Carbon based nanocomposite material for CO_2 capture technology

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ABSTRACT

Carbon capture and sequestration contains a group of technologies keeping the differentiation of CO_2 from large industrial and energy related sources, transport to a storage location and long-term isolation from the atmosphere. Previous studies of CO_2 adsorption on low-cost iron metal oxide surfaces strongly encourage the possible use of metal oxide as sorbents, but the tendency of magnetite particles to agglomerate causes a lowering of CO_2 sorption capacity. This work investigates the adsorption behavior of CO_2 on composite materials prepared coating a low-cost carbonized rice husk (cRH), commercial carbon black (CB) with magnetite fine particles. The CO_2 capture capacity of composites and based on rice husk materials was evaluated the basis of the breakthrough times measured at atmospheric pressure and room temperature in a lab-scale fixed bed micro-reactor. To this aim the reactor has been firstly operated for CO_2 adsorption data with obtained samples.

Keywords: Rice husk, Carbon black, Solid sorbent, CO_2 capture, Magnetite, Carbon-based composite, Fixed bed.

Introduction

After discovery high surface area, good porosity and mainly low-cost of carbonized biomasses, they become good candidates for supporting CO_2 capture and sequestration technology (CCS). CCS embodies a group of technologies containing the separation of CO_2 from huge industrial and point energy sources, transport to a storage location and long-term segregation from the ambient air. There are main three methods available for CCS technologies: post-combustion capture, pre-combustion capture and oxy-fuel combustion. Post-combustion is the most advantageous near-term CO_2 capture strategy, because it does not imply substantial modifications to the combustion process technologies currently used [1-6]. Using of solid sorbents offers a remarkable advantage over the other separation approaches because it offers selectivity, great capacity, reduced energy for regeneration. M. Zhu, G. Diao reported that performances of the solid sorbents toward CO_2 absorption are often studied at high pressures [7]. It was found that materials with a large capacity for CO_2 uptake at high pressure often do not perform well at low pressure and in particular it was established processes at low pressure (post-combustion conditions 1 bar and CO_2 10–15% vol.)

The CO_2 uptake capacity is influenced primarily by functionality effects rather than pore metrics. New materials with uncommon surface chemistry could find large applications in adsorption processes. Recent studies of CO_2 adsorption on low-cost hydroxylated metal oxide surfaces strongly encourage the possible use of metal oxide as sorbents [8–12]. Rice husk (RH) is a green material that has a great potential for technological applications since it can be converted to different types of fuels and chemical feedstocks through a variety of thermochemical conversion processes. Rice husks – is the outer shell of rice kernels that protects the internal components from external attacks of insects and bacteria, but also RH need to let in air and moisture for the growth of corn. Due this function, rice in the process of natural evolution has created in its husk unique nanoporous layers [13].

The adsorption properties of carbonized rice husk is interesting research subject in industrial and environmental context. Annually produced about 200 million tons of rice husk in the all rice producing countries. Kazakhstan – one of rice produced country, in our country grows more than 470 thousand tons of unmanufactured rice per year. Twenty percent of this value is residue – rice husk. The production of adsorbent materials on the base of the rice husk can solve two environmental problems: utilization of agricultural wastes and use it for CO_2 capture [14]. There are many

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studies of carbonized rice husk used for waste water remediation, also have a lot of adsorbent for oil products and blood. In this work we investigate adsorption behavior of composite materials based on rice husk and magnetite for CO_2 capture, compare that result with following the same approach presented in previous works on the CO_2 capture performances of FM loaded on a carbon-based reference material (carbon black) [15], also we investigate rice husk without magnetite in different condition for CO_2 capture.

Experimental part

2.1 Used materials

Carbonization process of raw RH was going on in auger furnace shown below with 500-800° temperature for 3 h [16]. Finished material-carbonized rice husk (cRH)- was taken from Innovative Enterprises "Zhalyn" in Almaty, Kazakhstan.

Installation Capacity:

- For the final product: more than 50 kg/day
- On the feedstock (humidity less than 100%) 150-160 kg/day
- Degree of processing of the carbonaceous raw material 80-85%
- Degree of purification of exhaust gas is not less than 98%
- Consumption of blow water (running or reverse) 5 l/h
- Flow activator (air) 0,005 m^3/kg
- The installed capacity of not more than 90 kW
- Power ~ 50 Hz, 380 V

CB N110 type (furnace CB) was obtained by Phillips Petroleum Co. Its density at 25 ºC is 1.8 g mL^{-1}, and the surface area (SA) is 143 m^2 g^{-1}. CB is a monodispersion of chain-like aggregates of spherical primary particles with average diameters of 15–20 nm [17]. All agents were used from Sigma–Aldrich, were analytical reagent grade and used as received.

