Thermal degradation of rice husks on a pilot plant

Utilization of the products as adsorbents for oil spill cleanup

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Abstract This study is an attempt to establish the possibilities to obtain black rice husk ash (BRHA) and white rice husk ash (WRHA) via pyrolysis of wasted raw rice husks in a pilot plant fluidized-bed reactor at different conditions. The process course auto thermally, without outer fuel. The released heat may be used for steam obtaining or drying. The solid products obtained (BRHA or WRHA) are characterized using X-ray diffraction patterns, thermal analysis, and low temperature nitrogen adsorption. Using batch adsorption technique, the kinetics was studied and the adsorption capacities of crude oil and diesel fuel at different temperatures as well as some hydrocarbons at 298 K onto BRHA and WRHA are determined. It was established that BRHA have been higher adsorption capacity than WRHA. At a given temperature, BRHA sorbed more crude oil than diesel fuel. The results obtained showed that the material studied has high adsorption capacity and low cost and may successfully be used as an effective adsorbent to cleanup of bilge water and spills of oil and oil products in water basins. Because the saturated BRHA with crude oil, diesel fuel or different hydrocarbons are characterized with high calorific, they can be burnt in incinerators, industrial ovens or steam generators. By this way, we attain not only ecological but also economical effect.

Keywords Rice husks · Pyrolysis ·
Fluidized-bed reactor · Rice husks ash · Adsorption ·
Crude oil · Diesel fuel

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Introduction

Rice husks are an important by-product of rice milling process and are major waste product of the agricultural industry. According to the statistical data of Food and Agriculture Organization (FAO), the world annual paddy production is ∼582 million tons. *Oryza sativa* L. husks (Rice husk) comprise 22–25% of the rice grain and, therefore about 145 million tons of rice husks residue are produced [1]. It is major constituents comprising of cellulose, hemicellulose, lignin, hydrated silica, and ash content. The chemical constituents are found to vary from sample to sample which may be due to the different geographical conditions, type of paddy, climatic variation, soil chemistry, and fertilizers used in the paddy growth [2]. Govindarao in an extensive review [3] has analyzed all the reported data on the chemical composition of rice husks from various countries, including western world and Asia and gives an average composition of dry basis as organic matter 80% and ash 20%. The organic part is composed approximately of 42.8% a-cellulose, 22.5% lignin, 32.7% hemicellulose, and other organic matter about 2%. Hemicellulose (xilan) is a mixture of D-xylose—17.52%, L-arabinose—6.53%, methylglutaconic acid—3.27% and D-galactose—2.37% [4–6]. The chemical analysis of the inorganic part in rice husks showed that the main component is amorphous silica and small amount from some oxides of alkali, alkali earth metals, aluminium, and iron. These husks are not of commercial interest and cause serious pollution problems for ecology. Rice husks has an average lower heating value of 13–16 MJ/kg and it is about one-third that of furnace oil, one-half that of good quality coal and comparable with sawdust, lignite and peat [7]. The world annual energy potential of rice husks is about 1.2×10^9 GJ, and thus, rice husks are good renewable

energy source. Milling of 1 ton of paddy produces about 220 kg of rice husks, which are equivalent to ∼150 kWh of potential power. This quantity of power is enough to produce electricity and steam for paddy drying. The energetic balance shows that utilization of rice husks as a renewable fuel may be convert paddy milling process from consumer to producer of energy [7–9].

The current practices to dispose of the large quantities of rice husks through open burning or rotting in field are not environmental-friendly. Open burning results in air pollution with the formation of smoke and particulate materials in the form of chair and ash. Rotting in field, on the other hand, results in formation of methane, which is a greenhouse gas 25 times more potent than carbon dioxide. Rotting in the field leads to a slow decay of the organic material, with eventual emission of approximately equal amount of CH_4 and CO_2 from the carbon that is released during the decay [7].

