



Efficient Utilization of Rice-wheat Straw to Produce Value –added Composite Products

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Abstract

Although the application of composites can be found back to the mid-nineteenth century, but renewed interest in these materials has been emerged only in the last decade or so. Wood has been the major source of raw material particleboards and fibreboards, but recently, rice-wheat straw (RWS) has gained more attention of researchers to be used as an alternative of wood. In Pakistan the Rice-Wheat grain production in 2006-07 was 5438 thousand tonnes and 23520 thousand tonnes respectively. For every 4 tonnes of rice or wheat grain, about 6 tonnes of straw is produced. Around 43437 thousand tonnes RWS is produced in Pakistan. RWS is primarily composed of cellulose, hemicellulose, and lignin. Use of RWS as a feedstock for producing materials, fuels, and chemicals still has been inadequate due to a number of factors including capital costs, waste streams, energy consumption, production logistics, and the quality of the biomass feedstock. RWS contain a relatively large amount of vessel elements, sclerenchyma fibers, epidermal cells (Dermal tissues) and parenchyma cells as compared to wood. The outer thin waxy layer of RWS lowers their wettability with water based formaldehyde resins. In addition to this, straw has a higher content of hemicelluloses and ash, but a lower content of lignin compared with wood.

Particleboards, medium and high density fiberboards like composite materials are mainly manufactured from wood using binders such as acid curing amino-formaldehyde resins, alkaline curing phenol-formaldehyde resins, using polyisocyanate adhesives. Wood-based materials including natural materials and composites are being used as construction materials for long and forest wood has been used in paper and wood-based panels industries. RWS have not been used before for Particleboards, medium and high density fiberboards manufacture with the use of conventional formaldehyde resins like urea-formaldehyde (UF) resins, melamine-urea formaldehyde (MUF) resins, phenol-formaldehyde (PF). Therefore, the main aim of this study is to review the literature on methods to improve the bondability of straw with conventional resins. The study will help in efficient utilizing wheat and rice straw as an alternate resource for the industrial manufacture of particleboards and fibreboards.

Keywords: Rice-wheat straw, Composite Products, Particle Boards, Formaldehyde resins, Pollution reduction

1. Introduction

Wood-based materials including natural materials and composites are being used as construction materials for long and forest wood has been used in paper and wood-based panels industries. In recent years, wood-based industry is facing difficulty for solid woods raw material. As a result the use of renewable resources such as agricultural residues, especially RWS, is now gaining increased interest in production of composite panels like paper products, particleboards and fibreboards and is now being reflected as attractive feedstock both economically and environmentally.

Agricultural lignocellulosic fibers such as RWS can be easily crushed to chips or particles, which are similar to wood particle or fiber, and may be used as substitutes for wood-based raw materials [1]. Use of RWS can help in protecting the virgin forests especially in regions

already facing a shortage of wood. In addition, due to environmental concerns, burning of straw has been prohibited since no proper uses for these wastes have been found yet and great quantities of straw residues are available today.

Ajiwe, V.I.E., et al., (1998) [2] produced ceiling boards from agricultural wastes and tested ceiling boards and commercial samples for moisture content, rate of water absorption, and tensile strength. The results of the tests confirmed that the boards produced were of similar standards to those commercially available [2, 3]. Han, G., et al., (1998) [3] examined the effects of particle size and board density on reed and wheat particleboard properties. They reported that the properties of particleboard produced from fine particles were better than those made from coarse particles. Yang et al. 2003 [1] prepared composite boards with rice straw without considering the

size and wood particles, with the specific gravities of 0.4 and 0.6, and found them suitable as a sound absorbing insulation material in wooden constructions.

RWS contain a large amount of fiber and have a great potential to replace wood for production of wide variety of composites. Producing composite materials from RWS is likely to contribute favorably to the disposal problem as well as to the overall CO₂ balance as a carbon sink. Converting RWS into value added products has also the potential to improve the performance of agriculture sector.

The better utilization of RWS will also benefit farmers as an additional income, which can be an important motivating factor in promoting an efficient harvesting, collection and management of RWS. Additionally, industry is also showing increased interest in the production of composite materials from agricultural residues due to the acute shortage of forest resources.