2.2 Preparation of the samples

Five different cRH-magnetite composites and five CB–magnetite composites were produced by varying the amount of cRH/CB (0.10 g for cRH/CB–FM-1, 0.35 g for cRH/CBFM-2, 0.60 g for cRH/CB–FM-3, 0.90 g for cRH/CB-FM-4 and 1.2 g for cRH/CBFM-5). These composites were produced adapting the co-precipitation strategy reported by Luo [18]. Briefly, material (cRH or CB) was suspended into 200 mL of de-ionized water by sonication for 20 min and then 50 mL aqueous solution of $FeCl_3*6H_2O$ (1.4 g) and $FeSO_4*7H_2O$ (0.70 g) was added. The mixture was kept at 30 ºC for 30 min under stirring. After that, 10 mL 28% ammonia solution was added in order to adjust the pH at 10. The mixture was kept for 1 h at 90 ºC under stirring. The workup of the cRH-NH_4OH and cRH-NaOH samples preparation produced without adding FM.

2.3 CO_2 adsorption tests

For test CO_2 adsorption used fixed bed (shown below in Fig. 2) with CO_2/N_2 gas mixture (15 Nl/h) at a fixed CO_2 concentration (3% vol), operating under atmospheric pressure. The CO_2 concentration in the inlet and outlet gas streams has been measured by online continuous ABB infrared gas analyzer.

Process of preparing 5 different composite material based on cRH or CB and magnetite was described in previous work previous work, cRH was used instead reference material carbon black (CB) [15]. A set of RH/FM composites were produced by varying the amount of carbonized RH from 20 to 80 wt.% in order to optimize the sorbent properties for CO_2 adsorption applications[15].

Fig. 1. View of auger furnace for carbonization raw rice husk [16].

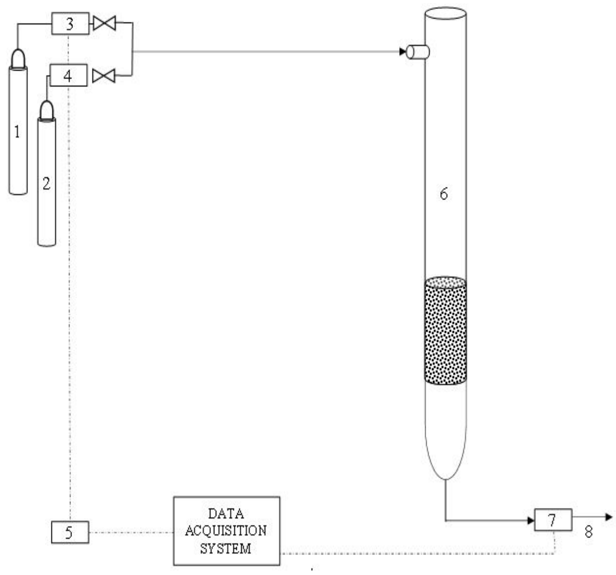

Fig. 2. Experimental apparatus: 1) N_2 cylinder; 2) CO_2 cylinder; 3) N_2 flow meter; 4) CO_2 flow meter; 5) multichannel control instrument; 6) 10 mm ID fixed bed reactor; 7) CO_2 analyzer; 8) stack

Table 1
Content of cRH and magnetite in samples

Sample	cRH,wt.%	FM, wt.%
cRH/FM-1	14,3	52,6
cRH/FM-2	36,8	39,9
cRH/FM-3	50	28,3
cRH/FM-4	60	23,3
cRH/FM-5	66,7	18,8
cRH-NH_4OH	100	0
cRH-NaOH	100	0

Also like this technology we prepare 2 sample with only cRH in presence at first NH_4OH, at second NaOH. We obtain 7 samples (Table 1): cRH/FM-1, cRH/FM-2, cRH/FM-3, cRH/FM-4, cRH/FM-5, cRH-NH_4OH, cRH-NaOH.

