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Development of Waterproof Cum Heat Resistant, Montmorillonite Clay Modified High-Pressure Plywood Composite from Renewable-Nonedible Agricultural Wastes – An Industrial Case Study of 'Flask to Reactor' Approach

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Abstract
A sustainable development model demands an economical transition of product synthesis from 'Flask to Reactor,' which demands synchronization between universities, industries and funding agencies. In our lab, we have successfully developed a prototype method for synthesizing adhesive phenol-furfural resin from extracts of *Saccharum munja* while biomass residues of this feedstock extraction were employed as filling materials for manufacturing plywood samples. This designed method has the advantage of no leftover waste material. Moreover, waterproofing, heat resistance and mechanical strength were improved by impregnating functionalized montmorillonite clay into these prepared plywood samples. Subsequently, water and fire-resistant wood composite (MDF) was developed from agricultural residue on a pilot plant scale (*Saccharum munja*). Green precursor furfural (for resin/glue synthesis) was extracted from agricultural residue (Saccharum munja and peanut plant) on a pilot plant scale. Organic functionalization clay was also synthesized and incorporated during resin (Phenol-Furfural) preparation. Plant materials left after furfural extraction were further used for wood composite (MDF) preparation by hot pressing of plant residue and resin. Characterization and evaluation of prototype wood composite products were also performed for fire and waterproof analysis. Results have shown that prepared samples have good fire and water-resistant activities. This product will be a good candidate for the wood composite market and is green. Furfural, used for resin synthesis, is a potential replacement for carcinogenic formaldehyde, which is largely used in wood composite and plywood industries. Pakistan is an agricultural country and is enriched with mineral reservoirs. Fortunately, raw materials required for this project, i.e. renewable biomass including agricultural residue and nonedible plants, and minerals, i.e. montmorillonite clay, are available in ample quantities. Thus, this project has good potential to develop cost-effective and improved quality plywood products that are marketable and can generate positive cash flow. TTSF platform was employed to support promising partnerships between academia (HEC & NUST) and industry (KDC Boards (Pvt) Ltd, Woodworld (Pvt) Ltd & TASCO Mines (LLP)) to facilitate the transfer of university-developed technological research to industry and the commercial sector.

Keywords: Green chemistry, sustainability, renewable feedstocks, pilot plant wood composite; *Saccharum munja*; phenol-furfural resin; montmorillonite; cum-heat resistant.

1. INTRODUCTION
Wood-based medium/high-density fiber board (MDF, HDF) is considered engineering wood used to fabricate furniture and building interiors, particularly Kitchens. Conventionally, it is manufactured from wood fiber that causes deforestation because trees are cut at a mass scale. These wood fibers are glued together through some adhesive resin. The most common adhesive resins used to manufacture plywood, MDF are urea-formaldehyde, phenol formaldehyde resins which are carcinogenic, causing dangerous health effects to human health. Conventional wood composites have no long service life due to medium resistance against hot and humid conditions, posing fire hazard risks.

Solutions to these problems may include replacing formaldehyde with plant-derived furfural to synthesize phenol-furfural resin. This is a green approach to synthesizing green resin with no carcinogenic reactants. Renewable and nonedible agricultural biomass like *Saccharum munja*, peanut shell, etc., could be used to extract furfural, which will further synthesize resin. The mass left behind after extraction could be reused, compressed and heated with resin to make plywood [1]. Cheap clay materials can be impregnated into plywood matrix to improve product thermo-mechanical and waterproofing properties. Previously many methods have been developed to extract furfural [2-6], but we have designed a modified extraction method with greater efficiency.

Plant wastes are good alternative feedstock for their ease of availability, economical cost, and renewable raw materials [3]. Phenol-formaldehyde (PF) resin owing to its superb mechanical properties, chemical resistance and thermal stability, has played an extensive role as engineered plastic in industry. PF resin is used on a large scale to manufacture plywood where veneers or thin layers of wood are hot-pressed using PF as an adhesive agent [4, 5]. In 2004, the World Health

