

Utilization of rice husks for the production of oil sorbent materials

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Received: 31 October 2013 / Accepted: 13 February 2014
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Abstract Rice is the third largest cultivated cereal crop in the world, making rice hulls one of the most abundant biowastes on Earth. In this manuscript, the rice husks have been subjected to alkali treatment at low temperatures aiming to produce a lignocellulosic sorbent material as well as removing their silica. This absorbent has been subsequently tested for marine diesel spill clean up. Various treatment conditions such as NaOH concentration, duration, and temperature have been investigated. The optimized cellulosic sorbents show high RMG380 marine diesel uptake due to low bulk density and their fluffy structure. It is argued that the bulk density is a critical factor in the excellent uptake capacity. As far as the authors are

aware, these results (as high as 20 g of RMG380 sorbed per gram of sorbent) show the highest oil sorption for rice husk derived materials reported in literature. Other advantages include higher yields and lower treatment temperatures compared to other studies. The proposed cheap and environmentally friendly method provides a simple and safe technique for the production of valuable products from lignocellulosic agricultural waste.

Keywords Rice husk/hull/chaff · Oil spill clean up and remediation · Marine diesel · High capacity sorbent · Adsorbent

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Introduction

Rice is an annual cereal plant which completes its entire life cycle from planting to harvesting within a single year. The husk (also known as the hull or chaff) is the protective outer layer of the grain containing large amounts of silica. About 20 % weight of the rice is disposed as husk (Kumagai et al. 2007). The exact composition of rice husk is highly dependent on many variables, most of which cannot be controlled such as the weather conditions (Van Nguyen and Ferrero 2006; Sweeney and McCouch 2007; Peter Rosner and McCulloch 2008; Peng et al. 2009; Stoop et al. 2009; Malekmohammadi et al. 2011). Annually about 200 million tons of rice is produced in China alone. India and Indonesia are the second and third largest rice

producers respectively. Rice is currently the third most widely produced crop in the world (700 million tons/year) standing behind sugar cane and maize (Khush 2005; FAOSTAT 2013a). In the past decade the production of paddy rice has increased by approximately 2.3 % (FAOSTAT 2013b). Rice hulls have a low percentage of protein and available carbohydrates, and a high percentage of crude fiber, crude ash, and silica (Hirotsu et al. 2007; Kamoshita 2007; Naing et al. 2008; Talpur et al. 2011). Rice husks have a low content of digestible nutrients (<10 %). Silica content has been reported at 12.4–22.9 % with the mean of 18.6 % in the dry season and 10.9–20.8 % with the mean of 15.4 % in the wet season (Juliano 1985). Various applications for rice husks have been suggested (Safa and Bhatti 2011a, b; Kamsonlian et al. 2012; Mehdinia et al. 2013; Lordan et al. 2013; Hongo et al. 2013; Pereira et al. 2013).

On the other hand, oil spills are a serious environmental threat that might take years or even decades to clean up. The detrimental effects of spills are not only limited to direct effects on coastal ecosystems, human health, and marine life, but also the indirect and chronic ones. Further study of regions prone to oil spills shows the necessity of establishing protocols for emergency operations (Asfad and Darabinia 2013). Susceptible areas of the world such as the Persian Gulf have been frequently studied [although some have incorrectly referred to the Persian Gulf with false names such as “the Persian-Arabian Gulf”, the “Arabian Gulf”, or just merely the “Gulf” (Elhakeem et al. 2007; Verma et al. 2008; Kirby and Law 2008) in contrast with the United Nations’ assertion against the use of such fabricated names (United Nations Group of Experts on Geographical Names 2006)].