1.1 Composite Materials

Composite materials such as particleboards and medium & high density fibreboards are mainly produced from wood using binders such as acid curing amino-formaldehyde resins, alkaline curing phenol-formaldehyde resins, using polyisocyanate adhesives. Generally, composites based on lignocellulosic particles or fibers can be divided into the following groups [4]: conventional panel-type composites like particleboards, fibreboards, insulating boards, etc. lignocellulosic-mineral composites, which are based on inorganic binders, natural fibers reinforced polymers, nonwoven textile-type composites.

Particleboards are prepared in the density range of 0.4 to 0.85g/cm³ depend upon their field of application and thickness. Boards with density lower than 0.59g/cm³ are low-density boards, between 0.45 and 0.8g/cm³ are medium density and greater than 0.8g/cm³ are high density boards. Also, in the case of particleboards, the requirements depend on the field of application and thickness of the boards [5].

1.2 Wheat Straw Production

The annual worldwide production of wheat straw (WS) was estimated to be approximately 540 million tons in 2007 [5]. Small portion of WS has been used as animal feed-stock and bedding. Farmers also use WS in construction of mud houses but still most of these agricultural byproducts are left on the ground to decompose [6]. In some parts of the world, WS is burnt in open fields, causing air pollution [7, 8]., industrial applications of WS are still under investigation. One of such applications is use of WS in composites.

1.3 Composition of Rice-Wheat Straw

Rice-wheat straw is primarily composed of cellulose, hemicellulose, and lignin. The main botanical fractions of straw are: nodes, internodes and leaves

(blades and sheaths) (Figure 1) [9]. The relative proportions of these fractions vary with species and with many other factors such as maturity at harvest, soil and climate conditions, etc. Since the chemical composition of the various fractions is different, the overall chemical composition of the straw changes as a consequence (Table 1).

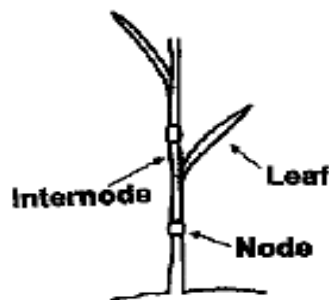


Figure 1. Sketch of wheat

Table 1. Physical content of wheat [9]

S. No	Part of Tree	Mass Percent
1.	Internodes	68.5
2.	Leaves-sheaths	20.3
3.	Leaves-Blades	5.5
4.	Nodes and Fines	4.2
5.	Grains and Debris	1.5

Straw has a higher ash content and lower lignin content when compared with wood (Table 2) and has not been used for board manufacture with the use of conventional formaldehyde resins (UF, MUF, PF, etc.), while other types of adhesives like polymeric isocyanates have been tried. However, the mechanical strength and the water resistance of the boards made from straw and isocyanates are much lower than those made from wood using the same bonding conditions.

Table 2. Main constituents of wheat and straw versus spruce wood

Main constituents of wheat and rice straw versus spruce wood				
Material	Hemi Celluloses %	Cellulose %	Lignin %	Ash %
Wheat Straw [10]	26.4	40.8	22.9	9.9
Rice Straw [11]	25.9	40.8	17.9	15.4
Spruce wood [12]	30.17	44.31	25.20	0.32

In the morphological structure, RWS are less homogeneous than wood and contain a relatively large amount of vessel elements, sclerenchyma fibers, epidermal cells (Dermal tissues) and parenchyma cells as compared to wood. In a cross section, the epidemic cells are the outermost surface cells and are covered by a thin

waxy layer (Figures 2 and 3) [13]. The waxy and silica layer encircling the straw stem inhibit sufficient direct contact between the binder and the straw fibers. This layer lowers the wettability of straw with water based formaldehyde resins. The chemical composition of crop fibers, especially high ash content, has limited the use of these crop materials as raw fiber materials for panel manufacture [14]. In addition, crop materials commonly contain high levels of extractives, which may influence the curing behavior of adhesives [15]. The pH and acid buffering capacity of aqueous extracts from the non-wood lignocellulosic materials are significantly higher than those of softwood, which increases the gel time of UF resin and causes bonding difficulty [16]. The presence of extractives can also influence the wettability of materials [17, 18]. The low wettability is related to the existence of non-polar extractives [19]. Generally, there is a waxy layer on the crop material surface [14, 15]. The water-soluble UF resin is chemically incompatible with the straw material and it is probably the main factor responsible for the reduction of bond quality.