Organization's 'International Agency for Research on Cancer' marked formaldehyde as carcinogenic to humans. For this reason, PF resin should be replaced to avoid the carcinogenic emission of formaldehyde [6]. This has driven the interest of various researchers for the substitution of PF resin with bio-based phenolic compounds, furfural, lignin and lignocellulosic biomass, etc. [7-11]. Pizzi et al. [12] have investigated the structure of traditional, linear phenol–resorcinol–formaldehyde (PRF) resins, urea-branched PRF resins, and phenol–resorcinol–furfural (PR-Furan) resins. They found that very different percentages of resorcinol were needed for equal performance of these resins as adhesives. PRF resin performance was improved by maximizing the proportion of resorcinol-containing oligomers or methylol groups containing oligomers. However, in PR-Furan resin, the determinant parameter is the higher molecular weight of furfural as compared to formaldehyde [11]. In another reported work, phenol-resorcinol-furfural, resorcinol-furfural and resorcinol-phenol-furfural cold-setting resins were prepared to substitute formaldehyde-based cold-setting resins. The phenol-resorcinol-furfural adhesive resin has the advantage of lower volumetric shrinkage on curing [12]. Oliveira et al.[13] have prepared resol-type resins with furfural obtained by acid hydrolysis of abundant renewable resources from agricultural and forestry waste residues. Composites were prepared with furfural–phenol resins and sisal fibers without formaldehyde, which showed excellent adhesion between resin and fibers [13]. Rapid curing of resin is desirable in many industrial applications. Increasing the ratio of furfural to phenol increases the curing speed, which may be attributed to increasing molecular weight [14]. Fire and degradation behaviour can be improved by blending phenol-furfural resin with some clay materials [15]. The presence of the aldehyde functional group and its extraction from renewable feedstock, furfural, has found its application in manufacturing green adhesive novolac-type PF resins [16, 17]. Montmorillonite (MMT) clay is hydrated sodium calcium aluminum magnesium silicate hydroxide $(NaCa)_{0.33}(AlMg)_2(Si_4O_{10})(OH)_2.nH_2O$ [18], having fundamental tetrahedral and octahedral sheets. MMT has a better heat-insulating property and thermal resistance when used as a substance stabilizer [19]. MMT clay has been applied as an inorganic synergist to prepare plywood's water-based intumescent flame retardant (IFR) ornamental coating. Analysis of heated products has revealed that residual nitrogenous polyaromatic structure and residual mass in the IFR coating were the result of effect of MMT on the antioxidation properties of the char layer [20]. Furfural, a green chemical, can be extracted from biomass by acid catalysis, ionic liquids, and by hydrothermal method using $AlCl_3$ as a catalyst [21-25].

In the proposed pilot plant work, the phenol-furfural resin would be synthesized using furfural that may be extracted from various plant wastes. Resin would be blended with organically modified montmorillonite clay to incorporate thermal stability. The resultant resin clay composite would be mixed with leftover plant material and pressed at high temperatures to manufacture a high-pressure composite. The end product will be a suite of engineering wood formulations employable in composite wood manufacturing. It will help to protect forests and vegetation and thus will be helpful to preserve nature. In-house economical production of composite wood will be helpful to press down the manufacturing cost by use of agricultural waste as raw materials; thus, the product will be cost-effective. This product will have improved mechanical strength, waterproofing and heat resistance. This will increase the service life of the product and will help avoid catastrophe failure. Replacing carcinogenic adhesive resin and using renewable agricultural waste will assist in technical compliance with the government's safety, health and environmental policies and the golden principles of Green Chemistry.

2. MATERIAL METHODS

2.1. Raw materials

Saccharum munja and peanut plants are purchased from the local market of Chakwal, Pakistan. These biomasses were ground to powder form in a pilot scale grinder. The shaded and crushed raw materials would be subjected to furfural extraction by our lab-developed method. NaCl (99% National Foods, Pakistan), $AlCl_3.6H_2O$ (99%, Daejung, Korea), Chloroform (99%, Daejung, Korea), DMSO (99%, Daejung, Korea), HCl (37%, Daejung, Korea), Phenol (99%, Daejung, Korea) and KOH (99%, Daejung, Korea). Montmorillonite clay was purchased from TASCO Mines (LLP), Pakistan. All solutions were prepared in tape water.

2.2. Grinding of Biomass

For each batch, the grinding of peanut plant biomass is carried out by an electrical grinder machine to extract furfural (Fig. 1). Grinding biomass to desired particle size is very important for a homogeneous reaction. Suitable Surface area of reactants also increased the rate of reaction. Crushed biomass was dried at 50 ^oC to remove moisture contents.