The controlled burning of raw rice husks in air in a fluidized-bed reactors leads to the production of white rice husk ash (WRHA) or so-called "white ash" containing almost pure (≥95%) silica in a hydrated amorphous form, similar to silica gel, with high porosity and reactivity. This biogenic silica with amorphous nature in the raw rice husks makes it extractable at a lower temperature range, and hence, thermal treatment of rice husks to produce amorphous silica is viewed as a more economical process having the potential to replace the conventional high temperature processes. This is because thermal treatment of rice husks actually produces energy instead consuming energy. The energy produced could be recovered in the form of heat or electricity [7–9].

The controlled thermal degradation of rice husks in inert or poor of oxygen medium leads to the production of black rice husk ash (BRHA) or so-called "black ash" which contains different amounts of amorphous carbon incorporated with silica. This material has very high porosity and may be used as an adsorbent for adsorption of non-polar molecules, such as hydrocarbons, contained in crude oil, or diesel fuel. WRHA and BRHA may be successfully used as fillers in rubber and plastic composites [10–14].

The sources of contamination of fresh and seawater are most often spills of oil and oil products by accidents with tankers or underwater pipes, as well as offshore oil platforms and oil refineries. According to data presented by the USA National Academy of Sciences, the annual amount of oil and oil products spilled into the seas and oceans by various sources is about 20 million tons [15]. Moreover, the ships produce a large amounts of oily wastewater such as bilge water which needs to be treated before being discharged. The bilge water is a difficult wastewater to treat as it contains seawater, particulates, used oils and detergents.

Micro- and ultra-filtration are often the methods of choice to treat this water. The pretreatment of this oily wastewater before ultrafiltration is desirable, as the used oils and particulates can block the feed channels of the ultrafilters spiral and hollow fiber modules. In this reason, at the last time different hybrid adsorbents with high adsorption capacity and appropriate porous structure are used. The main requirements for these sorbents are [15–17]:

– They should adsorb significant quantities of oil per unit mass.
– They should be hydrophobic and with low water sorption capacity.
– Their loose density should be low and they must remain in water as long as possible.
– The adsorption rate should be high enough.

The aim of this study is to study the structure of WRHA and BRHA obtained by thermal degradation of raw rice husks on a pilot plant fluidized-bed reactor and the possibilities to use these products as an adsorbents for cleanup of spilled crude oil, diesel fuel or bilge water.

Experimental

Rice husks were collected from suburb areas of Thrace (Pazardjik, Bulgaria). It was sun dried and the moisture content reduced to less than 10 mass%. These raw rice husks were used without any pretreatments.

X-ray diffraction

The diffraction patterns of the samples studied were recorded in a symmetrical reflection mode using URD-6 Seifert diffractometer and a copper target X-ray tube ($l = 0.154$ nm) operated at 40 kV and 30 mA. Cu K_α radiation was monochromized with a graphite monochromizer and a Ni filter. The XRD patterns were recorded in the 2θ range 4–60° at 0.1° steps. The samples for the experiments were powdered and pressed into a sample holder. Samples with the radius of 2 cm and the thickness of 1 mm thick were prepared.

Thermal analysis

The thermal analysis measurements (TG–DTG–DTA) were carried out on a Netzsch STA 449F3 Jupiter apparatus by increasing temperature from ambient to 1073 K. The measurements were performed in dry air atmosphere, at a heating rate of 10 K/min. The sample mass was about 10 mg placed in an aluminium crucible without pressing. Calcined α-Al_2O_3 powder was used as standard reference.

Nitrogen adsorption measurements

The nitrogen adsorption–desorption isotherms were obtained on a classical volumetric high-vacuum BET apparatus at 77 K. Spectrographically pure nitrogen (Matheson) was used as an adsorbate. The samples used for obtaining of the isotherms were heated at 393 K for 4 h and evacuated simultaneously by a mercury diffusion pump to a residual pressure of 5×10^{-5} Torr (1 Torr = 133.32 Pa).