Various methods such as mechanical, chemical, physicochemical, and biological can be applied for combatting oil spills and the use of dispersants, absorbents, solidifiers, booms and skimmers are common (Adebajo et al. 2003; Deymeh et al. 2012; Seyedi et al. 2013). Some studies suggest that large spills are first handled by trying to restrict the dispersion of the oil with booms, followed by collection of the oil with skimmers. The remaining oil which washes onto shores is mechanically collected either by suction or shovels. Sorbents are often applied for small-scale spills (Suni et al. 2004). To date, hundreds of different types of materials, including natural and synthetic ones have been tested as possible sorbents (Adebajo et al. 2003;

Suni et al. 2004; Sayed and Zayed 2006; Rajakovic et al. 2007; Rajaković-Ognjanović et al. 2008; Wahi et al. 2013). The type of petroleum product which is spilled is also of importance. Some can be flushed or cleaned up with porous surfaces, some are prone to weathering and evaporation of volatile components, and some sink to the bottom of the sea. The un-sunk fraction will form slicks that pollute rocky and sandy coastlines such as beaches, ports, wharfs, marinas, caves, historic and touristic sites, and nature reserves (El-Fadel et al. 2012).

Several studies have used rice husks as possible sorbent materials for oil spills. About a decade ago, a Japanese study reported the absorption of oil by carbonized rice husk (Kumagai et al. 2007). The husk was pyrolyzed in a vacuum (500 Pa) at 300–800 °C after pretreatment with steam and refining. A maximum uptake capacity of 6.7 g heavy oil/g as-prepared husk was obtained. In a Nigerian study (Nwankwere et al. 2010), rice husks were acetylated using N-bromosuccinimide (1 % NBS) as a catalyst. Acetylation for 1 and 3.5 h can increase the crude oil sorption from 1.9 g/g to 8.2 and 10.3 g/g, respectively. Bulgarian researchers have also published several papers in recent years, sometimes very similar, regarding oil absorption onto heat-treated rice husks (Angelova et al. 2011; Vlaev et al. 2011; Angelova et al. 2012; Dimitrov et al. 2012; Uzunov et al. 2012). Pilot plant operations have also been tested (Vlaev et al. 2011).

As far as the authors are aware, the highest capacity of oil sorption reported thus far for rice husks has been in a study which first pretreated and subsequently prepared the rice husks via thermal treatment under CO₂ (200 ml/min flow) at 300–800 °C for 1 h (Kenes et al. 2012). It was observed that the density of the sorbate had a direct effect on the sorption capacity. The lowest density hydrocarbon (gasoline $\rho = 0.734 \text{ g/cm}^3$) showed a sorption capacity of 4.5 g/g whereas the highest density hydrocarbon (heavy crude petroleum $\rho = 0.937 \text{ g/cm}^3$) showed a sorption capacity of 15 g/g (Kenes et al. 2012). Herein, we have used a simple method for the production of oil sorbent materials with uptake capacities higher than any previously reported in literature for rice husk-derived absorbents.

Materials and methods

The rice husks (also referred to as rice hulls) were harvested and collected in Mainland China. They were

Table 1 Specifications of marine fuel RMG380 as specified by ISO 8217: petroleum products–fuels (class F)

Parameter	Unit	Limit	RMG 380
Viscosity at 50 °C	mm ² /s	Max	380
Density at 15 °C	kg/m ³	Max	991
Water	% V/V	Max	0.5
Pour point (upper), summer	°C	Max	30
Pour point (upper), winter	°C	Max	30
Flash point	°C	Min	60

kindly donated to the research team by a Hong Kong based company (Peako Biomass Energy Ltd.). The husks are golden brown in color and averagely <1 cm in length. Residual (marine) diesel was used as the petroleum product to test the rice husk sorption capacities. The marine diesel was obtained from Gulf Oil Marine Ltd. (X 1L—M380, RMG ISO 8217). The nominal specifications of the fuel provided by the supplier can be seen in Table 1.

As can be seen from Table 1 the density of the fuel is indicated to be a maximum value of 991 kg/m³ at 15 °C. Since the experiments were carried out at room temperature (22–25 °C) it is expected for the marine diesel to be slightly less dense. However, it should also be noted that with time the volatile fraction of the marine diesel will evaporate leaving behind a thicker liquid.

The husks were first sieved by a stainless steel net to remove any powder or broken pieces of hull. All remaining pieces were fully in-tact hulls. The sieved husks were dried and kept at 90 °C in the oven. In each experimental run, husks were treated with various molarities of NaOH solution. After the reaction duration was fulfilled the husk was left to cool to room temperature, filtered, washed, dried and collected.