Figure 1. Preparation of biomass powder (a-b)

2.3. Pilot plant designing

Designing of pilot plant reactor plays an important role in industrial scale productions to overcome the extra expenditures to make all procedures cost-effective. It was very challenging for us to design and modify the reactor for specific desired reactions. In the early stages, we tried our best to overcome maximum problems, which important were, adjusting condenser length for proper condensation, oil heating pipes modification to gain proper heat for the maximum volume of reaction, protective insulation with glass wolves to reduce the heating losses, fan shaft redesigning for minimum and maximum volume stirring, condenser outlet modified for condensing and distillation during reactions, temperature-pressure gauges, glass mirrors were also fixed on suitable positions to monitor and observed the reaction conditions, random cooling water circulation for condensation and distillation, reactor outlet valve was designed for removal of different types of residue and products (solvent, semi-solid) after reactions completions, inlet point also modified for addition of reactant during reactions. We can proudly say that our designed reactor is suitable for 4 to 5 types of reactions starting from biomass digestion to resin synthesis. We can run maximum reactions, including digestion, distillation, extraction, solvent recycling, resin synthesis, clay modification on a single reactor. The important thing is that we tried to finalize maximum reactions in one reactor with suitable supporting apparatus (Fig.2).

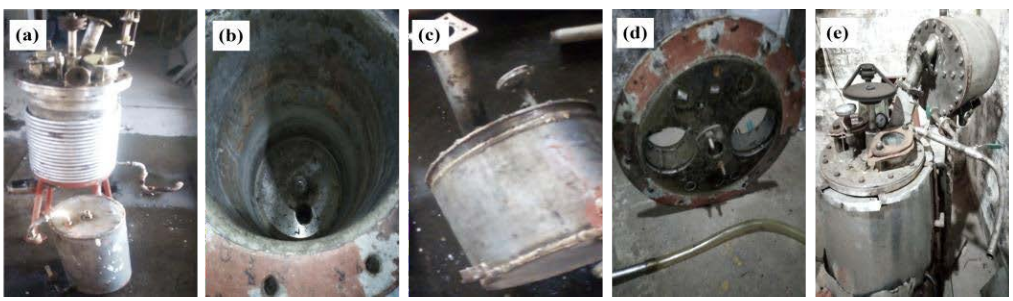

Figure 2. Pilot plant reactor preparation (a-e)

2.4. Extraction of Furfural

Different catalyst mixture was tested for furfural extraction from biomass. Overall findings show that an equal amount of $AlCl_3{\cdot}6H_2O$ and NaCl was fruitful for furfural extraction. An extraction medium was developed by preparing 2 w/v % catalyst material in 12% HCl solution. Plant powder was charged into this extraction medium in 1:10 proportion, mixed and stirred to ensure proper mixing of powder and extraction medium. Subsequently, an oil heating system heated this extraction system with an equipped condenser at 100 ◦C for 2.5 h. These digested plant material mixtures were distilled, and the distillate was collected into the airtight gallon. The distillate was poured into a separating gallon, and chloroform was used as a separating solvent to extract the furfural from the distillate. Recycle the chloroform and pure furfural were collected from the reactor, weighed, and stored in an airtight small gallon to prevent oxidation and evaporation. The higher yield (32%) of furfural from peanut plants was attributed to a higher percentage of pentosans in plant materials in a pilot plant. Extracted furfural was pure, as checked by FTIR and used for resin synthesis without further purification. Three batches (3 kg biomass) were completed for extraction of furfural. Meanwhile, the recovery of chloroform was also completed accurately (Fig.3).

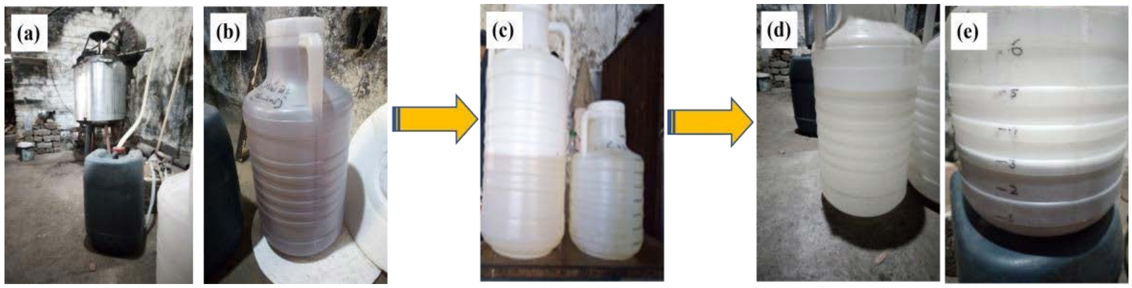

Figure 3. Extraction of furfural; Distillation to extraction (a-c), Recovery of chloroform (d), recovery of furfural (e)

2.5. Extrafoliation of montmorillonite clay (MMT)

Approximately 1 kg of MMT was first grinding and then organically extra foliated with DMSO for 1-2 h and then dried for the synthesis of modified phenol-phenol resin (Fig.4).

