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STUDY OF RICE HUSK ASK (RHA) –BASED SORBENTS FOR SIMULTANEOUS REMOVAL OF SULFUR DIOXIDE SO2 AND NITROGEN OXIDES NOX FROM FLUE GAS

DR. LEE KEAT TEONG

UNIVERSITI SAINS MALAYSIA
KAMPUS KEJURUTERAAN
2008

USM

UNIVERSITI SAINS MALAYSIA

Laporan Akhir Projek Penyelidikan Jangka Pendek

Study of Rice Husk Ash (RHA)-Based Sorbents for Simultaneous Removal of Sulfur Dioxide (SO$_2$) and Nitrogen Oxides (NO$_x$) from Flue Gas

by
Dr. Lee Keat Teong
Prof. Dr. Abdul Rahman Mohamed
Assoc. Prof. Dr. Azlina Harun @ Kamaruddin

UNIVERSITI SAINS MALAYSIA

LAPORAN AKHIR PROJEK PENYELIDIKAN JANGKA PENDEK

Nama Penyelidik

Dr. Lee Keat Teong
Prof. Dr. Abdul Rahman Mohamed
Prof. Madya Dr. Azlina Harun @ Kamaruddin

Tajuk Projek

Study of Rice Husk Ash (RHA)-Based Sorbents for Simultaneous Removal of Sulfur Dioxide (SO₂) and Nitrogen Oxides (NOₓ) From Flue Gas

LAPORAN AKHIR PROJEK PENYELIDIKAN JANGKA *PENDEK*
FINAL REPORT OF SHORT TERM RESEARCH PROJECT

Sila kemukakan laporan akhir ini melalui Jawatankuasa Penyelidikan di Pusat
Pengajian dan Dekan/Pengarah/Ketua Jabatan kepada Pejabat Pelantar Penyelidikan

UNIVERSITI SAINS MALAYSIA

1. **Nama Ketua Penyelidik:**   Dr. Lee Keat Teong
   Name of Research Leader

   ☐ Profesor Madya/   ☑ Dr./   ☐ Encik/Puan/Cik
     Assoc. Prof.   *Dr.*   *Mr/Mrs/Ms*

2. **Pusat Tanggungjawab (PTJ):**   Pusat Pengajian Kejuruteraan Kimia
   School/Department

   > 2 2 JAN 2008
   > **UNIT EITD**
   > Universiti Sains Malaysia

3. **Nama Penyelidik Bersama:**
   Name of Co-Researcher   Prof. Dr. Abdul Rahman Mohamed
                                    Prof. Madya Dr. Azlina Harun @ Kamaruddin

4. **Tajuk Projek:**   Study of Rice Husk Ash (RHA)-Based Sorbents for Simultaneous Removal of
   Title of Project

   Sulfur Dioxide (SO₂) and Nitrogen Oxides (NOₓ) From Flue Gas

5. **Ringkasan Penilaian/***Summary of Assessment***:**

	Tidak Mencukupi / *Inadequate* 1	Boleh Diterima / *Acceptable* 3	Sangat Baik / *Very Good* 4
i) Pencapaian objektif projek: *Achievement of project objectives*	☐ ☐	☐	☐ ☑
ii) Kualiti output: *Quality of outputs*	☐ ☐	☐	☐ ☑
iii) Kualiti impak: *Quality of impacts*	☐ ☐	☐	☐ ☑
iv) Pemindahan teknologi/potensi pengkomersialan: *Technology transfer/commercialization potential*	☐ ☐	☐	☑ ☐
v) Kualiti dan usahasama : *Quality and intensity of collaboration*	☐ ☐	☑	☐ ☐
vi) Penilaian kepentingan secara keseluruhan: *Overall assessment of benefits*	☐ ☐	☐	☐ ☑

6. **Abstrak Penyelidikan**
(Perlu disediakan di antara 100 – 200 perkataan di dalam **Bahasa Malaysia dan Juga Bahasa Inggeris**. Abstrak ini akan dimuatkan dalam Laporan Tahunan Bahagian Penyelidikan & Inovasi sebagai satu cara untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti & masyarakat luar).

Abstract of Research
(An abstract of between 100 and 200 words must be prepared in Bahasa Malaysia and in English).
This abstract will be included in the Annual Report of the Research and Innovation Section at a later date as a means of presenting the project findings of the researcher/s to the University and the community at large).

Penyingkiran gas-gas SO_2 dan NO dari gas serombong tiruan telah dikaji dengan menggunakan bahan penyerap dari bahan dasar abu sekam padi (ASP). Dalam kajian permulaan, bahan penyerap dibuat dari ASP dan CaO menggunakan kaedah hidro-terma telah diuji untuk kemampuan penyerapan SO_2 (KPS) di dalam reaktor palam termampat. Kesan perubahan pelbagai pembolehubah penyediaan bahan penjerap telah dikaji menggunakan perkaedahan permukaan sambutan (RSM). Berdasarkan model yang diterbitkan didapati jisim ASP, jisim CaO dan tempoh penghidratan yang digunakan dalam penyediaan bahan penjerap mempengaruhi KPS bahan penyerap dengan ketara. Untuk meningkatkan lagi KPS bahan penyerap, pelbagai jenis bahan tambah telah digunakan (seperti NaOH, $CaCl_2$, LiCl, $NaHCO_3$, NaBr, $BaCl_2$, KOH, K_2HPO_4, $FeCl_3$ and $MgCl_2$). Kebanyakan bahan tambah yang diuji meningkatkan KPS bahan penyerap ASP/CaO, kerana ia membolehkan penyingkiran SO_2 pada tahap yang lebih tinggi. NaOH didapati adalah bahan tambah yang terbaik diantara bahan tambah lain yang dikaji. Namun, bahan penyerap ini tidak dapat menyingkirkan gas NO. Oleh itu, pengubahsuaian telah dibuat menggunakan kaedah pengisitepuan dengan pelbagai jenis logam-logam oksida. Keputusannya menunjukkan bahawa bahan penyerap ASP/CaO yang telah diisitepu dengan CeO_2 memperlihatkan kemampuan penyerapan yang sangat tinggi terhadap SO_2 dan NO bagi penyingkiran serentak gas-gas SO_2 dan NO. Kajian spektroskopi inframerah menunjukkan pembentukan kedua-dua spesies sulfat (SO_4^{2-}) dan nitrat (NO_3^-); membuktikan penyerapan SO_2 and NO di dalam bahan penyerap.