Batch adsorption experiments

The sorption measurements with crude oil and diesel fuel were carried out gravimetrically. Samples of 1 g were placed in a stainless steel mesh basket and immersed in filled with crude oil or diesel fuel glass container equipped with a water jacket and electromagnetic stirrer. The measurements were carried out at 293 K. The temperature was kept constant with a precision of ±0.05 K using Ultra thermostat U-1 (Germany). After certain contact time between the sample and crude oil or diesel fuel, the basket was taken out of the glass container, strained and weighted. The used sorbates were diesel fuel commercial product of Lukoil, Bulgaria with relative density at 293 K = 828.0 kg/m^3 and viscosity at 313 K = 2.16 mm^2/s, and crude oil ''Russian export blend'' with relative density at 293 K = 869.8 kg/m^3 and viscosity at 313 K = 12.28 mm^2/s.

Results and discussion

The first purpose of this research was to produce rice husks ash from raw rice husks through thermal treatment at different conditions using the fluidized bed technology. In the literature, there are described three thermal treatment technologies which had been widely used to produce

amorphous silica from rice husks: muffle furnace, rotary kiln, and stepped grate furnace [7, 14, 18–21]. However, the fluidized bed technology is capable of achieving high carbon conversion efficiency at moderate operating temperatures (below the crystallization point of silica in rice husks ash) at rapid reaction times, which are the characteristics necessary in overcoming the major concerns in heat treatment of rice husks. Rice husks has low bulk density ($\sim$100 kg/m^3) poor flow characteristics and low ash melting point that render it unsuitable to be burned in conventional combustion systems, such as inclined grate furnaces. The bubbling action in the fluidized bed provides a high degree of turbulence and mixing in the bed region, which results in high heat transfer rates within the bed. Therefore, the heat evolved during the combustion process is distributed uniformly within the bed, with temperature variations within the bed region typically not exceeding 5–8 °C. The formation of hot-spots is thus eliminated. The presence of hot-spots in the combustion zone poses the risk crystallizing the silica in the rice husks ash. In addition, the high rates of heat transfer also leads to high combustion efficiency. As such, the combustion temperature can be kept low, typically in the range 600–800 °C, while enabling autogenous combustion to take place compared to other types of combustors, for example the inclined grate system. On these reasons, using the results obtained from the studies carried out with the laboratory equipment [2, 14], we build a pilot plant for pyrolysis of rice husks with productivity of 100 kg/h raw rice husks which a photograph and scheme are presented on Fig. 1a, b, respectively.

The main part of the pilot plant is fluidized-bed reactor with inner diameter of 0.3 m and height of 3.6 m. The fluidization or bubble formation characteristics affect the degree of mixing in the fluidized bed. The mixing behavior, in turn affects the combustion efficiency, with good mixing behavior promoting high combustion efficiency. This is because good mixing provides turbulence and higher residence time among the reactants and therefore, two of the


Fig. 1 **a** A photograph of the pilot plant for rice husks pyrolysis. **b** Overall schematic diagram of the 0.3 m inner diameter fluidized bed combustor system
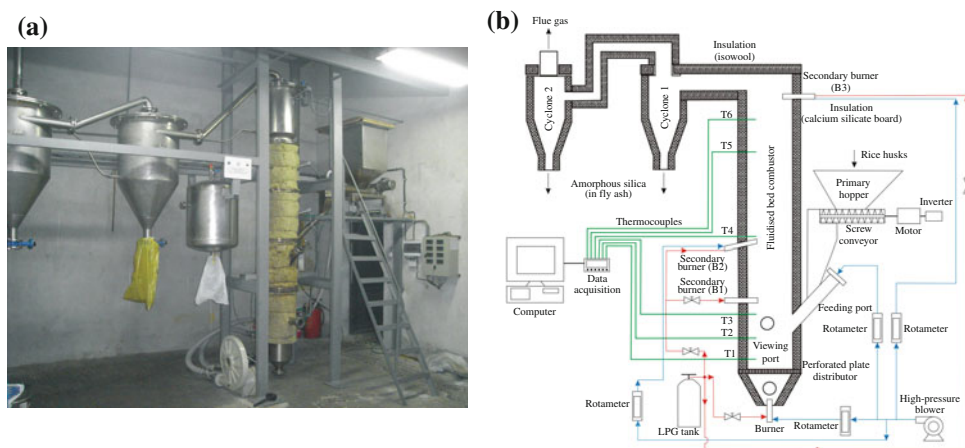
three fundamental requirements for the combustion reaction (temperature, turbulence, and residence time) could be fulfilled. Due to the specific shape of the rice husks (like boat), however, it is almost impossible to maintain a stable regime of the fluidized bed. Beside, it is quite difficult to ignite and burn only rice husks because of their low heat conductivity and heat capacity. All this indicates that auxiliary techniques and original approaches should be sought to solve the problem. The most efficiency way to overcome it turned out to be the use of quartz sand of suitable granulometric composition as heat carrier in the fluidized bed reactor. It is chose is stipulated by it is high thermal resistance and chemical inertness, as well as it is availability and low price. With the use of a same distributor design, the bubble formation characteristics and thus the mixing in the fluidized bed is governed by the fluidization parameters. For effective working of the fluidized bed reactors very important parameters are the fluidizing velocity of air, sand size fraction, and static bed height of sand [7].