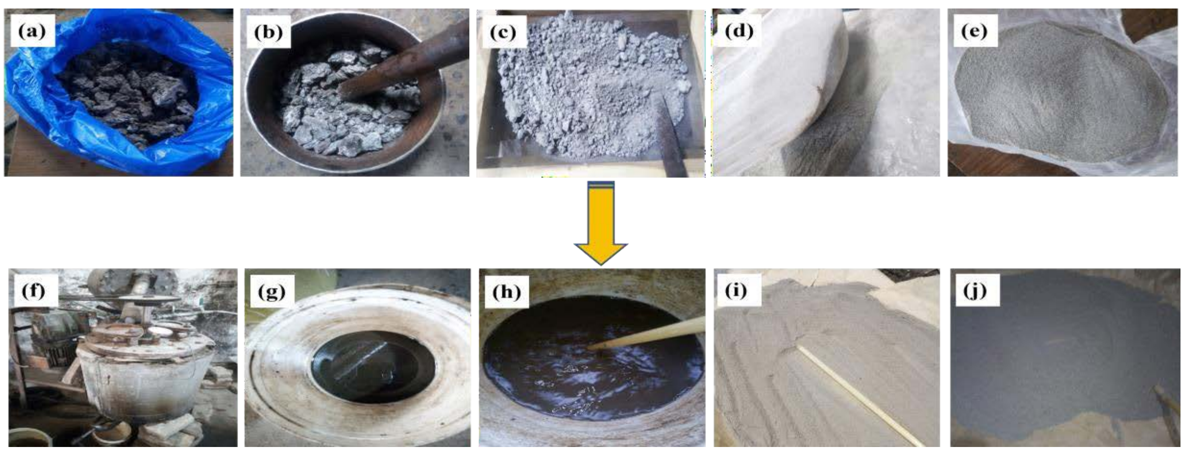

Figure 4. Grinding (a-e), modification in DMSO and drying of MMT (f-j)

2.6. Synthesis of MMT-modified phenol-furfural resin

Synthesis of a resin is always a challenging part of a particular reaction. We successfully completed the MMT-modified phenol-furfural resin reaction in the same reactor Fig. 5 (a-c). First, we melted the phenol in the reactor and added desired KOH to ionize the phenol and then added dropwise extracted furfural for a phenol-furfural reaction. When the reaction was completed after some cooling, the dark-brown coloured resin was collected from the reactor outlet and evaporated the unreacted phenol by heating. Successfully three batches of furfural were converted into Phenol-Furfural resin.

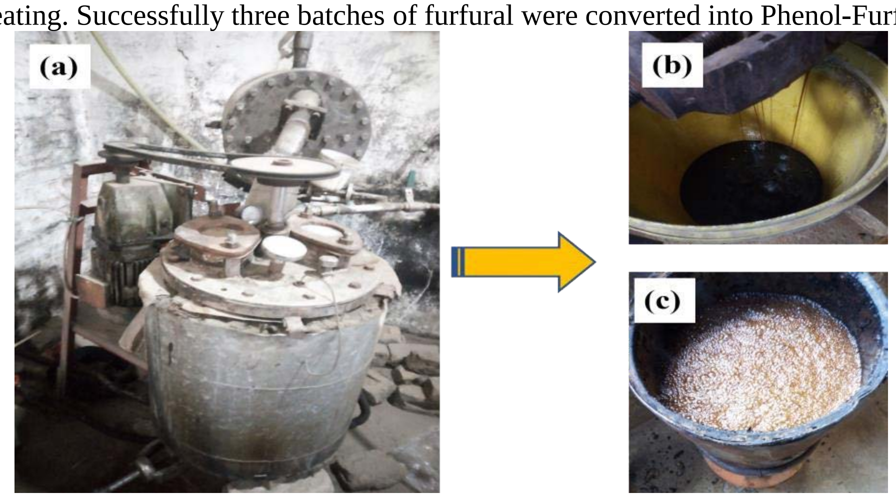

Figure 5. Preparation of MMT-modified resin (a, b) and removal of unreacted phenol (c)

2.7. Heating press designing

The heating press is designed to prepare 8" x 8" inches sheet of wood composite with a thickness of 20 mm **Fig. 6 (a-h)**.