The removal of SO_2 and NO from simulated flue gas were investigated utilizing rice husk ash (RHA)-based sorbent. In the preliminary study, sorbents were prepared from RHA and CaO using water hydration method and tested for SO_2 sorption capacities (SSC) using fixed bed reactor. The effect of various sorbent preparation variables were examined using response surface methodology (RSM). Based on the model developed, the amount of RHA, amount of CaO and hydration period used in the preparation of sorbent significantly influenced the SSC of the sorbent. To further increase the SSC of the sorbents, different type of additives have been utilized (i.e. NaOH, $CaCl_2$, LiCl, $NaHCO_3$, NaBr, $BaCl_2$, KOH, K_2HPO_4, $FeCl_3$ and $MgCl_2$). Most of the additives tested increased the SSC of RHA/CaO sorbent, because it allows for a higher degree of SO_2 removal. NaOH has been found to be the best additive among all the other additives studied. However, this sorbent was unable to remove NO gases. Therefore, further modification has been made to the sorbent by employing impregnation method with various metal oxides. The results showed that RHA/CaO sorbents impregnated with CeO_2 displayed the highest sorption capacity among other impregnated metal oxides for the simultaneous removal of SO_2 and NO. Infrared spectroscopic results indicate the formation of both sulfate (SO_4^{2-}) and nitrate (NO_3^-) species in the sorbent confirming the sorption of SO_2 and NO.

7. **Sila sediakan laporan teknikal lengkap yang menerangkan keseluruhan projek ini.**
[Sila gunakan kertas berasingan]
Applicant are required to prepare a Comprehensive Technical Report explaining the project.
(This report must be appended separately)

Please refer attachment for Comprehensive Technical Report.

Senaraikan kata kunci yang mencerminkan penyelidikan anda:
List the key words that reflects your research:

Bahasa Malaysia	*Bahasa Inggeris*
Bahan penyerap	Sorbent
Abu sekam padi	Rice husk ash
Kemampuan penyerapan	Sorption capacity
Bahan tambah	Additive
Logam oksida	Metal oxides

8. Output dan Faedah Projek
Output and Benefits of Project

(a) Penerbitan Jurnal
Publication of Journals
(Sila nyatakan jenis, tajuk, pengarang/editor, tahun terbitan dan di mana telah diterbit/diserahkan)
(State type, title, author/editor, publication year and where it has been published/submitted)

Refereed Journal

1. Dahlan, I., Lee, K.T., Kamaruddin, A.H. and Mohamed, A.R. (2006). Key factor in rice husk ash/CaO sorbent for high flue gas desulfurization activity. *Environmental Science & Technology*, Volume 40, Issue 19 : 6032-6037.

2. Dahlan, I., Mohamed, A.R., Kamaruddin, A.H. and Lee, K.T. (2007). Dry SO_2 removal process using calcium/siliceous-based sorbents: Deactivation kinetics based on breakthrough curves. *Chemical Engineering & Technology*, Volume 30, Issue 5: 663 – 666.

3. Dahlan, I., Mohamed, A.R., Kamaruddin, A.H. and Lee, K.T. (2007). Calcium-based with waste-derived siliceous materials as a sorbent for dry-FGD technology: Reactivity and characteristic. *Jurnal REINTEK (Rekayasa Innovasi Teknologi)*, Volume 2, Number 1: 117-120.

Conferences

1. Dahlan, I., Kansedo, J., Lee, K.T., Kamaruddin, A.H. and Mohamed, A.R. (2006). Effect of NaOH on Preparation and sorption capacity of rice husk ash (RHA)/CaO-based sorbents for flue gas desulfurization (FGD) at low temperature. In *Proceedings of the International Conference on Environment (ICENV2006)*, held on November 13-15, in Grand Plaza Parkroyal, Penang, Malaysia (organized by School of Chemical Engineering, Universiti Sains Malaysia), pp. 27.

2. Dahlan, I., Kamaruddin, A.H., Lee, K.T., and Mohamed, A.R. (2007). Effect of various additives on the SO_2 sorption capacities of rice husk ash/lime sorbents for dry-type flue gas desulfurization at low temperature. In *Proceedings of the 12th Asian Chemical Congress (12ACC) - International Symposium on Environmental and Green Chemistry (EGC 2007)*, held on August 23-25, in Putra World Trade Centre, Kuala Lumpur, Malaysia (organized by Institut Kimia Malaysia, IKM), pp.201 (EGC 055)

3. Dahlan, I., Mei, G.M., Lee, K.T., Kamaruddin, A.H., and Mohamed, A.R. (2007). Removal of SO_2/NO_x from flue gas over dry-type sorbent incorporated with metal oxide catalyst – A review. In *Proceedings of the 12th Asian Chemical Congress (12ACC) - International Symposium on Environmental and Green Chemistry (EGC 2007)*, held on August 23-25, in Putra World Trade Centre, Kuala Lumpur, Malaysia (organized by Institut Kimia Malaysia, IKM), pp. 225 (EGC 115).

Others

1. Lee, K.T., Mohamed, A.R., Kamaruddin, A.H., and Dahlan, I. (2007). Rice husk ash-based sorbent/catalyst as a novel industrial gas cleaning technology. *International Exposition of Research and Inventions of Institutions of Higher Learning 2007 (PECIPTA 07)*, held on August 10-12, in Kuala Lumpur Convention Centre (KLCC), Kuala Lumpur, Malaysia (Gold Medal & Minister of Higher Education award for Sustainable Development).

2. Jibrail Kansedo (2006). Study of flue gas desulfurization using adsorbent made from rice husk ash/CaO/NaOH. *Final Year Thesis*, Universiti Sains Malaysia.