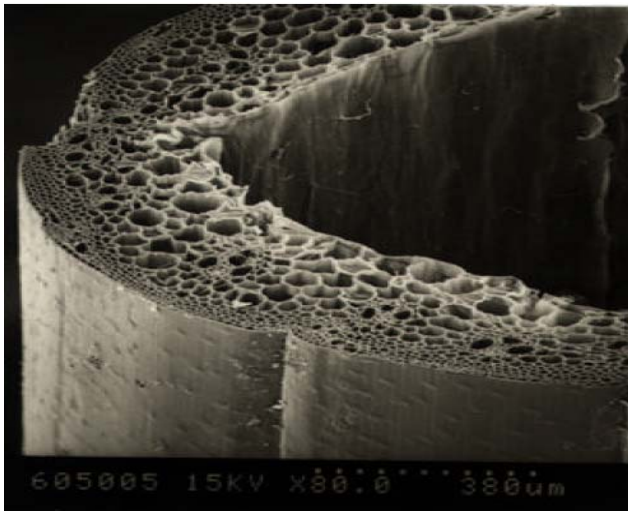


Figure 2. Electron micrograph of a straw stem cross-section. [13]

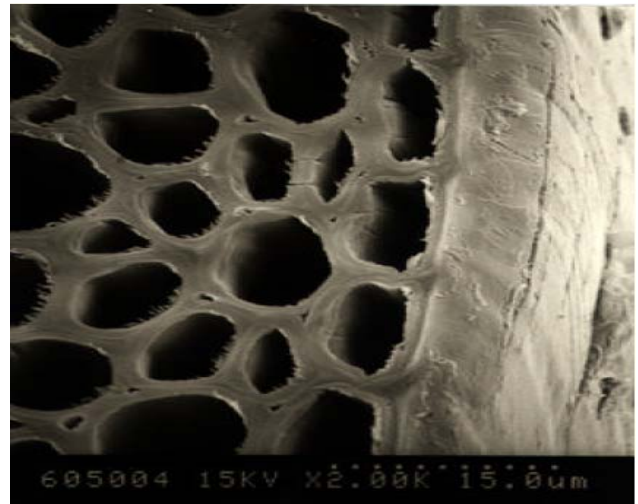


Figure 3. Electron micrograph of a straw waxy/silica layer. [13]

The properties of the lignocellulosic composites are dominated by the interfacial interaction between the lignocellulosic filler and polymer matrix. Generally, there are two types of interaction at the interfacial region, i.e. primary and secondary bonds. Primary and secondary bonds include covalent and hydrogen bonds, respectively. Whilst, covalent bonding at the interfacial region exists in thermoplastic-wood composites with the incorporation of a coupling agent, such bonds are more prevalent in the thermoset-lignocellulosic composites. This is because lignocellulosic hydroxyl (OH) groups could serve as reaction sites with various functional groups in the thermoset system.

According to Hatakeyama, H., et al., (1993) [20] natural polymer having more than two OH groups per molecule could be used as a polyol for polyurethane (PU) preparation if the groups could be reacted with isocyanate. PU is one of the most useful three dimensional polymers due to its unique features. It can be produced in the form of sheets, foams, adhesives etc. Recently, many attempts have been made to utilize lignocellulose as raw materials for PU synthesis [21].

1.4Wheat and Rice Straw as Composite Material

Recently, interest has been developed on using agricultural residues like wheat and rice straw as a starting material for particleboards and medium density fibreboards (MDF). Many studies have been carried out on the utilization of biomass, such as, particle board, MDF, pulp and composites [22-26]. In general, utilization of biomass in lignocellulosic composites has been attributed to several advantages such as low density, greater deformability, less abrasiveness to equipment, biodegradability and low cost. Other advantages of straw

particleboard are its rigidity and strength, built-in insulation, and low cost [27].

2. Manufacture of Straw Medium Density Fibreboard (SMDF)

The processing of straw differs from that of wood in the initial stage of the composite material process (Figure 4). The harvested and baled wheat straw is size-reduced (chopped), hammer-milled, screened, and pre-wetted before defibration (the fiber-refining process). The subsequent processing steps are similar to those in conventional wood-based systems and involve resination, drying, mat-forming, pre-pressing and, finally, hot pressing. During hot pressing a synthetic resin binder (adhesive) is usually added to glue the fibers together to form a composite material [28].

MDF is produced in a dry fiber process. The strength of MDF depends on its fibers and on the adhesive bonds between them. Thereby, the adhesives are necessary to ensure effective bonding between the fibers. The most common types of resins used for MDF-products are based on formaldehyde, for example UF, MUF, and PF resins [29]. Typical MDF-products are cabinet doors, shelves, laminated floors, furniture and panels for building construction.