The choice of sand size to be used for the operation of the fluidized bed reactor affects the amount of air input required in order to maintain a certain fluidizing conditions. The velocities at which a materials is in it fluidizing state lay within the range of it is minimum fluidizing velocity (U_{mf}) and it is terminal velocity (U_t). It was reported by Rozainee [7, 21, 22] that a fluidization number (U_t/U_{mf}) of 3, was necessary to produce the turbulence regime crucial in attaining good mixing behavior in a fluidized bed. In his study, it was found that incineration was stable at a fluidization number of 3 and that at fluidization number of 5, the combustion efficiency was similar to that of fluidization number of 3. The velocities range obtained from experiment for the fluidizing state of rice husks, it is chair and ash, as well as sand samples was compared in Fig. 2.

It was established that the operating velocity of air for combustion of rice husks in a fluidized bed was optimum at 0.185–0.37 m/s at room temperature and pressure for sand particle sizes between 350 and 420 μm. After some trial runs with different sand sizes, we conclude that this sand size was deemed the most suitable for the combustion of
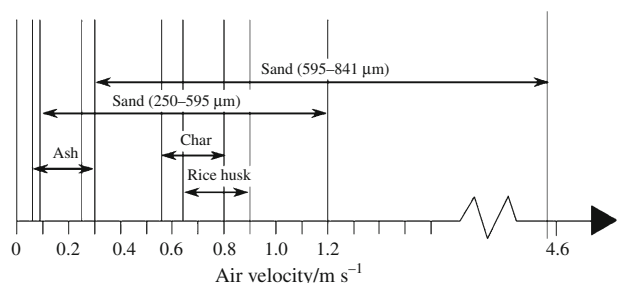
Fig. 2 Experimental values of velocities range for the fluidizing state of raw rice husks, rice husks chair, or ash and sand samples

rice husks in fluidized bed as there was considerable sand entrainment with sand size much smaller than 350 μm. On the other hand, sand particles that are too large would not mix well with rice husks, resulting in poor combustion behavior. This was found to be consistent with other studies which reported the use of sand with sizes less than 830 μm, mostly in the range 300–500 μm [14].

Depending on the combustor operating conditions, particle combustion may be controlled by chemical reaction or transport phenomena. At low temperatures, chemical reaction is a dominant factor, but not at high temperatures, where chemical kinetics are fast. At high temperatures, intra- and extra-particle mass transfer resistance of the oxidizing agent plays a major role in determining the combustion rate. Combustion at these high temperatures regime, therefore, is diffusion limited. In fluidized bed reactor, the combustion process was widely believed to be limited by the char oxidation stage [7] as the conversion of carbon to CO_2 generates three times the heat released in comparison to it is conversion to CO. Chair from biomass materials such as rice husks belong to the most reactive of technical carbon material due to their porous and highly disordered carbon structure. Therefore, it is expected that the temperature regime for diffusion-limited combustion of rice husks char is lower. It was established that below the temperature 773 K, the combustion of rice husks char is kinetically controlled process.