3. Gui Meei Mei (2007). Simultaneous removal of SO_2 and NO using impregnated CaO/Rice husk ash sorbent with metal oxide. *Final Year Thesis*, Universiti Sains Malaysia.

(b)   **Faedah-faedah lain seperti perkembangan produk, pengkomersialan produk/pendaftaran paten atau impak kepada dasar dan masyarakat.**
State other benefits such as product development, product commercialisation/patent registration or impact on source and society.

The results from this study showed that sorbent prepared from rice husk ash (RHA) can be utilized to remove SO_2 and NO simultaneously and effectively. Utilization of RHA will definitely bring benefits to the rice mill operators in Malaysia. Apart from solving the disposal problem of RHA by converting RHA into a sorbent that has a high SO_2 and NO_x sorption capacity, it will also convert a waste into a value added products, *i.e.* mainly gypsum, which is a raw material used in the manufacturing of building materials, ceramic products, coagulating agent and even fertilizer. On the other hand, utilization of waste material to synthesize sorbent will eventually reduces the cost of the dry-type FGD technology. With the development of this cheaper and efficient process, it is hope that all industries will implement this technology on their combustion unit, and thus reducing the emission of air pollutants (especially SO_2 and NO_x) to the environment.

* Sila berikan salinan/*Kindly provide copies*

(c)   **Latihan Sumber Manusia**
Training in Human Resources

i)   Pelajar Sarjana:
Graduates Students
(Perincikan nama, ijazah dan status)
(Provide names, degrees and status)

Pelajar Siswazah
1. Irvan Dahlan (P-JD0027) PhD Program, Status: in progress

Pelajar Prasiswazah
1. Jibrail Kansedo (70495) Bachelor Degree, Status: completed
2. Gui Meei Mei (73121) Bachelor Degree, Status: completed
3. Mohd Ashraf Abd Jalil (83824) Bachelor Degree, Status: in progress

ii)   Lain-lain:
Others

9.   **Peralatan yang Telah Dibeli:**
Equipment that has been purchased

None

_____

Tandatangan Penyelidik
Signature of Researcher

28/9/07
_____

Tarikh
Date

Komen Jawatankuasa Penyelidikan Pusat Pengajian/Pusat
Comments by the Research Committees of Schools/Centres

Penyelidikan telah dijalankan dengan jayanya seperti yg terkandung dalam cadangan asal penyelidikan

PROFESOR ABDUL LATIF AHMAD, CEng FIChemE
Dekan
Pusat Pengajian Kejuruteraan Kimia
Kampus Kejuruteraan
Universiti Sains Malaysia, Seri Ampangan
14300 Nibong Tebal, Seberang Perai Selatan
Pulau Pinang.

12/1/08

TANDATANGAN PENGERUSI
JAWATANKUASA PENYELIDIKAN
PUSAT PENGAJIAN/PUSAT
Signature of Chairman
[Research Committee of School/Centre]

Tarikh
Date

304.PJKIMIA.6035192

JUMLAH GERAN :- 18,792.00

NO PROJEK :-

PANEL :- J/PENDEK

PENAJA :- JANGKA PENDEK

UNIVERSITI SAINS MALAYSIA
KAMPUS KEJURUTERAAN
SERI AMPANGAN
PENYATA KUMPULAN WANG

TEMPOH BERAKHIR 31 OGOS 2007

Tempoh Projek:06/01/2006 - 31/05/2008

STUDY OF RISE ASH(RHA)-BASED SORBENTS FOR SIMULTANEOUS REMOVAL OF SULFUR DIOXIDE(

Vot	Peruntukan (a)	Perbelanjaan sehingga 31/12/2006 (b)	Tanggungan semasa 2007 (c)	Perbelanjaan Semasa 2007 (d)	Jumlah Perbelanjaan 2007 (c + d)	Jumlah Perbelanjaan Terkumpul (b+c+d)	Baki Peruntukan Semasa 2007 (a-(b+c+d)
11000 GAJI KAKITANGAN AWAM	4,423.00	0.00	0.00	0.00	0.00	0.00	4,423.00
21000 PERBELANJAAN PERJALANAN DAN SARAHI	800.00	45.40	435.00	413.00	848.00	893.40	(93.40)
23000 PERHUBUNGAN DAN UTILITI	200.00	51.10	0.00	0.00	0.00	51.10	148.90
24000 SEWAAN	1,224.00	0.00	0.00	0.00	0.00	0.00	1,224.00
27000 BEKALAN DAN ALAT PAKAI HABIS	7,896.00	271.65	0.00	8,449.00	8,449.00	8,720.65	(824.65)
28000 PENYELENGGARAAN & PEMBAIKAN KECIL	1,500.00	1,750.00	0.00	0.00	0.00	1,750.00	(250.00)
29000 PERKHIDMATAN IKTISAS & HOSPITALITI	2,749.00	1,298.00	1,110.00	3,770.00	4,880.00	6,178.00	(3,429.00)
	18,792.00	3,416.15	1,545.00	12,632.00	14,177.00	17,593.15	1,198.85
Jumlah Besar	18,792.00	3,416.15	1,545.00	12,632.00	14,177.00	17,593.15	1,198.85

COMPREHENSIVE TECHNICAL REPORT

Comprehensive Technical Report

The main aim of this work is to synthesize a sorbent that can remove simultaneously SO_2 and NO present in the flue gas of industrial combustion system utilizing rice husk ash (RHA). This report consists of three sections; (1) Experimental method, (2) Results & discussion, and (3) Conclusions. The background/ introduction of this study will not be given as this has already been presented in previous research proposal.

1. Experimental Method
This section divided into five sub-sections.

1.1 Sorbent prepared from RHA and CaO

The sorbents were prepared from lime (CaO) and rice husk ash (RHA). The CaO was obtained from BDH Laboratories, England while the RHA was provided by Kilang Beras & Minyak Sin Guan Hup Sdn. Bhd., Nibong Tebal, Malaysia. The RHA used was collected directly after the burning of rice husk without any pre-treatment. However, it was sieved prior to use in order to obtain ash with particle less than 200 μm particle size. The BET specific surface area of RHA and CaO is 56.3 m^2/g and 5.62 m^2/g respectively. The chemical composition of RHA is 68.0% SiO_2, 2.30% K_2O, 1.20% P_2O_5, 0.71% MgO, 0.59% CaO, 0.32% SO_3, 0.32% Cl_2O, 0.16% Al_2O_3, 0.40% others and 26.0% ignition loss (LOI).