For the sorption tests 0.2 g of the alkali treated husk was sieved, weighed, and submerged into the marine diesel. The sieving process is carried out so that no powder product will fall through the net during the experiment and contaminate the marine diesel bath. Unless otherwise specified, the sieve is left submerged in the oil for 30 min before it is removed and left to drain. The weight of the wet net and sorbent are measured after 15 min of drainage. The amount of RMG380 taken by the empty net (without any husk) is measured in a separate blank run. The final oil sorption

capacity of the rice husk is calculated after the weight of the marine diesel uptaken by the net and the weight of the dry husk are deducted from the final measured weight with Eq. 1:

$$C = \frac{M_{total} - M_{empty} - M_{husk}}{M_{husk}} \quad (1)$$

where C is the sorption capacity of the as-prepared husk [gRMG380/gsorbent], M_{total} is the total weight of the experimental apparatus, M_{empty} is the weight of the liquid taken by the net, and M_{husk} is the weight of the dry sorbent used.

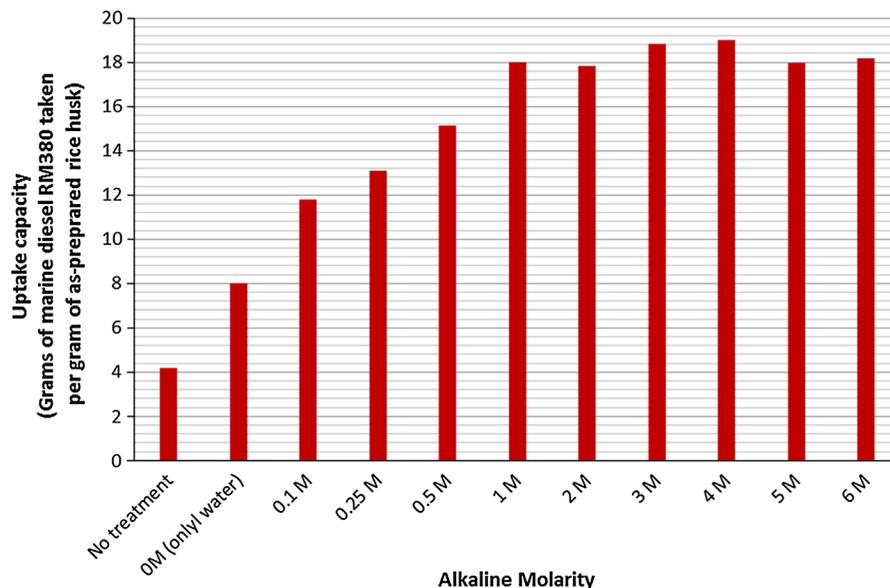
The FTIR spectra were obtained for a wave number range of 4,000–400 cm⁻¹ on a Nicolet 550 Magna-IR spectrometer (Nicolet Instrument Corp., Madison, WI) equipped with OMNIC software. The experiments were repeated several times and the results were normalized after acquisition for comparative purposes. The specific surface area of the materials was characterized by adsorption–desorption of N₂ (Brunauer-Emmett-Teller method, BET) at the temperature of liquid nitrogen (77 K) using an Autosorb1-Quantachrome instrument. The gas used for the analysis was 99.9 % pure.

Results and discussion

Compared with other technologies, alkali treatment processes utilize lower temperatures and pressures because they can be carried out at ambient conditions. However, the times required for alkali treatment are much longer than some other technologies which may require only minutes. When compared with acid treatments, alkali treatments lead to less sugar degradation. Sodium hydroxide is the most widely studied caustic material for lignocellulose treatment (Kumar et al. 2009).