Depending from the reaction conditions in a fluidized-bed reactor, two type products were produced—WRHA [23–25] and BRHA [25–29], respectively, which were characterized with X-ray diffraction, thermal analysis, nitrogen adsorption measurements, and batch adsorption experiments. WRHA and BRHA obtained under these conditions have good quality and may be used as adsorbent, filler of polymers, rubbers, cement, and concrete or for other purposes [10–14]. We study the possibility to be used as adsorbents for sorption of crude oil and diesel fuel.

In Fig. 3 are presented the TG, DTG, and DTA curves obtained by pyrolysis of raw rice husks and BRHA in air at heating rate of 10 K/min.

As can be seen from Fig. 3, the thermal degradation of raw rice husks in air occurred in two stages: The first one with maximum rate at 573 K and the second one at about 693 K. These processes are strongly exothermic and the heat generated was about 4.4 kJ/g. The remaining quantity of WRHA was about 22 mass%. The burning of BRHA in air atmosphere occurs in one stage with maximum rate at 773 K. This process is also exothermic and the heat generated was 6.8 kJ/g. The residue at the end of this process was about 54 mass% WRHA consisting of almost pure amorphous SiO_2.

The XRD patterns of raw rice husks (RRH), BRHA and WRHA showed a broad diffused peak centred at about $2\theta = 22.5°$. No reflexes characterizing cristobalite or

tridymite phase of silicon dioxide were noticed in the sample studied, indicating the absence of any crystalline phases. A broad hump around $2\theta = 22.5°$ was noticed, indicating the presence of amorphous silica (disordered cristobalite).

The pore structure of the products of the thermal degradation of rice husk was studied using low temperature adsorption of nitrogen. In Fig. 4 are shown the typical nitrogen adsorption–desorption isotherms of BRHA and WRHA and pore size distribution curves of both samples.

As can be seen from Fig. 4, the adsorption isotherms of BRHA and WRHA are of type IV and each had hysteresis loop (associated with capillary condensation) from type H1 according IUPAC classification [30, 31]. According to these observations, both the samples were mainly microporous (mean radius 1.8–2.0 nm) with narrow pore size distribution. It can be seen from Fig. 4 that the nitrogen adsorption isotherms and the curves of pore volume distribution in white and BRHA were identical. According to the classification of Brunauer–Deming–Deming–Teller

Fig. 3 TG, DTG and DTA curves of pyrolysis of raw rice husks (*1*) and BRHA (*2*) in air

[30], they are type IV with clearly manifested hysteresis loop H-1 by IUPAC [30, 31]. This indicates for mesoporous structure with cylindrical or almost cylindrical pores open at both ends. The shape of the curves representing the distribution of pore volume by effective size, however, shows bimodal distribution with a pronounced maximum at about 2.0 nm and smaller second one at about 3.0–3.5 nm. It means that the porous structure of the samples is composed of both micro and mesoporous characteristic for many globular adsorbents and particularly amorphous silica gel [32, 33]. The uniformity of the adsorption isotherms for WRHA and BRHA shows that the presence of certain amount of amorphous carbon did not result in substantial changes in the amorphous SiO_2 porous structure. This is sustained by the fact that the specific area of both samples was in the order of 230–240 m^2/g, and pore volume—0.22–0.25 cm^3/g. This was considered to be a sound basis to expect that both products could be used as adsorbents, although, it should be kept in mind that hydrophilic WRHA will adsorb predominantly polar molecules while hydrophilic will adsorb mostly non-polar molecules. Taking into account these differences and characteristics of BRHA and WRHA, we carried out studies on the adsorption of diesel fuel and crude oil onto BRHA and WRHA, obtained in our pilot plant fluidized bed reactor. The evaluation of adsorption process as a function of contact time between adsorbate and adsorbent was carried out with both the adsorbents. In Table 1 is shown some physicochemical characteristics of the products studied, as well as these of Aerosil A200 Degussa for comparison.
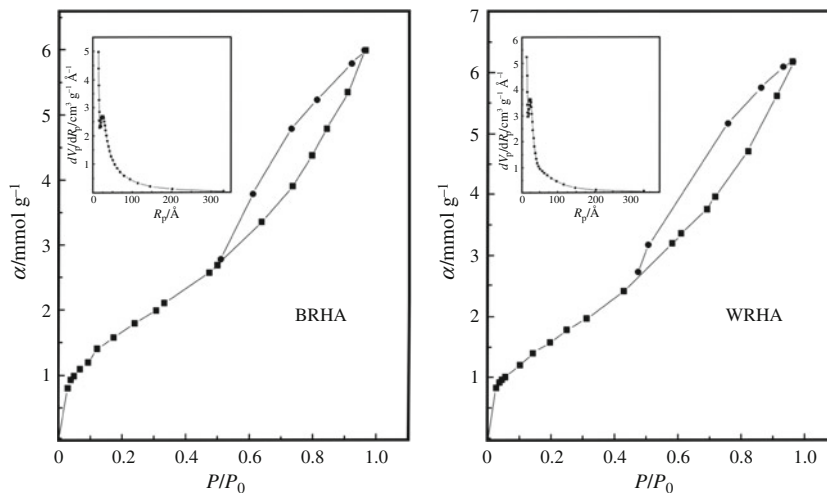
The kinetics curves of adsorption of diesel fuel at 298 K onto BRHA and WRHA are presented in Fig. 5.