The sorbents were prepared using the water hydration method [1]. A specified amount of RHA and CaO were added into 100 ml deionized water which was previously added with (or without) a certain amount of NaOH (according to experimental designs described below). Then the conical flask which contains the mixture (covered with aluminium foil) was inserted into a shaking water bath at 65 °C with a rotating stirring rate of 150 rpm for a specified time. After that, the slurry was then filtered and dried at 150 °C for 2 h. The sorbents were then pelletized, crushed and sieved to obtain the required particle size range of 250-300 μm. The sorbent prepared was then tested for the SO_2 sorption capacity (SSC) by subjecting it to simulated flue gas.

1.1.1. Experimental Design.

Response surface methodology (RSM) was used to study the individual and interaction effects of various sorbent preparation variables (independent variables) towards the desulfurization activity of the sorbent (dependent variables). In this study, a half-fraction five-variable central composite rotatable design (CCRD) with replicate in each point and α = 2 was adopted [2]. Table 1 presents the range and levels of the five sorbent preparation variables studied.

Table 1. Coded and actual values of the variables used in the design of experiment

Variables	Units	Coding	Levels of Variables				
			-2	-1	0	1	2
Hydration period	h	x_1	1	6	11	16	21
Amount of RHA	g	x_2	0	5	10	15	20
Amount of CaO	g	x_3	0	2	4	6	8
Amount of water	ml	x_4	80	90	100	110	120
Hydration temperature	°C	x_5	100	150	200	250	300

In order to use CCRD to study the five sorbent preparation variables, 16 factorial points (A1-A16), 10 axial points (A17-A26) and 6 replicates at the center point (A27-A32) are required for a total of 32 experiments. Table 2 shows the complete experiment design matrix. Six replicate runs at the centre of the design were performed to allow the estimation of pure error. All experiments were carried out in a randomized order to minimize the effect of unexplained variability in the observed responses due to extraneous factors. The data from Table 2 were utilized to develop a correlation between the sorbent preparation variables with its SSC by fitting it to a second order polynomial equation as shown below:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \qquad (1)$$

where Y is the predicted SSC (mg SO_2 captured/g sorbent), b_0 is the offset term (constant), b_i is the linear coefficients, b_{ii} is the quadratic coefficients, b_{ij} is the interaction coefficients, x_i, x_j are the coded values of the various sorbent preparation variables and n is the number of sorbent preparation variables.

Table 2. Experimental Design Matrix and Result of the CCRD

Run (Solid Code)	x_1	x_2	x_3	x_4	x_5	Experimental SSC (mg/g)	Predicted SSC (mg/g)
A1	-1	-1	-1	-1	1	5.15	4.77
A2	1	-1	-1	-1	-1	8.58	8.41
A3	-1	1	-1	-1	-1	7.72	7.41
A4	1	1	-1	-1	1	10.3	9.77
A5	-1	-1	1	-1	-1	6.01	6.05
A6	1	-1	1	-1	1	10.3	10.1
A7	-1	1	1	-1	1	12.0	11.7
A8	1	1	1	-1	-1	15.4	15.3
A9	-1	-1	-1	1	-1	6.01	5.69
A10	1	-1	-1	1	1	8.58	8.05
A11	-1	1	-1	1	1	7.72	7.05
A12	1	1	-1	1	-1	10.3	9.84
A13	-1	-1	1	1	1	6.86	6.55
A14	1	-1	1	1	-1	10.3	10.2
A15	-1	1	1	1	-1	12.0	11.8
A16	1	1	1	1	1	17.2	16.7
A17	-2	0	0	0	0	7.72	8.35
A18	2	0	0	0	0	14.6	15.2
A19	0	-2	0	0	0	6.86	7.20
A20	0	2	0	0	0	13.7	14.6
A21	0	0	-2	0	0	1.72	2.77
A22	0	0	2	0	0	9.44	9.63
A23	0	0	0	-2	0	6.86	7.20
A24	0	0	0	2	0	6.86	7.77
A25	0	0	0	0	-2	7.72	7.92
A26	0	0	0	0	2	6.86	7.92
A27	0	0	0	0	0	6.86	6.94
A28	0	0	0	0	0	6.86	6.94
A29	0	0	0	0	0	7.72	6.94
A30	0	0	0	0	0	6.86	6.94
A31	0	0	0	0	0	6.86	6.94
A32	0	0	0	0	0	7.72	6.94

1.1.2. Statistical Analysis and Model Fitting.

Design Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, USA) was used to develop the mathematical model that correlates the sorbent preparation variables with its SSC based on the data presented in Table 2. The accuracy of the model was evaluated by the coefficient of determination (R^2), lack-of-fit test and analysis of variance (ANOVA), all performed using the Design Expert software.

1.2 Sorbent prepared from RHA (un-treated and pre-treated), CaO & various additives

In the first experiment, the sorbents were prepared using water hydration method [1] by slurrying untreated RHA, CaO and different type of additives based on the optimum hydration conditions reported in the previous experiment. The additives studied are NaOH, $CaCl_2$, LiCl, $NaHCO_3$, NaBr, $BaCl_2$, KOH, K_2HPO_4, $FeCl_3$ and $MgCl_2$.

