch) and casein either by incorporation or by surface treatment. Generally, incorporation treatment gave less free HCHO content percent than surface one compared with control (UF-bonded hardened lignocellulosic composites from different raw materials). HPAN-g-starch showed less free HCHO percent than casein did compared with conventional hardener UF-bagasse composite. In case of mechanical properties, incorporation of HPAN-g-starch and casein to UF gave better results than surface treatment compared with control. HPAN-g-starch gave better results than casein did. Rice straw, reed, and cotton stalks gave fewer improvements than bagasse composite owing to their differences in chemical composition of raw material and presence of highly waxy layer that prevents penetration of resin into fibers, and consequently decreased mechanical strength increased water absorption and thickness swelling.