Results and discussion

cRH features presented at the Fig. 2 show good porosity and developed surface area (SEM) and contain about 66.09% of carbon (EDAX) (was investigated in Nanolaboratory, al-Farabi Kazakh National University, Almaty, Kazakhstan), cRH have amorphous structure with crystalline includes (XRD) (was investigated in Institute of Research Combustion, Napoli, Italy). Due to contain of silica (13.36%) rice husk can be saved for long time, without decay and that reason make cRH unique carbon material.

Magnetite (Fe_3O_4, FM) and CO_2 interaction proceeds through acid–base interactions involving unsaturated metal and O sites exposed on FM surface [15]. The FM sorption capacity is lowered by the tendency of magnetite particles to agglomerate that lowers the exposed surface area. The dispersion of magnetic particles on carbon-based solid matrices has been proposed to face this limitation [19].

Preliminary results (Table 2) performed amount of absorbed CO_2 and time need for saturation of the samples. As we can see composite material RH/FM don't show best result like it be with reference materials CB (CB/FM-3 mads = 16.5) (Table 3). The highest result we get from samples only with rice husk (without magnetite) after treatments NaOH and NH_4OH. Also with samples cRH-NH4OH and cRH-NaOH increased saturation time of sorbent, 21 s and 13 s accordantly.

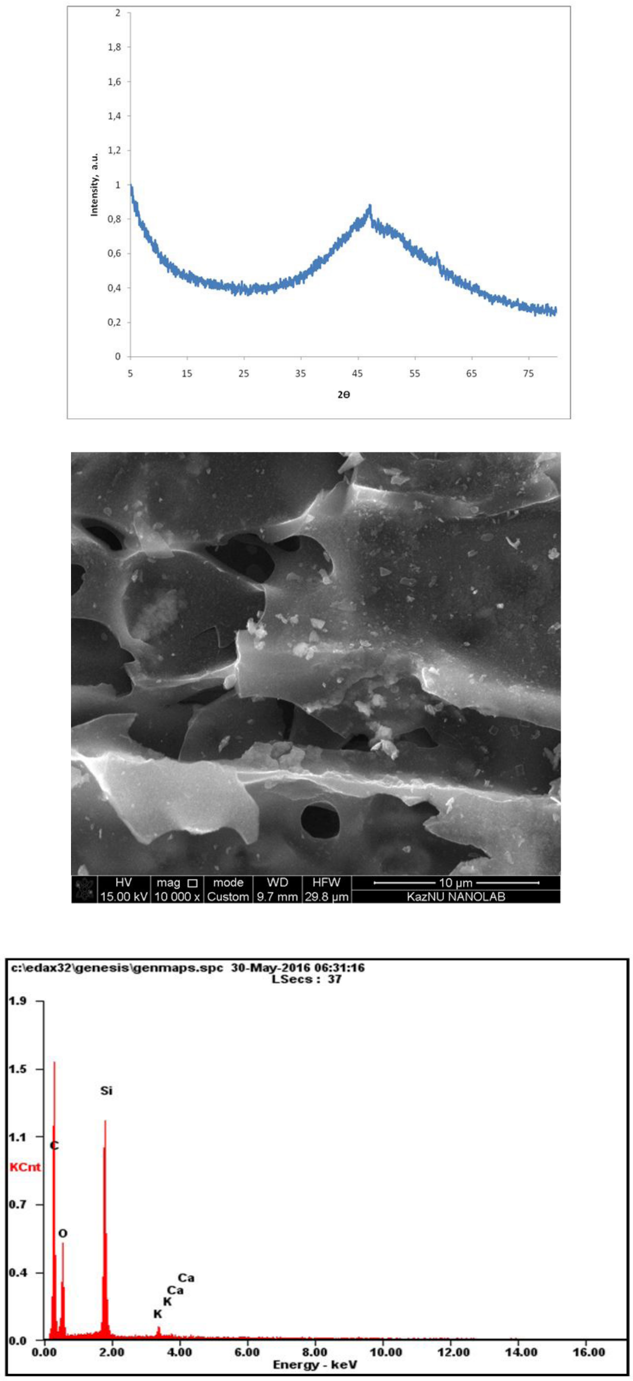

Fig. 3. Physicochemical properties of carbonized rice husk (XRD, SEM and EDAX)

Table 2
CO_2 adsorption tests results

Sample	m_{ads} ($mgCO_2/g$)	t_b (s)
FM	10.87	4
cRH	11.26	8
cRH/FM-1	8.39	4
cRH/FM-2	12.00	7
cRH/FM-3	8.87	4
cRH/FM-4	7.43	4
cRH/FM-5	7.38	3
cRH-NH_4OH	29.23	21
cRH-NaOH	21.88	13

Table 3
CO_2 adsorption tests results with carbon black [4]

Sample	m_{ads} ($mgCO_2/g$)	t_b (s)
FM	10.6	3
CB	6.5	13
CB/FM-1	11.1	15
CB/FM-2	16.1	25
CB/FM-3	16.5	24
CB/FM-4	14.9	27
CB/FM-5	7.2	3

The increase of sorption capacity in samples with cRH is primarily due to the fact that the silica is washed out, as well as possible, so that the elemental carbon content increases more than 80% after the leaching process (Table 4).