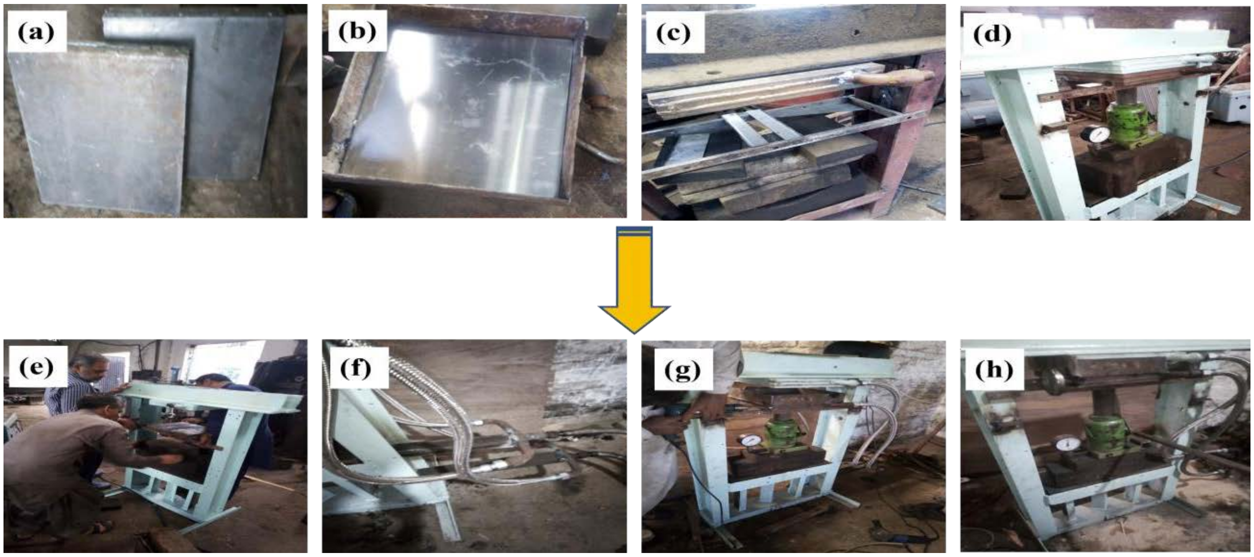

Figure 6. Heating press manufacturing (a-h)

3. RESULTS AND DISCUSSION

In-house economical production of wood composite will be helpful to press down the manufacturing cost using agricultural waste as raw materials; thus, the product will be cost-effective. This product has improved mechanical strength, waterproofing and heat resistant. This will increase the service life of a product and will be helpful in avoiding catastrophe failure. Replacing carcinogenic adhesive resin and using renewable agricultural waste will assist in technical compliance with the government's safety, health and environmental policies and golden principal green chemistry. It will help to protect forest and vegetation and thus will be helpful to preserve nature. 8″ x 8″ inches sheet of wood composite with a thickness of 20 mm is prepared and laminated for good representation Fig. 7 (a-d).

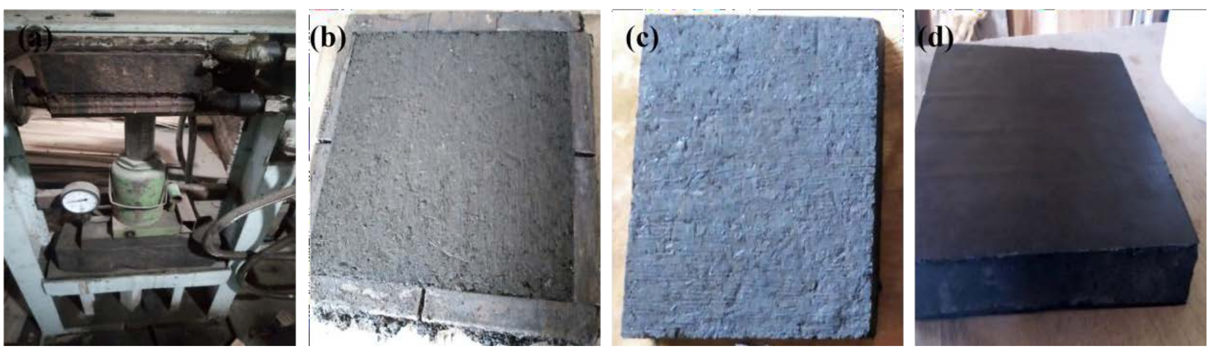

Figure 7. Sample preparation by heating press (a-d)

