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Short communication

Alternative fuels from waste cellulosic substrates and poly furfuryl alcohol

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This paper provides methods for manufacturing alternative fuels from waste cellulosic substrates reinforced by poly furfuryl alcohol (PFA). PFA, as a matrix, is obtained from the condensation polymerization of furfuryl alcohol - a waste of sugarcane bagasse. The processes provided herein can utilize a variety of natural cellulosic substrates derived from, for example, plants such as hemp, ramie, pineapple, abaca but not limited to these. Forest residues and wood chips can also be used as the cellulosic substrates. ISO 5660-1 standards were used to compare the calorific values of the PFA reinforced cellulosic alternative fuels and the existing fossil fuels especially coal as well as cellulosic materials. The calorific value of the cellulosic substrates in any form varies from 5.4 MJ/kg to 16.3 MJ/kg. Reinforcement of cellulosic substrates with PFA increases the calorific values in the range of 18.9-25.09 MJ/kg. We have shown by our novel research that PFA based cellulosic fuels provided herein can be used as effective alternative fuels with heat release/calorific values comparable to any varieties of existing coal.

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1. Introduction

The low calorific values (14–15 MJ/kg) of the cellulosic biomass 38 compared to that of any variety of coal (17-31 MJ/kg) as described 39 in US patent limits their uses in generation of electricity or in steel 40 41 industry [1]. Hence, the interest for upgraded wood fuels as alternative fuels increased in the last decade [2] and it is still growing as 42 a consequence of improved awareness for sustainable develop-43 ment as well as behavior of the market of traditional fossil fuels. 44 There are many different types of fossil fuels especially important 45 are coal, petroleum, and natural gas [3]. However, a problem with 46 fossil fuels is depleting resource base. 47

48 After the advent of petroleum oil as the leading source of electrical power, the importance of coal also diminished due to its po-49 tential in environmental pollution. However, coal has recently 50 experienced a "comeback", both because of the increasing costs 51 and exhausting petroleum resources besides new development 52 called "Clean Coal Technology" (CCT) [4]. 53

Since decades, with the advent of 'green revolution', annually 54 55 harvested agro-wastes like corn cobs, sugarcane bagasse, cereal 56 by-products or pulping wastes make up a bottomless renewable feedstock for furfural production. Most of the furfural produced 57 worldwide is converted into furfuryl alcohol (FA) - a monomer 58 for poly furfuryl alcohol (PFA) - by simple reduction processes. Re-59 cently an article has been published regarding protecting FA and 60 61 enhancing its uses [5].

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ABSTRACT

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In this paper, we are reporting the uses of PFA resin to reinforce waste cellulosic substrates in forms of fibers, chips, sheets, and blocks to fabricate new alternative fuels. The calorific values of cellulosic substrates, PFA reinforced cellulosic substrates and coal are compared and reported. The proposed fuels will find application in the areas of generating energy and also in steel industries. Indian patent related to this invention has been filed in June 2010 [6].

2. Experimental

2.1. Materials

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FA and *p*-toulene sulfonic acid (PTSA) were procured from Sigma-Aldrich, Germany. Waste cellulosic fiber was collected from the agricultural field. Waste flax nonwoven web, prepared by needle punching technique on a pilot plant at CSIR, Port Elizabeth, South Africa, was taken as another cellulosic substrates. Coal, used for cooking purpose, was purchased from the local supermarket.

2.2. Reinforcement of cellulosic fiber by poly furfuryl alcohol

Controlled polymerization of PFA was carried out using PTSA as 78 a catalyst at room temperature for 3 days to obtain PFA resin of de-79 sired viscosity. PFA resin, obtained after 3 days of polymerization, 80 was poured on the waste cellulosic fibers placed in the container 81 with holes allowing the extra resin $t\bar{0}$ come out and get collected. 82 The purpose of the holes in the container is to recollect the extra 83 PFA resin coming out after cellulose is saturated with PFA resin 84

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Fig. 1. Thermal stability of the cellulosic fibers and PFA reinforced cellulosic fuels.

and reuse it. Subsequently cellulosic fiber absorbed with PFA resin was placed on a silicon rubber mold and cured at <u>170–180</u> °C for <u>1</u> h to get PFA reinforced cellulosic fuels. The black coloured PFA reinforced cellulosic fuels were obtained upon curing PFA. For comparison fully cured PFA without cellulosic substrates was also prepared.

91 2.3. Characterization

Thermogravimetric analysis (TGA) of approximately 5 mg samples was carried out at a heating rate of 10 °C min⁻¹ between room temperature and 700 °C in nitrogen atmosphere on a thermogravimetric analyzer (Perkin Elmer, Buckinghamshire, UK). The water uptake of the cellulosic substrates and PFA reinforced cellulosic

substrates was evaluated according to ASTM D570-81 as described elsewhere [6].

ISO 5660-1 standards were used to compare the calorific values of the newly manufactured alternative fuels and the existing fossil fuels especially coal as well as cellulosic materials. The samples of dimension 100 mm × 100 mm were cut and wrapped in one layer of heavy duty aluminum foil, shiny towards the sample, covering the sides and bottom and leaving the testing surface exposed. After that samples were placed in a clean horizontal specimen holder which contains fire blanket and the flammability tests were conducted on Dual Cone Calorimeter, Fire Testing Technology, UK.