In the second experiment, the best additive was used in the preparation of sorbent. In this work, the effect of un-treated RHA and pre-treating RHA (by combusting at 600°C) was also investigated using central composite face centered design (CCFCD) with a quadratic model and $\alpha = 1$ coupled with RSM [2]. The un-treated and pre-treated RHA hereinafter is referred to as $RHA_{300\ °C}$ and $RHA_{600\ °C}$, respectively. The pre-treated RHA ($RHA_{600\ °C}$) had the following composition: 89.0% SiO_2, 2.60% K_2O, 1.50% P_2O_5, 0.86% MgO, 0.68% CaO, 0.40% SO_3, 0.26% Cl_2O, 0.21% Al_2O_3, 0.29% others and 4.20% LOI. Four independent variables namely hydration period (x_1), RHA/CaO ratio (x_2), amount of NaOH (x_3) and hydration temperature (x_4) were studied for each type of RHA ($RHA_{300\ °C}$ and $RHA_{600\ °C}$, respectively). Each independent variable was varied at 3 levels represented by -1, 0 and +1. The experimental design in the coded and actual levels of variables is shown in Table 3. A total of 21 different combinations (including five replicates of the center point) were performed for each type of RHA prepared in random order according to the CCFCD configuration as shown in Table 4. Three replications were carried out for all design points except the center point.

Table 3. Coded and actual values of variables employed for CCFCD

Variables	Units	Coding	Levels -1	Levels 0	Levels 1
Hydration Period	h	x_1	4	12	20
RHA/CaO Ratio	g/g	x_2	0.3	1.65	3
Additive Amount	mol/l	x_3	0	0.25	0.5
Hydration Temperature	°C	x_4	150	200	250

The resulting sorbents were tested for SSC and the results are also presented in Table 4. The SSC of sorbents prepared from $RHA_{300\,°C}$ and $RHA_{600\,°C}$ were represented by Y_3 and Y_6, respectively. The data obtained were then fitted to the second-order polynomial equation (1). Again, Design Expert Software was used in this optimization process using the point prediction capability of the software whereby it can predict the experimental variables leading to the synthesis of sorbent with an optimum SSC. Additional experiments were also carried out to verify the predicted optimize conditions.

Table 4. CCFCD matrix of the four variables in coded units with the experimental and predicted values of SSC

Run	x_1	x_2	x_3	x_4	Y_1 ($RHA_{300\,°C}$), mg/g Experimental	Predicted	Y_2 ($RHA_{600\,°C}$), mg/g Experimental	Predicted
D1	1	1	1	-1	13.73	13.74	15.44	15.39
D2	1	1	-1	-1	11.15	11.12	9.44	9.68
D3	1	-1	1	1	12.01	12.02	12.87	12.81
D4	-1	1	-1	1	5.15	5.12	6.86	7.11
D5	1	-1	-1	1	10.30	10.27	7.72	7.96
D6	-1	-1	1	-1	9.44	9.45	10.30	10.24
D7	-1	1	1	1	14.59	14.60	13.73	13.67
D8	-1	-1	-1	-1	3.43	3.40	8.58	8.82
D9	-1	0	0	0	14.59	14.62	18.02	17.66
D10	1	0	0	0	18.88	18.91	24.02	23.66
D11	0	-1	0	0	12.87	12.91	18.88	18.51
D12	0	1	0	0	19.73	19.77	21.45	21.09
D13	0	0	-1	0	6.01	6.13	9.44	8.47
D14	0	0	1	0	11.15	11.10	12.87	13.11
D15	0	0	0	-1	15.44	15.48	19.73	19.37
D16	0	0	0	1	15.44	15.48	18.88	18.51
D17	0	0	0	0	15.44	15.75	18.88	19.83
D18	0	0	0	0	16.30	15.75	19.73	19.83
D19	0	0	0	0	15.44	15.75	19.73	19.83
D20	0	0	0	0	16.30	15.75	19.73	19.83
D21	0	0	0	0	15.44	15.75	18.88	19.83

1.3 Sorbent prepared from RHA and CaO and various metal oxides

Two steps sorbent preparation were used. Water hydration method [1] was used to prepared RHA/CaO sorbent based on the optimum hydration conditions reported in previous studies. Then, pore volume impregnation method [3] was separately employed to obtain various RHA/CaO-supported metal oxides (5 wt.%), which were prepared by thermal decomposition of the metal nitrates, i.e: $Mg(NO_3)_2$. $6H_2O$ (Acros, 99%); $Co(NO_3)_2$. $6H_2O$ (Acros, 99%); $Al(NO_3)_3$. $9H_2O$ (Fluka, 98%); $Mn(NO_3)_2$. $4H_2O$ (Fluka, 97%); $Zn(NO_3)_2$. $6H_2O$ (Fluka, 99%); $Fe(NO_3)_3$. $9H_2O$ (Fluka, 97%); and $Ce(NO_3)_3$. $6H_2O$ (Fluka, 98%). The sorbent obtained in the powder form was then pelletized, crushed and sieved in order to achieve the required particle size (250 – 300 µm) for the sorption capacity/activity test toward SO_2/NO by subjecting it to simulated flue gas.

1.4 Activity (sorption capacity) study

The activity of the sorbent toward SO_2 or NO is express here as SO_2 or NO sorption capacity and is defined by the weight of SO_2 or NO captured from the flue gas per gram sorbent [4]. The sorption capacity experiments were conducted in a fixed bed reactor attached to an experimental rig as shown in Figure 1.
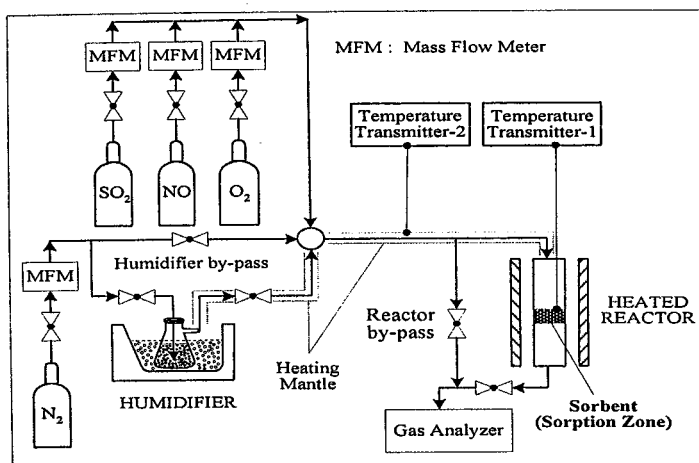

Figure 1. Schematic diagram of the experimental set-up for simultaneous removal of SO_2 and NO