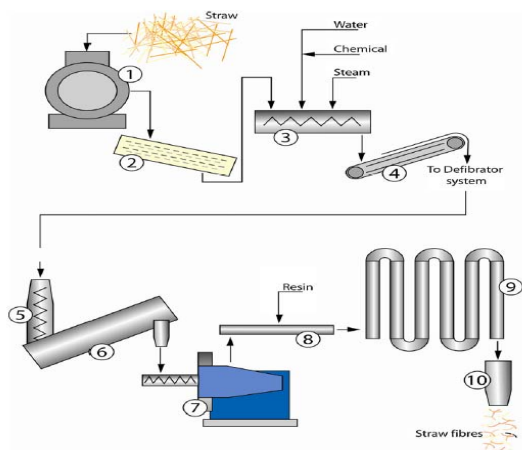


Figure 4. Electron Schematic of a straw fibre preparation system in an MDF pilot plant for handling wheat straw: (1) hammermill, (2) dry screen, (3) pre-treatment screw, (4) conveyer, (5) infeed screw, (6) pre-heater (digester), (7) Defibrator™ (refiner), (8) blowline, (9) dryer, and (10) fibre outlet (cyclone) [28]

RWS have not been used before for board manufacture with the use of conventional formaldehyde resins like UF, MUF, PF, etc. The main obstacle is their poor bondability particularly using UF resins. The mechanical strength and water resistance of the boards made from RWS and isocyanates are much lower than those made from wood using the same bonding conditions.

Binders or bonding agents are those conventionally employed in forming composite products and include both acidic and alkaline type binders. Typical bonding agents are amino resins, phenolic resins, resorcinol resins, tannin resins, isocyanate adhesives or mixtures thereof. Thus resins which can be used to bond treated straw fibers include UF-resins MUF-resins, PF-resins, resorcinol-formaldehyde resins (RF-resins), tannin-formaldehyde resins (TF-resins), polymeric isocyanate binders (PMDI) and mixtures thereof. The resins can be added in the amount of 5-15% based on dry straw materials employed in the final composite.

The reason for poor bondability of straws is probably the specific morphological structure of the straw, where the waxy and silica layer encircling the straw stem inhibit sufficient direct contact between the binder and the straw fibers. Other types of adhesives for example polymeric isocyanates have been tried. However, the mechanical strength as well as the water resistance of the boards made from straw and isocyanates are much lower than those made from wood using the same bonding conditions.

One possible way to improve the adhesion is to chemically activate the fiber surface by oxidation. Binding between and within the fibers can then be promoted during hot pressing by activated (reactive) components that are part of the lignocellulose [30, 31].

Paraffin wax or wax emulsions are added in small quantities (approximately 0.5–1.0%) to improve the poor water resistance of MDF. Fibreboards made using annual plant materials and agricultural waste have even worse water-resistant properties than wood [13, 14, 32-35]. Another way to improve the hydrophobic properties of the fiber is to add small quantities of salts containing di- or trivalent cations [36]. The most frequently used salt in the papermaking industry is aluminum sulphate. Below pH 9, the cations are primarily adsorbed to the pulp fibers by electrostatic interactions with the carboxyl groups in the lignocellulose material. The electrostatic interactions result in adsorption of small species or colloids on the fiber surface, altering the surface properties of the fibers [37]. Improved swelling-resistance in wood-based fibreboards has been reported after the addition of CaCl_2 [36, 38].

Other properties of the boards made from straw can be further improved if the straw is treated with various chemicals which are fibrous property lignocellulose modification agents. These reagents can be used either alone or in combination and include metal hydroxides, such as lithium, sodium, potassium, magnesium and aluminum hydroxide, organic and inorganic acids, such as phosphoric, hydrochloric, sulphuric, formic and acetic acid, salts, such as sodium sulphate, sodium sulphite and sodium tetraborate, oxides, such as aluminum oxide; various amines and urea, ammonia, as well as ammonium salts. These reagents can be used in the form of water

solution or suspension in quantities of from 0.01 to 10% based on dry material.

The chemical treatment and the defibration can be carried out in one step, by subjecting the straw to a stream of water during the high shear stage, containing the amount of chemical needed to upgrade the properties of the amino resin bonded boards. After the defibration, the fibers produced can be dried using conventional dryers used in particleboard factories, e.g. a drum dryer or a tube dryer, like that used in medium density fibreboard mills. From then onwards, the dried fibers follow the conventional procedures as for the production of particleboard or medium MDF.

