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A Feasibility Study of Synthesizing Zeolitic Material from Locally Available Waste Materials

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Abstract

The increasing ingestion of rice and use of coal in coal based power plant in Bangladesh have been producing rice husk ash (RHA), rice straw ash (RSA) and coal fly ash (FA) as byproducts in a massive amount. The current energy scenario of our country is resulting in a sustainable increase in the FA generation, whose proper management has become a cause of concern. Similarly, Bangladesh annually produces millions of tons of rice husk (RH) and rice straw (RS) after milling of the paddy, which produces ash in high amount after being used as a fuel in rural areas. All these ashes currently have limited or no use. Producing a micro porous solid acid adsorbent catalyst (Zeolite) from these locally available alternative sources would be a smart approach of waste utilization. This study is focused on the suitability of synthesizing certain types of low cost zeolite from these waste ash materials. The Si/Al ratio of FA, RHA and RSA is 1.96, 200.54 and 156.35 respectively, which is suitable for Zeolite synthesis. FA having higher (27.33%) alumina content needs only NaOH but RSA, RHA and FSA (0.35%, 0.37%, 6.5% alumina) needs also $NaAlO_2$ for zeolite preparation. This study also suggested a probable breakthrough in finding the feasibility of fecal sludge (human waste) ash (FSA) as a raw material in the synthesis of zeolites.

Keywords: Zeolite, Synthesis, Feasibility, Coal fly ash, Rice husk ash, Fecal Sludge ash, Bangladesh.

1. Introduction

The rapidly growing energy sector in Bangladesh has prompted increased consumption of coal to meet the demand. Due to the current energy policy [1], more coal based power plant will emerge in the near future. Fly ash (FA) is a byproduct of power generation from pulverized coal combustion. Barapukuria coal fired thermal power plant is now the only FA producing facility in the country. At present, there are few more public and private sector coal-fired power plants in the planning, implementation and construction phases. The projected annual production of FA will rise to 3.77 million tonnes per annum from 2018 onwards occupying nearly 0.27 million m^3 under loose condition [1]. FA is mostly used is cement industries. The other usage of FA is in landfilling, roads and embankments, brick manufacturing etc. Only a small portion of the current FA production is utilized and hence management of FA is going to be a challenge for the coal-based power plants. As alumina and silica are the major components of FA, a highly potential use of it is to produce zeolite, a valuable solid acid catalyst.

Bangladesh also has a vast amount of accessible and non-accessible biomass energy sources i.e. crop residues. The total supply of biomass fuel was 236 PJ in 1980 and has increased over the next 20 years to 360 PJ (1.73% growth) [2]. RH contributes the biggest share of biomass energy. In 1991, the production of RH energy was 76PJ and it increased to 106PJ in 2004 [2]. The RH is generally used as fuel in rural areas and a small quantity is used as animal feed. Large quantity of rice husk ash (RHA) is generated in Bangladesh during per-boiling of rice in rice mills. This ash, treated as a waste material, is usually dumped freely causing unanticipated environmental and health hazards. In Bangladesh, about 39.3 million ton of rice is produced annually which generate about 9.83 million tonnes of RH after milling of the paddy [3]. Assuming an ash to husk ratio of 18%, 1151.1 thousand tonnes of RHA is produced per annum in Bangladesh [4]. No planned efforts have yet been made for proper management of RH/RS or RHA/RSA on a commercial basis.

Recent experiments on fecal sludge (FS) have revealed its usefulness as a fuel source [5]. Ash from FS (FSA) has also been proved a good candidate as a raw material for synthesizing zeolite because of having nearly same chemical composition like FA/RHA/RSA.

As proper management of the mentioned waste ash materials has become an issue, an attempt has been made in this study to find out the suitability of these locally available waste materials in synthesis of valuable zeolitic materials in perspective of Bangladesh.

2. Materials and Method

FA was collected from the ESP (Electrostatic Precipitator) of 250 MW Barapukuria coal-fired thermal power plant of BPDB (Bangladesh Power Development Board) located at Dudhipur, Dinajpur. The power plant used coal from Barapukuria Coal Mining Company Limited (BCMCL). RH and RS were collected from rural areas of Comilla district. Treated FS was collected from a research team under IRC Water and Sanitation Centre and BRAC WASH program focusing on feasible and sustainable approach of FS management in Bangladesh, which was pre-treated by drying (sand-bed drying/bio drying) and post-treated by co-composting method [5].