In the current research rice husk samples were treated with alkali followed by subsequent testing of their diesel sorption abilities. Although hundreds of articles have targeted oil sorption with various sorbents, as far as the authors are aware there is no account in the literature of employing this simple yet effective method for preparing oil sorption materials from rice husks. After the oil is uptaken by the as-prepared husks it can either be recovered (Asadpour et al. 2013; Wang et al. 2013), or, the oil-rich rice husk sorbent could be directly used as a

Fig. 1 RMG380 Marine diesel uptake versus the concentration of the NaOH used in the treatment process



solid fuel with high calorific value (Karakasi and Moutsatsou 2013). Another added benefit of alkali treatment is the possibility to leach and chemically remove the silica content from the biowaste in the form of sodium silicate. The soluble sodium silicate could in turn be precipitated and used as a raw material for the production of silica gel and other valuable products.

Effect of NaOH concentration

The alkali concentrations tested to treat the husks at 90 °C were 0.1, 0.25, 0.5, 1, 2, 3, and 6 M. One sample was also treated only with hot water and denoted as 0 M. Raw rice husks without any treatment were used as control samples. The marine diesel uptake values can be seen in Fig. 1. Observably even treatment with hot deionized water increases the oil uptake of the rice husk. This is thought to be because of the removal of water-soluble impurities. Nearly 15 % weight of the sample is removed with water-treatment which results in brisk brown (less golden) husks. The solid yield of the treated husks is seen to decrease as the caustic concentration increases. The sizable effect of alkali treatment on the yield can be best seen from the 0.1 M sample. Even the mild 0.1 M NaOH treatment results in more than 50 % weight reduction. This is because even mild concentrations of NaOH can remove natural

fat and wax on the husk surface as well as some other components such as hemicellulose (Ndazi et al. 2007a, b). Oil uptakes of samples in the range of 2–6 M NaOH treatment give more or less the same results. Higher concentrations than 2M do not decrease the yield considerably. This is thought to be due to removal of all alkali soluble materials. As the molarity of the alkali is increased, the macroscopic and physical state of the husk becomes more broken down resembling mercerization.

Effect of reaction time

As seen in Fig. 2, RMG380 marine diesel sorption capacity increases with the increase of reaction duration. However, after about 12 h of reaction further continuation does not increase marine diesel uptake. This can be explained as follows: with the increase of time, the alkali solution has more opportunity to break-down the husk structure. Since lignin is known to be what gives cellulosic materials their rigidity, the loss of lignin results in smaller and fluffier fibrous fragments. When sufficient time has passed, all alkali soluble components are removed and so the remaining treatment is ineffective in making the structure of the as-prepared material any more suitable for RMG380 uptake. Evidently there is an inverse relationship between the yield and marine diesel uptake. This is