3. Results and discussion

3.1. Thermal behavior and water uptake

Fig. 1 represents the thermal stability of the cellulose and PFA 110 reinforced cellulosic (PRC) fuels. The thermal stability of the PRC 111 fuels is very high with around 44% char yield at 700 °C as compared 112 to the cellulosic substrates which show almost 8% char yield at 113 700 °C. Cellulosic substrates show water uptake of 28–30% upon 114 24 h immersion in water while same cellulosic substrates rein-115 forced by PFA, under same conditions, show only 5-6% of water 116 uptake. It is a well known fact that the moisture sensitivity of 117 the biomass obstructs the burning process and emits toxic fumes, 118 thus making the biomass as such as less preferred source of energy. 119 Therefore the property of PFA, as 100% hydrophobic reinforcement 120 matrix, gives another advantage to the proposed alternative fuels 121 [7]. 122

3.2. Flammability properties and production of gases

Fig. 2 shows the heat release rate of alternative fuels as compared to coal. Waste cellulosic fiber burns in 50 s with very low124125125



Fig. 2. Heat release rate for the PFA reinforced cellulosic fuels in form of fiber (a), nonwoven sheet (b), and nonwoven flakes (c).

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Table 1

Summarised results of all the important parameters for proposed alternative fuels. cellulosic biomass and coal.

Specimen	Total heat release (MJ/ m ²)	Calorific values (MJ/ kg)	CO (kg/ kg)	CO ₂ (kg/ kg)
Cellulosic fiber Nonwoven cellulosic fiber Charcoal flakes Charcoal sheet Poly furfuryl alcohol flakes Poly furfuryl alcohol sheet Poly furfuryl alcohol-fiber composite	0.6 2.5 5.5 13.1 9.4 8.4 28.2	5.4 16.31 14.93 17.87 20.58 24.95 19.48	0.1473 0.0771 0.2446 0.1846 0.3036 0.2690 0.0657	11.08 5.57 2.78 2.73 2.91 3.60 2.07
Poly furfuryl alcohol– nonwoven fiber composite sheet Poly furfuryl alcohol– nonwoven fiber composite flakes	33.0 29.3	18.90 25.09	0.0598 0.2430	1.95 2.82

peak heat release (166 kW/m²). Same cellulosic fiber in the form of 126 nonwoven web burns for longer time (330 s) with almost same 127 128 peak heat release rate. While in form of flakes, peak heat release 129 rate of the cellulosic fiber is low but it burns for same time as sheet. Fully cured PFA in form of sheet and flakes shows peak heat release 130 rate as 264 kW/m² and 372 kW/m², respectively. PFA burns with 131 almost same heat release as that of coal except in the initial stage 132 133 of ignition (25-50 s). Coal in form of flakes or sheet shows consistency in the heat release which makes it as a good fuel for several 134 applications. Interestingly, coal does not show peak heat release 135 136 rate but the average heat release rate for coal was found to be about 30 kW/m² for almost entire burning period. 137

138 PRC fuels show even higher peak heat release rate that is 600 and 400 kW/m² for sheet and flakes, respectively. For PRC fuels in form 139 of sheet there is single heat release while for flakes there are two 140 peak heat releases. Interestingly, the heat release rate for PRC fuels 141 based flakes or sheet for entire burning period are almost similar to 142 143 that of the coal except in the initial stage of ignition (25-150 s). 144 Alternative fuels burn for longer time compared to coal which 145 shows that for less amount of material consumed we can have more 146 energy for longer period of time. The heat release rate in charcoal 147 (CC) is almost linear whereas in the case of PRC fuels it shows a peak 148 just after ignition and then it dropped to the same level as CC and remains almost constant. On this basis it can be said PRC fuels show 149 150 promise in terms of desirable heat release and the burning time. The incorporation of PFA resin on waste nonwoven fiber mat in-151 creases the calorific values from 16.31 MJ/kg to 18.90 MJ/kg (Table 152 1). On the other hand the incorporation of PFA resin on cellulosic 153 fiber, collected from the agricultural field, increases the calorific 154

values from 5.39 MJ/kg to 19.48 MJ/kg (Table 1). Cellulosic biomass in the form of flakes as wood chips and forest residues are the commonly available substrates worldwide but they are burned to get rid off as they provide less thermal energy. From our proposed research we can add values to these categories of significant biomass.

Table 1 provides the important properties of the proposed alternative fuels, coal and the cellulosic biomass in different forms. It can be seen that our proposed alternative fuels have high calorific values than the cellulosic biomass. Interestingly, the release of CO₂ is higher for the cellulosic biomass but upon reinforcement with PFA the release of CO₂ decreased for the same cellulosic biomass. Even the levels of CO release after burning these alternative fuels are not very high. The calorific values of the alternative fuels are at par with all the varieties of the currently consumed coal. The mean heat release rates for PRC fuels are higher than that for coal and are well confirmed from Table 1. The release of smoke, CO and CO₂ upon burning alternative fuels and coal are almost same except at the point of highest heat release rate.

4. Conclusion

We conclude from this research work that the wastes from the two agricultural sources will be used in the best effective way with minimal environmental impact in fabrication of PRC fuels. The calorific values of the cellulosic substrates can be increased significantly by reinforcing the substrates with PFA. PFA reinforced cellulosic fuels provided herein can be used as effective alternative fuels with heat release/calorific values comparable to any varieties of existing coal. On the cost side, presently these fuels will be expensive than coal but with the advancement in technology and full Government/Industry support for sugarcane cultivation the price of FA can be significantly reduced to give cheap alternative fuels.

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