3. Literature Review of Work to Improve the bondability of Straw

Many treatments have been described in the literature to improve the bondability of lignocellulosic materials in both particle and fiber form with synthetic resins. Wax can usually be extracted by the organic solvents like ethanol/benzene (EB) [39-41]. Gardner and Elder, (1990) [42] added hydrogen peroxide, nitric acid or sodium hydroxide to enhance bonding characteristics of flakes using PF resins as a binder. Dimensional stability and internal bond strength were significantly reduced and it was shown that the chemicals did not change the wood surface, but rather they reacted with the resin.

Mclaughlan and Andersen, (1992) [43] tried many treatments to enhance the bondability of fibers towards bonding with UF resins for the production of MDF. The treatments include exposure to wet and dry heat, compression with heat and heat in combination with chemicals. The chemicals include 1% and 10% addition of aluminum sulphate, which is used in the hard board manufacture to control the pH value of the stock and 1% and 10% chromium trioxide. Almost all the treatments resulted in boards with reduced properties compared to the control.

Zhengtian and Bingye, (1992) [44] mentioned that slight improvement of bondability of straw can be achieved by destroying the waxy layers encircling the stem of straw, however, the bondability was still very poor and the boards made still could not meet the requirements of common standards. Simon and Pazner, (1994) [45] investigated the influence of the hemicellulose content of the self-bonding behavior of different raw materials including annual plants and concluded that there is a straightforward relation between the hemicellulose content in the raw materials and the bonding strength of composites prepared there from. According to this work hemicelluloses do have adhesive properties; however, bonds created using hemicellulose adhesives have almost no wet strength.

The studies by Markessini, et al., (1997) [32] and Mantanis, et al., (2000) [46] have shown that the bondability of straw can be improved if its surface structure is opened up and thus made more accessible to

wetting by aqueous adhesives such as conventional acid-curing UF resins [13].

Han, et al., (1998) [3] reported that the wettability of wheat straw surface was improved through EB treatment and the bondability of particleboards made from EB-treated wheat straw was significantly enhanced due to the removal of wax-like substances and other non-polar extractives from the straw surface.

According to Mantanis and Berns, (2001) [13] application of high shear forces in a refiner and an extruder made the bonding of straw fibers exclusively with UF resins possible. By applying high shear forces, the wax and silica layer is destroyed and allows bonding with formaldehyde-based resins. For the above-mentioned technical and economical reasons, this work was aimed at developing a strawboard technology that will be based exclusively on UF resin bonding. Extruding straw with a twin-screw extruder or refining with a pressurized refiner has rendered panels with characteristics comparable to standard particleboard, except for their swelling properties. Producing panels from refined fibers needs several precise adjustments of pre-treatment and refining conditions as well as a good density profile program. A combined treatment by extruder and refiner has rendered improved panel properties comparable to MDF. Although, the swelling figures were improved, the 24 hour swell standards for MDF and particleboard could not yet be fulfilled. Special care also needed to be taken in relation to the inherent timely and regional variability of straw.

Ndazi, B.S., et al., (2007) [47] suggested that chemical modification of rice husks by NaOH improves the adhesion properties of rice husks in composites made from these with PF resin due to removal of surface impurities such as silica and carboxylic compounds, which blocks reactive chemical groups. Low temperature steam treatment carried out removes carbonyl groups but does not remove silica. The increase in the Modulus of elasticity (MOE) and Modulus of rupture (MOR) of the steam treated composite panels observed could be associated with the stiffness of the particles and partly due to improved interfacial bonding.

Work by Mo, X., et al., (2003) [48] suggested that WS particleboard with 4% methylene diphenyl diisocyanate (MDI) gave superior mechanical performance, water resistance, and lowest thickness swell than formaldehyde (UF), soybean flour (SF), and soybean protein isolate (SPI), because MDI molecules were small and had better mechanical and chemical bonding ability. Same work also suggests that mechanical properties of particleboard made from bleached straw with SPI resin were similar or higher than those of UF resin.

High temperature steam treatment has been also been used to improve dimensional stability of wood products [39, 49-51]. Lawther, et al., (1996) [52] reported that some portion of pectic substances and hemicellulose can be removed from steam-treated wheat straw. Since the pectic substances and high content of hemicellulose in

non-wood lignocellulosic materials usually result in poor adhesion between adhesive and these materials, the extraction of these substances would contribute to the improvement of board properties. So far, there are limited studies on the bondability improvement through steam explosion pretreatment.