Fig. 2 The effect of reaction time on RMG380 uptake capacity

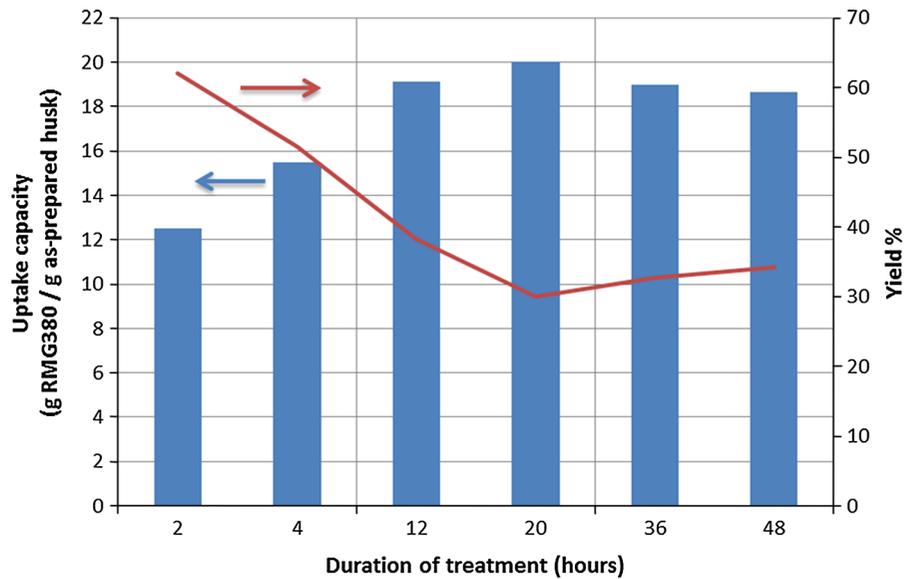
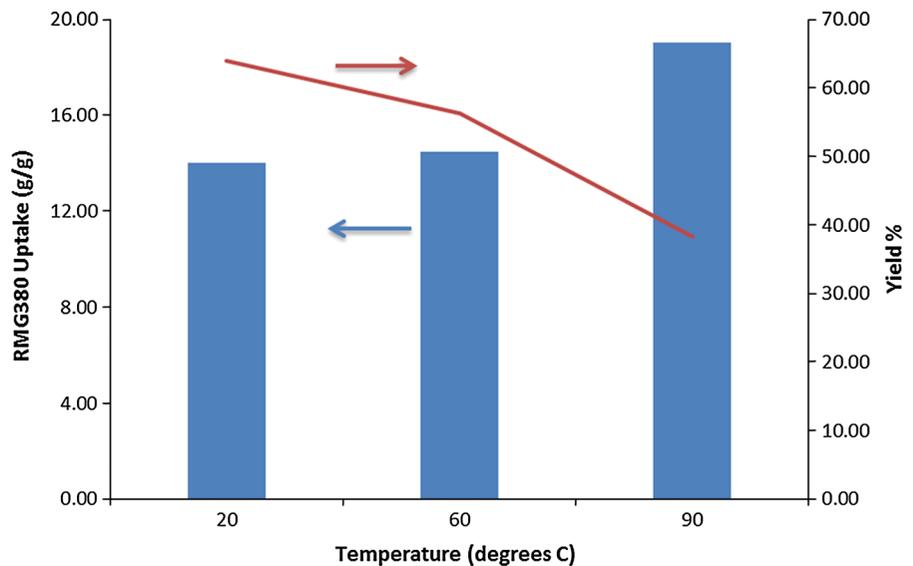


Fig. 3 The effect of treatment temperature on yield and RMG380 uptake. The samples have been treated with 1 M NaOH solution for 12 h. Solid loading is 16 g/l



because lower yields result in more macroscopic void spaces for retaining the liquid.

Effect of reaction temperature

Figure 3 shows the effect of treatment temperature on the marine diesel uptake. Evidently, the higher the temperature is, the more efficient the break-down of the husk will be. More extensive break-down (and hence lower yields) result in a lower bulk density and higher liquid uptake.

Overall analysis

Endwise degradation or peeling of cellulose can occur in alkali media. This reaction is also called endwise depolymerization. Reports have shown that the final product still contains noticeable amounts of reducing endgroups (Li et al. 2007). This is ascribed to the fact that the degradation has reached a crystalline region which is inaccessible to alkali and hence stopped. The alkali concentration affects both the physical accessibility and the relative rates of peeling and stopping

reactions. It is speculated that the degradation first increases due to higher accessibility, and is impeded due to the formation of stable endgroups at higher alkalinity. The hydrogen bond of cellulose is disrupted as a result of alkali treatment and thereby the surface roughness of the samples increases. Also, wax and oils covering the external parts of the fiber cell wall are removed. So alkali treatment increases both the surface roughness resulting in better mechanical interlocking, and the amount of cellulose exposed on the fiber surface (increasing the number of possible reaction sites) (Li et al. 2007).

Various constituents of the lignocellulosic materials are cemented together by lignin. The integrity, structural rigidity, and resistance towards swelling are due to the presence of lignin. Compared to most other biowastes rice hulls have high lignin content. Logically the delignification processes can improve the rate and extent of rice husk break-down. Lignin type, content, and distribution are of importance. The reason for improved rate of hydrolysis by removal of lignin might be related to a better surface accessibility (Tahezadeh and Karimi 2008). Since C–C bonds are usually very resistive to chemical attack the degradation or fragmentation of lignin is largely limited to breakage of ether units. Similar to cellulose and hemicellulose, lignin has a tendency to form hydrogen bonds. Both lignin and cellulose form strong hydrogen bonds when dried and therefore their subsequent adsorption of water is diminished (Lai 1996).