As can be seen from Fig. 5, the adsorption process occurred very fast on both adsorbents to reach adsorption equilibrium for about 2–3 min. It should be noted that both
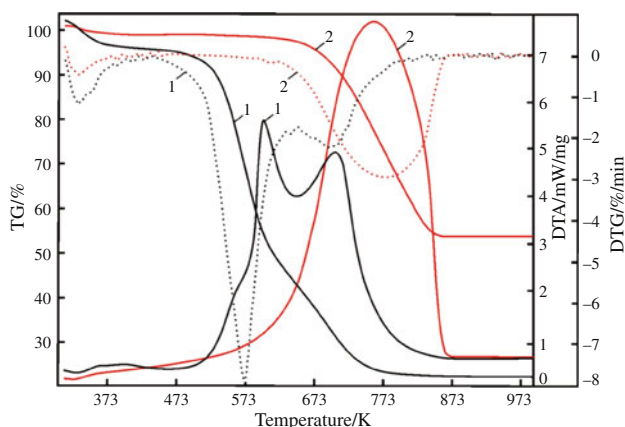
Fig. 4 Adsorption–desorption isotherms of BRHA and WRHA and pore size distribution curves
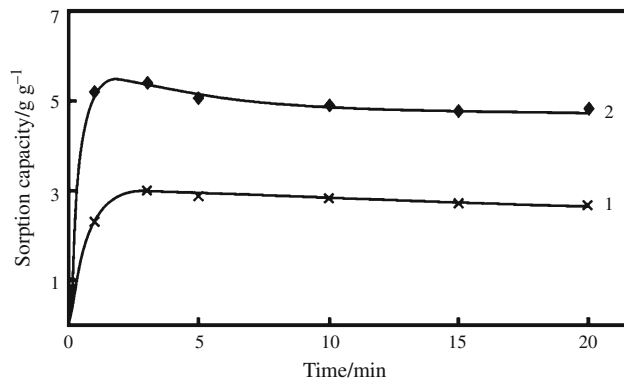
curves have weak local maximum at the beginning of the process. This rapid and exalted adsorption at the beginning of the process was attributed to the strong non-compensated forces on adsorbent pure surface [34] which provoke selective adsorption of some of the diesel fuel components. Further on, some rearrangements take place and thermodynamic equilibrium is established between the adsorbate and the adsorbent. The equilibrium sorption capacity of diesel fuel onto BRHA was estimated to be about 5 g/g, while onto WRHA it was only 2.8 g/g. Understandably, since BRHA surface is non-polar and that of WRHA is polar, the curve representing the adsorption of diesel fuel onto BRHA was above that for WRHA, as the main components of diesel fuel have non-polar molecules. A confirmation of the discussion above were the kinetic curves of adsorption of water onto BRHA and WRHA at 298 K presented in Fig. 6.