Proximate analysis of all the raw materials was done for their characterization. RH was taken in a porcelain crucible and heated in an electric muffle furnace at 550°C for ~4 hours to get RHA. From the difference of the weight of RH and RHA, the ash% of RH was measured. RSA was produced similarly by combustion at 600°C and came out along with some black unburnt particles. So, it was further heated at higher temperature (~700-750°C) to ensure the complete conversion of ash. Ash% of RS was calculated similarly. For making FSA from treated FS, method similar to RHA was followed (5 hour at 550°C and ash% was calculated. Moisture content of RH, RS was measured by finding the weight differences of the samples before and after keeping them in a dryer at 105-110°C for 4-5 hours in Petri dishes in single layer. For measurement of %volatile matter (in wet basis), RH/RS was taken in four identical (but somewhat different in weight) fused silica crucibles and burnt at 900°C for 7 minutes and then the weight difference before and after burning was measured. Volatile % in dry basis was calculated for each sample by subtracting the % moisture from volatile% in dry basis.

Chemical compositions of the ash samples was analysed by sequential X-ray fluorescence (XRF) spectrometer-1800. A high energy incident X-ray is collided with the atom of sample in a XRF and it produces energy as electron moves between levels and from this, the chemical composition of a sample is analysed. For XRF analysis, the ash samples were first grinded, mixed with a binder and pelletized for convenience.

3. Results and Discussion

The proximate analyses of coal, RH, RS and treated FS, are shown in Table 1. As shown in the table, as the primary raw material FS would be a good choice rather than others because it has the highest ash content (69.34%) where RH/RS/Coal has similar ash content (~13-14%). Coal has the lowest volatile content% (30.69%) where RH and RS have much higher values (65.85% and 68.29% respectively). Moisture content is low in amount for RH and RS and is absent in coal in dry basis. Also, it is evident that coal has the highest FC% (54.57%) whereas RH/RS has very lower values (14.30% and 14.45% respectively).

Table 1. Proximate analysis Coal, Rice Husk, Rice Straw and Treated Fecal Sludge (dry basis) sample

Component	Ash Content (%)	Volatile Content (%)	Moisture Content (%)	Fixed Carbon (%)
Coal	14.74	30.69	-	54.57
Rice Husk	14.08	65.85	5.77	14.30
Rice Straw	13.41	68.29	3.85	14.45
Treated Fecal Sludge	69.34	*ND*	*ND*	*ND*

* *ND= Not determined*

Table 2. Chemical Composition of Ash Samples (FA, RHA, RSA, FSA)

Constituents	% composition by weight			
	FA	RHA	RSA	FSA
SiO_2	61.04	79.50	65.33	69.35
P_2O_5	0.69	10.19	2.27	4.01
K_2O	1.34	4.37	16.83	3.03
MgO	0.31	3.76	4.31	1.62
CaO	0.83	1.00	5.08	3.77
Al_2O_3	27.33	0.35	0.37	6.50
Fe_2O_3	2.93	0.32	0.64	3.35
SO_3	0.55	0.26	1.87	6.40
Na_2O	0.21	0.18	3.22	1.29
TiO_2	4.78	0.07	0.09	0.67

Table 2 shows the compositions of ash samples. From the XRF analysis, FA has the highest Al_2O_3% (27.33%) yielding the lowest Si/Al of all the samples (1.96). On the other hand, RHA, RSA and FSA has much higher Si/Al ratio (0.35%, 0.37% and 6.5% Al_2O_3 respectively), which can be attributed to lower amount of Al_2O_3% in these samples. There are impurities in the ash samples (oxides other than silica and alumina) which need to be removed. Removal of impurities, prior to zeolite synthesis, can be done by acid treating the samples, as oxides other than silica and alumina dissolves in acid. These impurities are low in FA (11.64 wt. %) and are higher in RSA (34.31%) whereas FSA and RHA have 24.154% and 20.15 % impurities, respectively. Also, it is evident that FSA contains oxides similar to FA/RHA/RSA with some slight exceptions in mass fractions of certain oxides. Other than this, FSA is nothing but a waste material which is rich in silica (also has a favourable high ash content) and could be a potential candidate as a raw material for synthesis of zeolites.

Zeolites are actually crystalline aluminosilicates that consist of a tetrahedral framework of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$, linked each other with the corners by sharing oxygen atoms.

Composition of zeolite:

$$M_xD_y\,[Al_{x+2y}Si_{n-(x+2y)}\,O_{2n}].\,mH_2O$$

Where,

M = monovalent cation, D = divalent cations, m = number of water molecules per unit cell, x = numbers of cations (Monovalent), y = number of cations (Divalent). [6]

Zeolites have a wide range of industrial applications, e.g. - in ion exchange, as molecular sieves, catalysts, and adsorbents [7]. FA, RHA, RSA all have the potential to be converted into zeolites. The most important use of zeolites is catalysis, for several important reactions such as cracking, isomerization and hydrocarbon synthesis. The other importance of zeolites include gas separation by adsorption (the porous structure of zeolites can be used to 'sieve' molecules having certain dimensions and allow them to enter the pores; also known as "molecular sieve") and ion exchange (applications in water softening devices, in detergents and soaps, also it is possible to remove radioactive ions from contaminated water) [8]. Depending on the chemical composition (e.g. - final Si/Al ratio) and crystal structure, zeolites can be of many different types.