In rice husks, alkali treatment has shown to break the cell wall by dissolving hemicellulose, lignin, and silica; by hydrolyzing uronic and acetic acid esters; and by swelling cellulose. The degree to which each of the constituents dissolves depends on various parameters such as alkali concentration and temperature (Juliano 1985). The treated rice husk exhibits a decreased bulk density which allows more oil to seep inside the sorbent. The majority of the absorbed oil is not directly in contact with the walls of the solid, but rather is retained due to cohesion, surface tension, and capillary forces. It is important to keep in mind that the uptake capacity observed is mainly a function of bulk absorption, and not surface adsorption. Hence the internal BET surface area will not have a considerable effect on the sorption capacities. In order to show the effect of various parameters, the relevant information of three representative samples has been compared in Table 2. The three samples are raw rice hulls, those

Table 2 Comparison of alkali treatment effects

	No treatment	Weak alkali treatment	Strong alkali treatment
Yield (%)	100	42.8	35
BET surface area (m ² /g)	2.3	2.6	3.5
Bulk density (kg/m ³)	82	62	35
Highest measured uptake capacity (g RMG380/g as-prepared husk)	4.5	17.5	20.1

which have undergone mild alkali treatment, and those which have been treated with concentrated alkali.

Evidently, even concentrated alkali treatment has no considerable effect on the BET surface area of the sample. Hence the macroscopic feature of the samples (i.e. the bulk density) appears to be the main factor regarding marine diesel uptake. Contact angle measurements (not shown here) also revealed that the hydrophobicity of the surface is not beneficially altered due to the treatment. This is because the waxes and other hydrophobic materials have been removed and the as-prepared sample is comprised of mainly hydrophilic cellulose.

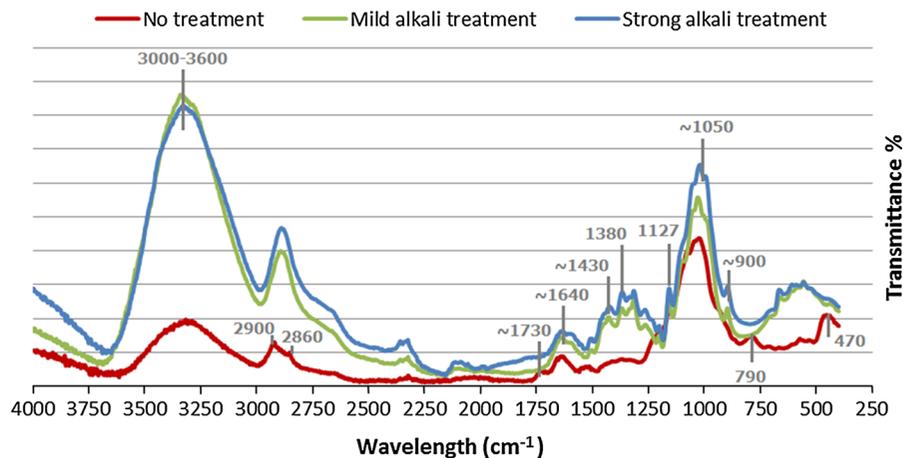
To further investigate the claim of the importance of bulk density, the sample treated with strong alkali was compressed followed by subsequent testing of the uptake capacity. Table 3 clearly shows that the physical compression of the sample considerably reduces the uptake capacity. The compressed samples lost their fluffy structure and turned into flat sheets which remained flat even after 5 months.

The surface functional groups of the alkali treated samples were also further analyzed with FTIR spectra

Table 3 The effect of physical compression on RMG380 uptake capacity

	Average measured RMG380 uptake capacity (g/g)	Highest measured RMG380 uptake capacity (g/g)
Strong alkali treated sample	19.5	20.1
Compressed strong alkali treated sample (500 bar for 10 s)	10.3	11

Fig. 4 FTIR Spectra of treated and untreated rice husk



analysis. Figure 4 compares the FTIR results of the untreated, mildly alkali treated, and strongly alkali treated husks.