The sorbent (0.5 g) was dispersed on the borosilicate glass wool (0.05 g) in the center of the reactor. The simulated flue gas with flow rate 150 ml/min was normally composed of 2000 ppm SO_2, 500 ppm NO, 10% O_2, 50 % H_2O and N_2 as a balance was subsequently passed through the sorbent at a reaction temperature of 87 °C. Prior to each run, the sorbent bed was humidified for 15 min by passing N_2 gas through the humidification system with 50% relative humidity. The concentration of the flue gas was measured using a Portable Flue Gas Analyzer IMR 2800P before and after the sorption process. The amount of SO_2/NO captured by the sorbent was evaluated from the time the sorbent could maintain 100% removal of SO_2/NO until it shows negligible activity (when the outlet SO_2/NO concentration becomes the same as the inlet SO_2/NO concentration). The weight of SO_2/NO captured by the sorbent was measured by integrating the difference between the inlet and outlet concentration. The desulfurization activity in this work is also reported as the breakthrough curves of the desulfurization/denitrification reaction (C/Co versus t), where C is the outlet concentration of SO_2/NO (ppm) from the reactor and Co is the initial concentration of SO_2/NO (ppm).

Every experimental run was repeated at least three times to increase the precision of the results, and only the average value was reported. The reproducibility of the experimental data was found to be sufficiently high with relative error between repeated runs was less than 5%.

1.5 Characterization (chemical and physical analysis).

The chemical composition of RHA and metal loading of the RHA-based sorbent were determined using a Rigaku RIX 3000 X-ray Fluorescence (XRF) spectrometer. The specific surface area and pore size distribution of the sorbents and raw materials were determined using the BET and BJH methods, respectively, on an Autosorb-1 Quantachrome analyzer. A Leo Supra 35 VP Scanning Electron Microscope (SEM) was used to examine the sorbent surface morphologies. X-Ray Diffraction (XRD) spectrum were recorded on a Siemens D5000 X-ray diffraktometer for the powdered samples with Cu-Kα radiation in the range of diffraction angle (2θ) 10–70° at a sweep rate of 1°/min to determine the phases present in the sorbent. The Fourier transform infrared (FTIR) spectrum was carried out on a Perkin-Elmer FTIR 2000 spectrometer over the frequency range of 4000 to 400 cm^{-1}.

2. RESULTS & DISCUSSION

The results and discussion in this section is devided into two main sub-sections; (1) Identified key factor for SO₂ removal, and (2) Improvement of RHA/CaO sorbent toward SO₂/NO removal.

2.1. Identified key factor for SO₂ removal

2.1.1 Effect of Specific Surface Area.

To elucidate the role of specific surface area on the SSC of the sorbents prepared from RHA, sorbents with surface areas ranging from 9.52 to 134 m^2/g were subjected to activity study. Figure 2 shows the SSC of the sorbent versus their specific surface area. The SSC of the sorbent did not correlate with the specific surface area of the sorbent. This indicates surface area may not be the key factor that influences the desulfurization activity of sorbents prepared from RHA. Other factors in sorbents prepared from RHA are thus more important to having a high SSC.
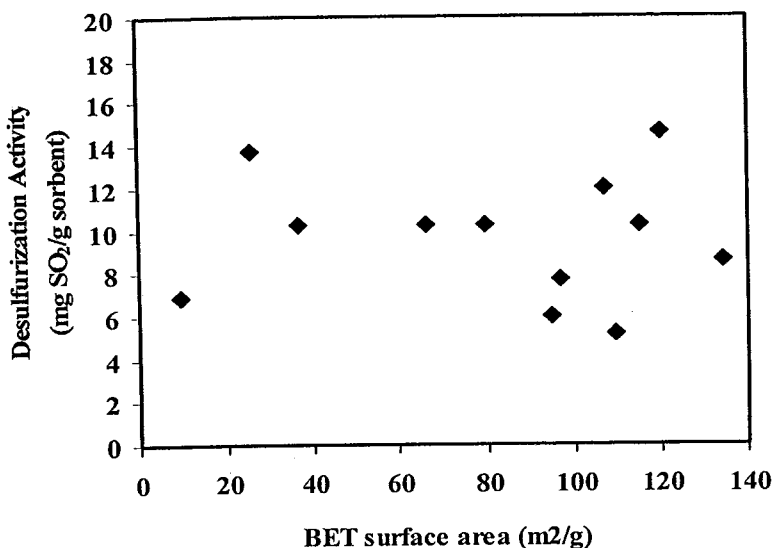
Figure 2. Desulfurization activity (SSC) as a function of the BET specific surface area.

2.1.2. Correlation Between Sorbent Preparation Variables to SSC.

To identify the key factor in sorbents prepared from RHA involved in high SSC, a statistically designed set of experiments were conducted to study the effect of five sorbent preparation variables and their interactions on the SSC of the sorbent. From the data presented (Table 2), sorbent A16 exhibited the highest SSC at 17.2 mg SO₂ captured/g sorbent. Sorbent A21 exhibited the lowest SSC at 1.72 mg SO₂ captured/g sorbent. Visual inspection of the data tabulated in Table 2 also reveal the sorbent preparation variables have a significant effect on the SSC of the sorbent. Since there are five sorbent preparation variables that were studied simultaneously, a more systematic method to study the influence of the various sorbent preparation variables on the SSC would be to develop a mathematical model that correlates the sorbent preparation variables to the SSC of the sorbent.

Using multiple regression analysis, the response (SSC) obtained in Table 2 was correlated with the five sorbent preparation variables using the mathematical model as shown in Equation (1). The coefficients of the full regression model equation and their statistical significance were determined and evaluated using Design-Expert software. The final regression model equation obtained in terms of coded value after discarding the insignificant effects (identified using the Fisher F-test) is given as

$$Y = 7.11 + 1.72\,x_1 + 1.86\,x_2 + 1.72\,x_3 + 1.20\,x_1^2 + 0.980\,x_2^2 + 0.970\,x_2 x_3 \tag{2}$$

A positive sign in front of a term indicates a synergistic effect. The statistical significance of Equation (2) was verified by the Fisher test (F-test) using analysis of variance (ANOVA) as shown in Table 5.