As can be seen from Fig. 6 the kinetic curve of water adsorption onto WRHA is above that for BRHA which means that the BRHA surface is indeed hydrophobic and, therefore, it would adsorb predominantly the non-polar hydrocarbon molecules contained in crude oil and diesel fuel. While thermodynamic equilibrium of water adsorption onto WRHA was reached in quite short period (after about 2 min), for BRHA it was reached after about 10 min. Besides, the maximal adsorption capacity of BRHA turned

out to be nearly 3 times lower than that of WRHA. The lower water adsorption capacity of BRHA was the reason for preferring it as adsorbent for collecting spills of oil and oil products. In practical, since crude oil is most often spilled, the kinetic curves of adsorption of diesel fuel and crude oil by BRHA are shown in Fig. 7 for comparison.

The kinetic curves, presented in Fig. 7 showed that the adsorption capacity of BRHA is higher for crude oil than for diesel fuel. The reason for this tendency is the fact, that crude oil contains more hydrocarbons of high molecular weight than diesel fuel. The results obtained from our study showed that the BRHA may be used as an effective adsorbent for oil or oil products. The temperature dependence of the sorption capacity of diesel fuel onto BRHA may be assessed from Fig. 8.

As can be seen from Fig. 8, the amount of diesel fuel sorbed onto BRHA gradually decreased with the increase of temperature. This can be interpreted as a proof that diesel fuel was sorbed physically onto BRHA, i.e., the process is exothermic. It should be noted also that the local

Table 1 Physicochemical characteristics of the RRH, WRHA, BRHA, and AR

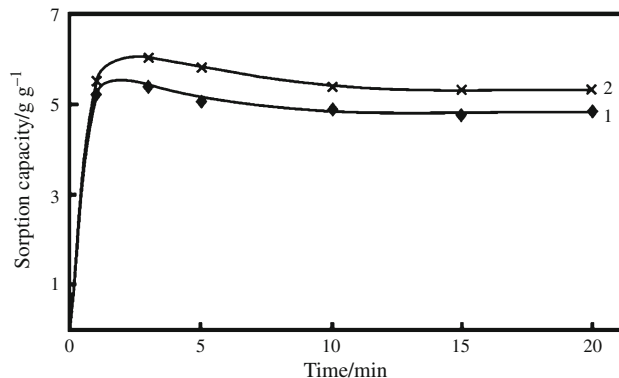| Parameter	RRH	WRHA	BRHA	AR
SiO_2/mass%	20.2	94.2	54.0	100
Moisture/mass%	7.1	0.8	0.6	–
Mean particle size/μm	800	15	20	5
Surface area/m^2 g^{-1}	<1	228	241	273
True density/g cm^{-3}	1.47	2.2	1.8	2.2
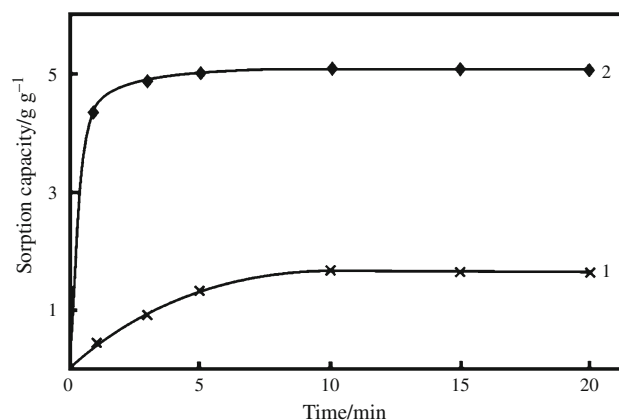
Fig. 6 Kinetic curves of adsorption of water onto BRHA (*1*) and WRHA (*2*)

Fig. 5 Kinetic curves of adsorption of diesel fuel onto WRHA (*1*) and BRHA (*2*)