According to Han, et al., (2010) [39] Steam explosion treatment can be a feasible approach to improve the bonding strength between wheat straw material and adhesive binders. After steam explosion treatments, the proportions of large particles decreased while fiber bundles increased. Higher steam temperature and longer retention time resulted in more homogeneous fiber-like material. It was found that the pH values and acid buffer capacities of straw were greatly reduced, indicating the increased acidity of the treated straw. The straw material before treatment was more hydrophobic. The dynamic contact angles after steam explosion treatments decreased significantly, indicating that the surface wettability of the treated straw was improved. The ash and silicon contents of the treated straw were significantly reduced through steam explosion. The improved acidity and wettability as well as the decreased silicon content would contribute to the improvement in bondability between straw particles and water-soluble UF resins.

4. Rice–Wheat Cropping System in Pakistan

In Pakistan, RWS is an abundant byproduct from rice–wheat cropping system. Agriculture accounts for nearly 20.9% of Pakistan’s national income (GDP), employs 43.4% of the country’s workforce.[53]. Moreover, this sector provides raw material to domestic agro-based industries, such as sugar, cooking oil, leather, and textiles. Most importantly, 65.9% of the country’s population living in rural areas is directly or indirectly dependent on agriculture for their livelihood [54]. Rice–wheat cropping system has been practiced in Pakistan since 1920 [55]. Wheat is an agricultural crop grown in cool dry season between November and March while rice is grown during warm, humid season between June and October. Both crops are grown for the grain portion of the plant that is a valuable food product, rest of the rice-wheat plant is in the rice-wheat straw consisting of stems and leaves, chaff that is a protective cover over the grain, and the underground root system. Rice-Wheat grain production in 2006-07 was 5438 thousand tonnes and 23520 thousand tonnes respectively. For every 4 tonnes of rice or wheat grain, about 6 tonnes of straw is produced [56]. These ratios of residue/product were verified from field data collected from farmers. It suggests around 43437 thousand tonnes RWS is produced in Pakistan.

In Pakistan wheat and rice straw form the basis of animal feed resources and are used in high rates. Straw is also used in paper and packaging material, mat, wall construction etc. Due to impulsive time span between harvesting of rice/wheat and planting of wheat/rice and moreover, performance of each crop is highly susceptible to any delay in planting therefore part of collected straw

left unutilized is burned, due to lack of high speed harvesting equipment.

Pakistan is facing problem of deforestation and lost 14.7% of her forest habitat between 1990 and 2005 interval [57]. Converting rice-wheat straw into value added products has the potential to improve the performance of agriculture sector. Farmers can also realize an additional income, being an important factor for promoting the efficient collection and management of straws at field.

5. Conclusion

A new environmentally friendly technology is being developed to convert agricultural residues like straw into quality value-added composite products using conventional formaldehyde-based resins. The implementation of the new technology will promote efficient use of agriculture byproduct as a sustainable resource for commercial production of commodity products like particleboards and fibreboards and help in reducing the amounts of agricultural wastes and eliminating the pollution caused by the burning of such straw. It will also help in reducing the stress on forest wood resources.

Straw particleboard has broad applications because of its rigidity, strength, and low cost. By bonding with UF resins, good mat stability, a pressing process without sticking problems and significant resin cost savings can be realized. Particleboard made from bleached straw had improved mechanical performance compared to particleboard made from untreated straw under similar conditions. However more research work is required to improve the bondability of straw fibers to produce even higher quality strawboards, specifically with lower swelling figures.

Present use of wheat straw as a feedstock to produce materials, fuels, and chemicals has been limited applications due to obstacles like capital investment, energy consumption, waste streams, production logistics, and the quality of the biomass feedstock.

Further research is required to make progress in utilization of wider range of lignocellulosic raw materials for composites and in technologies of their economic manufacturing to eliminate the question of availability of feedstock.. Such research should particularly concentrate on methods to improve the surface activation of refined ligno-cellulosic material to reduce the water absorption and to improve mechanical strength of fibreboards. Non-wood fibreboards have huge potential for future board applications since wood resources for such applications are already under great stress.

Pakistan is facing problem of deforestation and. converting rice-wheat straw into value added products has the potential to improve the performance of agriculture sector and help in its prompt removal from field to make field ready for next crop.

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