Based on a 95 % confidence level, the mathematical model developed was found to be significant in predicting the SSC of the sorbent as the computed F-value (20.8) is higher than the theoretical $F_{0.05\,(20,11)}$ value (2.65). Furthermore, the probability value (P-value) of the model was less than 0.0001, indicating the model is highly reliable. Each significant term in the model was also found to be significant at a 95 % confidence level as the computed F-values for the respective terms are higher than the theoretical $F_{0.05\,(1,11)}$ value (4.84). The validity of the mathematical model was also checked using the lack-of-fit test and the coefficient of determination (R^2).

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The P-value of lack-of-fit test demonstrates that considerable improvement was achieved after the exclusion of the statistically insignificant terms. The P-value of lack-of-fit for the model after excluding the insignificant terms is 0.0769 (an increase from 0.0319 when all the terms were included in the model). This value is greater than 0.05 indicating that the lack-of-fit for the mathematical model is insignificant. Insignificant lack-of-fit is good because the model fit the data well. Apart from that, the coefficient of determination (R^2) of the model is 0.952 indicating that 95.2% of the variability in the response (SSC) could be explained by the mathematical model. When all the terms (significant and insignificant) are included in the mathematical model, the R^2 value is increase by only 0.0221. This result justifies dropping the insignificant terms from the mathematical model as the insignificant terms only contribute 2.21% to the variability in the response (SSC).

Table 5. ANOVA for the Regression Model Equation and Coefficients

Source	Sum of squares	Degree of freedom	Mean of square	F-test	Prob > F
Model	313	20	15.7	20.8	< 0.0001*
x_1	70.7	1	70.7	93.8	< 0.0001*
x_2	82.9	1	82.9	110	< 0.0001*
x_3	70.7	1	70.7	93.8	< 0.0001*
x_4	0.490	1	0.490	0.650	0.437
x_5	0.00	1	0.00	0.00	1.00
x_1^2	42.9	1	42.9	56.9	< 0.0001*
x_2^2	29.0	1	29.0	38.5	< 0.0001*
x_3^2	1.01	1	1.01	1.34	0.272
x_4^2	0.550	1	0.550	0.730	0.413
x_5^2	1.74	1	1.74	2.31	0.157
$x_1 x_2$	0.00	1	0.00	0.00	1.00
$x_1 x_3$	1.66	1	1.66	2.20	0.166
$x_1 x_4$	0.00	1	0.00	0.00	1.00
$x_1 x_5$	0.180	1	0.180	0.240	0.631
$x_2 x_3$	14.9	1	14.9	19.8	0.001*
$x_2 x_4$	0.00	1	0.00	0.00	1.00
$x_2 x_5$	0.180	1	0.180	0.240	0.631
$x_3 x_4$	0.180	1	0.180	0.240	0.631
$x_3 x_5$	0.740	1	0.740	0.980	0.344
$x_4 x_5$	0.180	1	0.180	0.240	0.631
Residual	8.29	11	0.750	-	-

* Significant term

The mathematical model developed was also inspected for its validity using visual inspection by plotting the experimental versus the predicted sorbent desulfurization activity (Figure 3). The predicted values of the desulfurization activity of the 32 sorbents synthesized are also given in Table 2. The results demonstrated that the model provided a very accurate description of the experimental data, indicating that it was successful in capturing the correlation between the five sorbent preparation variables to the desulfurization activity of the sorbent. In addition, the R value (multiple correlation coefficient) for the plot was found to be 0.974, indicating a very good correlation between the experimental and predicted values. From all these validity tests, the model was found to be adequate for predicting the SSC of the sorbent within the range of the sorbent preparation variables studied.
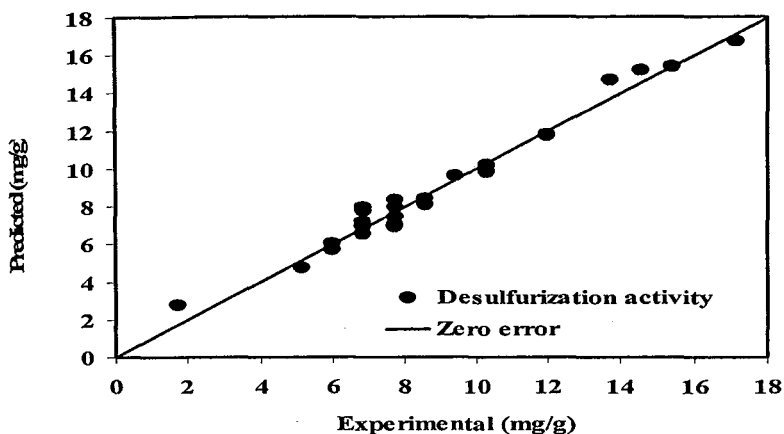
Figure 3. Experimental versus predicted desulfurization activity.

2.1.3. Effects of sorbent preparation variables.

Based on the mathematical model, it was observed that the linear terms of hydration period (x_1), amount of RHA (x_2) and amount of CaO (x_3) were found to have significant positive effect (P values < 0.05) on the SSC of the sorbent. Contrary, amount of water (x_4) and hydration temperature (x_5) did not have significant effect on the SSC. The quadratic term of x_1 and x_2 also effect the SSC, but less pronounced than the linear term. The interaction between variables, amount of RHA (x_2) and amount of CaO (x_3) was also found to have significant effect on the SSC. Among all the significant variables that affect the SSC, amount of RHA (x_2) was found to have the largest effect (due to the highest F-value). Hydration period (x_1) and amount of CaO (x_3) have almost similar effect while the interaction between x_2 and x_3 have the least significant effect on the SSC. In the previous study [5], hydration temperature had the largest effect on the sorbent surface area prepared from RHA. However, as indicated in the discussion earlier, hydration temperature was found to have negligible effect on the SSC. Therefore, this result further supports the conclusion that high surface area may not be the key factor for sorbents having high SSC.