Fig. 7 Effect of time contact between BRHA and diesel fuel (*1*) and crude oil (*2*)
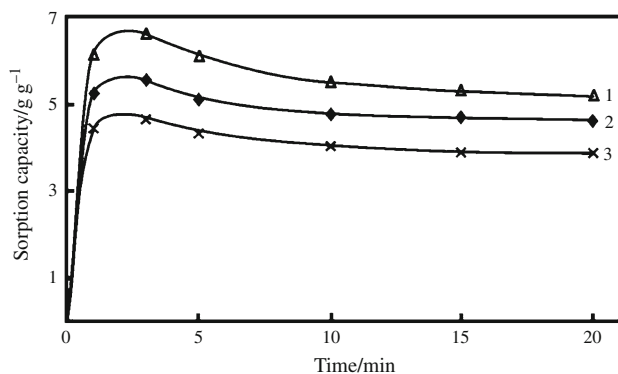
Fig. 8 Kinetic curves of adsorption of diesel fuel onto BRHA at: *1* 288, *2* 293 and *3* 298 K

Table 2 Sorption capacity of BRHA and WRHA at 298 K

Sorbate	Boiling point, T/K	BRHA, α/g g^{-1}	WRHA, α/g g^{-1}
Water	373	0.82	1.23
Benzene	353	2.15	1.32
Toluene	383	2.78	1.82
n-Octane	399	3.38	2.86
m-Xylene	411	3.58	3.12
Diesel fuel	–	5.02	2.78
Crude oil	–	6.22	2.98

maximum shifts the left hand side with the increase of temperature while it is height decreases. The reason for this behavior is faster rearrangement of the sorbed hydrocarbon molecules sorbed from the multicomponent system and the establishment of equilibrium between the adsorbate and the adsorbent. Considering the hydrophobicity of BRHA and the practical unmixability of crude oil and the oil products with water, was established that BRHA floats over the diesel fuel and adsorbs it without mixing with water. The experiments showed that the adsorption of water under these conditions is very slow and it took 10–12 days for the adsorbent to become saturated, grow heavier and precipitate spontaneously to the bottom leaving the water surface clear of diesel fuel. This observation indicates that crude oil or oil products spilled in open basins can be cleaned up using BRHA as collector. Besides, there are two methods which can be applied—leave the sorbent to become saturated and settle down to the bottom where the petroleum products can be degraded naturally by aerobic and anaerobic bacteria or collect the material after certain period from the surface and dry it. The material will be highly caloric and can be burnt in industrial ovens or steam generators to attain double effect—ecologic and economical. Since the bilge waters content different hydrocarbons, we have studied sorption capacity of some of them on BRHA and WRHA, respectively. In Table 2 for comparison are presented the maximal sorption capacity of BRHA and WRHA for these compounds at 298 K.

As can be seen from Table 2 the sorption capacity of water for BRHA is less than those of WRHA, because BRHA is more hydrophobic. In all cases sorption capacity of BRHA concerning studied hydrocarbons, diesel fuel and crude oil is higher than those of WRHA. This tendency may be explained with the non-polar character of surface of BRHA. Moreover, there is a clear dependence between sorption capacity of hydrocarbons and it is boiling point. Based of the presented results may be concluded, that BRHA is more appropriate adsorbent for cleaning of bilge

water from crude oil and different hydrocarbons. Because the saturated BRHA with these hydrocarbons are characterized with high calorific value, they can be burnt in incinerators, industrial ovens or steam generators. By this way, we attain double effect not only ecological but also economical.

Conclusions

This study was an attempt to establish the possibilities to obtain BRHA and WRHA via pyrolysis of raw rice husks in a pilot plant fluidized bed reactor at different conditions. The products obtained were used as an adsorbent for purification of crude oil and diesel fuel from water surfaces and for cleaning of bilge water. The results showed that BRHA has high adsorption capacity and low cost and may successfully be used as an effective sorbent for purification of crude oil or oil products spilled in water basins or bilge water. The saturated BRHA with crude oil, diesel fuel, or different hydrocarbons are characterized with high calorific value and they can be burnt in incinerators, industrial ovens or steam generators. By this way, we attain not only ecological but also economical effect.

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