These samples were investigated for waterproof and heat resistant. A waterproof analysis is conducted in 24 h in hot and cool water Fig, 8 (a, d). Results show that after 24 h the samples have the same weight and good representation. Further fire resistance is investigated for low and high flame Fig. 8 (e-h). Fire-resistant analysis shows that with low flame Fig. 8 (e, g), the prepared sample is almost fully protected from fire damage compared to the plywood sample. High flame test Fig. 8 (f, h) also indicated that investigated sample is well protected and inhibited the fire burning as compared to the plywood sample. In the plywood sample, the fire is continued, and the surrounding temperature increases, favoring fire promotion. The fire-resistant analysis confirmed that the prepared sample is less affected by direct fire flame and does not elevate the surrounding temperature.

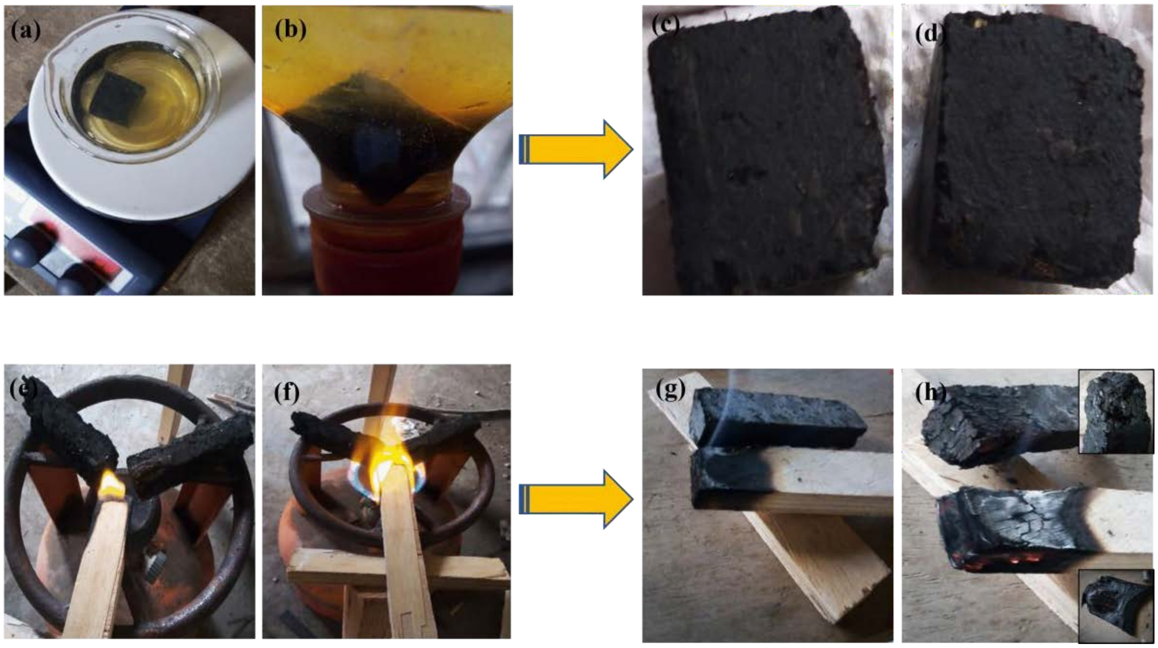

Figure 8. Waterproofing (a-d) and heat/fire resistant analysis of the prepared sample (e-h)

These benefits will save millions of dollars annually by ensuring a cheap and stable supply of waterproof and heat-resistant good quality wood composite by in-house production. The initial market for engineering wood products within Pakistan is estimated to be worth more than $100 million with annual sales of close to $40 million.

4. CONCLUSION

Pilot plant scale wood composite (MDF) is made from agricultural residue (*Saccharum Munja*). Furfural is extracted and used for resin/glue (Phenol-Furfural) synthesis. Montmorillonite clay was also modified and incorporated with phenol-furfural resin. Final samples of the wood composite are made by hot pressing with resin and left after residue from furfural extraction. Test analysis showed these prepared samples have good water- and fire-resistant properties. A pilot scale trial for wood composite manufacturing is completed. Customization and optimization of processes for industrial-scale production are further required. This product has good potential in the international market and is green. The product should have better quality in terms of hardness and compressibility as compared to already available products.

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