Conclusion

Carbon dioxide capture testing results with adsorbent obtained from RH get a good possibility to be investigate as a new interesting material in this area. Sorption capacity showed approximately more than 10 $mgCO_2/g$ performance. Also that efficiency opens up the possibility to widely use and study derived biomass as a low cost materials for CO_2 capture. Unlike of CB, composite materials based on cRH and FM showed decreased sorption capacity than pure cRH. But samples treated by NH_4OH and NaOH performed excellent characteristic of CO_2 adsorption, enhanced more than 77% and 32% respectively.

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Table 4
Elemental analysis of cRH-NH_4OH and cRH-NaOH CO_2 sorbents

Element (wt.%) / Sorbent	C	O	Si	Ca	Mg	Fe	Cu	Other
cRH-NH_4OH	81.48	13.19	4.49	0.28	0.25	0.13	0.12	0.05
cRH-NaOH	87.44	8.29	2.05	0.44	0.35	0.27	0.34	0.82

Нанокомпозитный материал на основе углерода для технологии улавливания CO_2

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АННОТАЦИЯ

Улавливание и секвестрация углерода содержит группу технологий, обеспечивающих дифференциацию CO_2 из крупных промышленных и энергетических источников и транспортировку к месту хранения в долгосрочную изоляцию от атмосферы. Предыдущие исследования адсорбции CO_2 на недорогих поверхностях из оксида металла железа настоятельно рекомендовали возможное использование оксида металла в качестве сорбентов, но склонность частиц магнетита к агломерации вызывает снижение способности к сорбции CO_2. В данной работе исследуется адсорбционное поведение CO_2 на композиционных материалах, приготовленных с покрытием из дешевой карбонизированной рисовой шелухи (cRH), технической сажи (CB) с мелкими частицами магнетита. Способность улавливать CO_2 композитными материалами на основе рисовой шелухи оценивали с помощью времени прорыва, измеренного при атмосферном давлении и комнатной температуре в лабораторном микрореакторе с неподвижным статическим слоем. С этой целью данный реактор впервые эксплуатировался для определения сорбционной способности по диоксиду углерода с полученными образцами.

Ключевые слова: рисовая шелуха; техническая сажа; твердый сорбент; улавливание CO_2; магнетит; композит на основе углерода; статический слой.

CO_2-ні аулау технологиясына арналған көміртек негізіндегі нанокомпозитті материал

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АҢДАТПА

CO_2-ні ірі өндірістік және энергетикалық көздерінен дифференциясын қамтамасыз етіп, атмосферадан ұзақ уақыт изоляциялануын қамтамасыз ететін сақтау орнына транспорттау технологиясы дамуда. Бұрын жарияланған CO_2-нің қымбат емес темір оксиді бетіне адсорбциясы жөніндегі зерттеулер металл оксидінің сорбент ретінде қолданылуын ұсынды. Бірақ магнетит бөлшектерінің агломерацияға бейімдігі CO_2 сорбциясына қабілетін төмендетеді. Берілген жұмыста CO_2-нің, арзан карбонизацияланған күріш қауызынан, техникалық күйеден, магнетиттің ұсақ бөлшектерімен алынған композициялық материалдарға адсорбциондық қабілеті зерттелген. Күріш қауызы негізіндегі композициялық материалдармен CO_2 аулау қабілетін атмосфералық қысымда және бөлме температурасында лабораториялық микрореакторда өлшенген уақыт айырмашылығымен зерттелінді. Осы мақсатта берілген реактор көміртек диоксидін, алынған үлгілермен сорциялық қасиетін анықтау үшін бірінші рет қолданылды.

Кілттік сөздер: күріш қауызы, техникалық күйе, қатты сорбент, CO_2 аулау, магнетит, көміртек негізіндегі композит, статикалық қабат.