The large peak at 3,000–3,600 cm^{-1} is representative of strong hydrogen bonding due to hydroxyl (OH) groups of the cellulose. The absorbance ratio of the bands at about 1,430 and 900 cm^{-1} is referred to as the crystallinity index. The larger band denotes the crystalline absorption, while the smaller shows the amorphous part. The more broad these peaks are, the more disordered the structure of the cellulose is. One might conclude that the results show that by alkali treatment, the crystallinity of the rice husk samples increases. However, this is in contrast with general knowledge regarding the mercerization of pure cellulose which is known to decrease the crystallinity index. Also, since the absorbance at approximately 900 cm^{-1} is shown to increase as cellulose I transforms into cellulose II, we can conclude that this transformation has not occurred prevalently here (Oh et al. 2005). Further scrutiny of XRD patterns (not shown here) affirms the fact that no conversion to cellulose II has occurred (French 2013). The overlapping band at 1,050 cm^{-1} has also been ascribed to Si–O stretching (He et al. 2013). Hence the untreated rice husk which contains a high silica content shows a high intensity at this wavelength. After alkali treatment, the silica is removed in the form of sodium silicate, and therefore the relative intensity of this band decreases.

The small peak at around 1,640 cm^{-1} corresponds to the absorption of water. Some hemicellulose and lignin material have clearly been removed. For

example, the shoulder observed at around 1,730 cm^{-1} seen in the raw rice husk is no more present after the treatment. This is ascribed to the removal of acetyl and ester groups in hemicellulose or carboxylic acid groups in the lignin (Johar et al. 2012). The bands at 1,473 and 1,380 cm^{-1} show the C–H symmetric and asymmetric deformations, respectively (Sun et al. 2005). Similarly, the bands at 2,900 and 2,860 correspond to asymmetric and symmetric stretching vibrations of the aliphatic C–H bonds in $-\text{CH}_3$ and $-\text{CH}_2$ groups in the structures of cellulose, hemicellulose, and lignin, respectively (He et al. 2013). The bands at approximately 470 and 790 cm^{-1} which exist in the raw husk but are removed with the alkali treatment can be associated with Si–H bonds (Nakbanpote et al. 2007). The band at 1,127 cm^{-1} could be indicative of C–O stretching in Na^+ -lignosulfonics (Shen et al. 2008).

Further studies could be carried out to make use of the silicon which is leached during the alkali treatment process in the form of sodium silicate. The silicon can be recovered in the form of a silica gel by reducing the PH (Foletto et al. 2006). Initial experiments have been done and suitable results have been obtained. Porous silica with BET surface areas exceeding 200 m^2/g and good purity has been recovered. Various reviews and studies regarding the recovery of porous silica from rice are available in the literature (Sun and Gong 2001; Chandrasekhar et al. 2003). Hence another benefit of the current proposed process is the production of two products at the same time: the first being an oil absorbent, the other a siliceous product. Considering

the total silica content within various batches of rice husks, the total amount of soluble silica (in the form of sodium silicate) would be 10–20 % weight of the raw rice husk. Considering the fact that about 20 kg of husk are produced per 100 kg of rice paddy product, this would amount to 2–4 kg of soluble silica per 100 kg of rice grain produced. Alongside other value-added applications (Santamaría et al. 2013; Shao et al. 2013; Kim et al. 2013), the sodium silicate could also be used for catalytic purposes for biodiesel and fatty acid production (Fan et al. 2013; Long et al. 2014).

Conclusion

Rice husks have been used as feedstock for the production of oil sorbent materials. Simple, safe, and cheap alkali treatment was shown to break-down the rice husk structure and produce as-prepared products with satisfactory oil uptake capacities. The proposed method uses low temperatures and results in high product yields. BET and FTIR analysis have shown that micro- and nano-porosity as well as surface functional groups are not determining factors in the superior uptake capacities. The marine diesel sorption capacity is shown to have a strong inverse relation with the bulk density.

Acknowledgments The authors would like to sincerely thank the staff at the MCPF and AEMF departments at the Hong Kong University and Technology, as well as Mr. Ronnie Lo of Peako Biomass Energy Co. for their assistance.

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