From the study it can be seen that the initial Si/Al ratio is 1.96 for the given coal FA sample which is somewhat close (1.57) to the FA used for preparing zeolite described by Kondru *et al.* and could be used to make Na-Y type zeolite [9]. The composition of RHA and RSA is also compatible for synthesizing Na-Y zeolite by the method described by Jan-Jezreel and Rizalinda, 2011 [10] and the initial Si/Al ratio (200.54 for RHA, 156.35 for RSA) of the samples of this study also supports this fact. As the alumina content is in an appreciable amount (27.33%) in FA, zeolites can be produced through fusing the ash only with NaOH followed by hydrothermal crystallization. But due to lower initial Si/Al ratio in RHA/RSA/FSA (0.35%, 0.37%, 6.5% alumina respectively) samples, $NaAlO_2$ solution is needed in these cases to balance the final Si/Al ratio in the synthesized zeolite. FSA sample, which contains initial Si/Al ratio of 9.4, would need $NaAlO_2$ much less than RHA/RSA.

3.1 Proposed preparation techniques

Ash samples were pre-treated before synthesizing zeolites. FA was first sieved and calcined at 800°C for 2 hours before acid treatment. Ashes was treated with 10% H_2SO_4 and kept for 24 hours before washing with excessive water and filtering by vacuum filtration. Filtered ashes were dried at 105°C for ~4 hours and later, stored in a desiccator.

Figure 1 shows the general procedure for zeolite synthesis from waste ash materials.

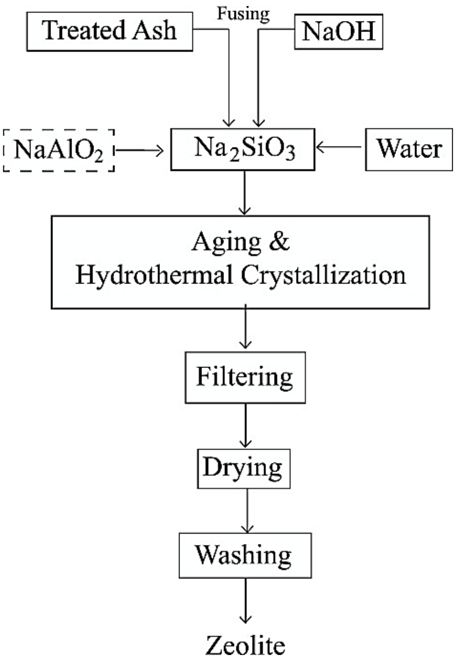

Fig. 1. General preparation technique for Zeolite synthesis ($NaAlO_2$ have to be added for RHA/RSA/FSA)

For zeolite synthesis FA would have to be added, mixed, grinded and fused with NaOH (alkali source) and then mixed with distilled water. Then the slurry sodium aluminate solution would have to be aged and hydrothermally crystallized (without disturbance) which would yield the final product after filtering, washing and drying.

For preparing zeolite from RHA/RSA, first, extraction of silica from the ashes would have to be done by refluxing with acid solution, washing, drying and finally through calcination. Then rice husk ash silica (RHAS) or rice straw ash silica (RSAS) would have to be dissolved in NaOH solution to produce sodium silicate (Na_2SiO_3) solution, which would be added with $NaAlO_2$ solution to produce a seed gel solution by stirring and aging. The feedstock gel, prepared in the same way as seed gel would have to be instantly mixed into the seed gel under vigorous stirring followed by aging and crystallization to get the final product. Lastly, filtering, washing and drying would have to be done to get the final product.

Zeolite could be synthesized from FSA same as the procedure of RHA/RSA but the ratio in which NaOH and $NaAlO_2$ have to be mixed with FSA would be slight different.

4. Concluding Remarks

FA/RHA has been proved previously by many researchers as a suitable source for synthesizing various types of zeolites. Correspondingly, in this research, locally available FA/RHA has successfully been converted to certain type of zeolite. Synthesizing zeolite from FSA could a major breakthrough. FSA has been found to be a good primary source as it has higher ash content than FA/RHA/RSA. RHA/RSA/FA has similar ash content but the first two has more volatile% with similar moisture%. FA could be the best source for synthesizing certain type zeolite for its lower Si/Al ratio due to higher Al_2O_3%. The other ashes, being the opposite, therefore, would need $NaAlO_2$ for preparing zeolite to gain a certain Si/Al ratio at the end product. The impurities of the ashes are similar in nature but different in mass fractions, which have been suggested to be removed by pre-treatment. Successful conversion of these wastes not only gives a feasible and sustainable approach to waste management of Bangladesh but also brings an economic value by making a valuable adsorbent solid catalyst. Future work by the authors involves characterization and performance evaluation of the produced zeolites.

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