To facilitate a straight-forward examination of the effect of amount of RHA (x_2) and amount of CaO (x_3) and their interaction, the mathematical model developed was utilized to construct three-dimensional response surfaces. Figure 4 (a) & (b) shows the SSC response surface and contour plot respectively with varying amount of RHA (x_2) and amount of CaO (x_3) at constant hydration period (11 h), amount of water (100 ml) and hydration temperature (200 °C). A significant interaction was observed between amount of RHA (x_2) and amount of CaO (x_3) (Figure 4). This observation is in agreement with the ANOVA results presented in Table 5 where the interaction term between x_2 and x_3 was found to have a prominent effect on the sorbent SSC (high F-test value). When the amount of CaO was held constant at 2 g, an increase in the amount of RHA did not significantly affect the SSC of the sorbent. However, when the CaO was held fixed at a higher amount (6 g), an increase in the amount of RHA increases the SSC of the sorbent significantly. Thus, the ratio of the amount of RHA to the amount of CaO used in the preparation mixture significantly influenced the SSC of the resulting sorbent. A similar result can also be obtained by observing the data trend tabulated in Table 2. Among the 32 different types of sorbent that were tested for its respective SSC, only sorbent A8 and A16 exhibited significantly high SSC. Comparing the sorbent preparation variables that is used to synthesize these two sorbents, the only similarity between them is the ratio of amount of RHA to CaO that is at 2.5. This observation indicates that the ratio of RHA to CaO used in the preparation mixture is an important factor that could lead to the synthesis of sorbent with a high SSC. Although sorbent A7 and A15 were also prepared using the same ratio, the SSC was found to be significantly lower. This is most probably due to the low hydration period used in the preparation step that limits the formation of the reactive species in the sorbent.
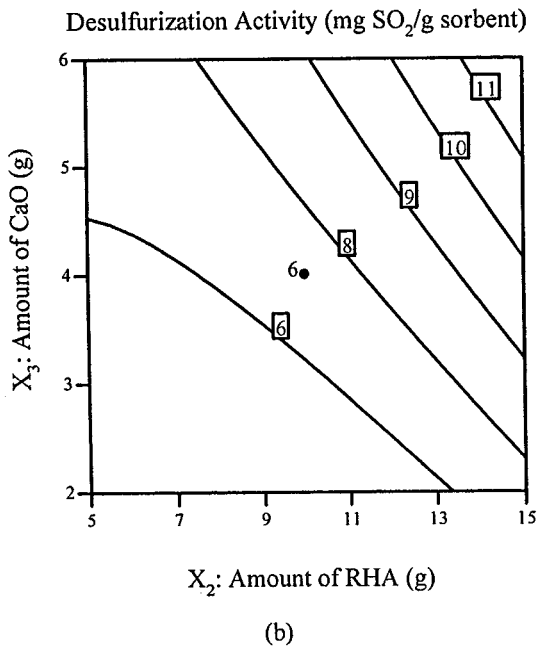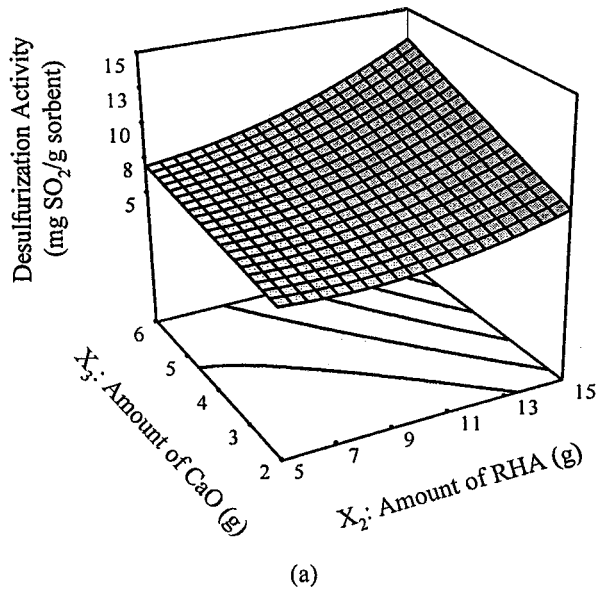
7

(a)

(b)

Figure 4. Effect of amount of RHA and amount of CaO on the desulfurization activity; (a) response surface plot and (b) contour plot.

The effect of hydration period on the SSC can be obtained directly by observing the data in Table 2. An increase in hydration period always increases the SSC of the sorbent. It has been reported that the reaction between calcium based materials and siliceous material involves a pozzolanic reaction that is very slow [6]. Thus, longer hydration period is required for the dissolution of silica from RHA to react with CaO to form the reactive species that is responsible for SO_2 sorption. Consequently, hydration period becomes the limiting factor for the formation of the reactive species in the sorbent. The SSC of the sorbent could be influenced by either the amount or type of reactive species formed in the sorbent. The total amount of raw materials used in the preparation mixture is not crucial in determining the total amount of reactive species formed in the sorbent, but it is the hydration period that is more crucial. Sufficient hydration period is required to ensure that the pozzolanic reaction between the starting materials can proceed to completeness [7].

2.1.4. Physical and Chemical Characterization.

Up to this point, the results have indicated the significant sorbent preparation variables that affect the SSC of the sorbent are somehow related to the formation of specific reactive species in the sorbent. Therefore, sorbents that exhibited significantly high and low SSC were subjected to X-Ray Diffraction (XRD) analysis in order to identify the various phases present in the sorbent. Figure 5 (a) & (b) shows the XRD spectrum of sorbent A8 and A16 respectively (high SSC), while Figure 5 (c) & (d) for sorbent A1 and A21 respectively (low SSC). The peak characteristics of vaterite ($CaCO_3$), silica (SiO_2), mountainite ((Ca, Na_2, K_2)$_2$ $Si_4O_{10}.3H_2O$) and iron oxide (Fe_2O_3) were detected in all the four sorbents except in sorbent A21 where iron oxide is not detected (Figure 4 (d)). Other than the four phases that were detected, additional phase were also detected in sorbent A8 and A16 which exhibited high SSC. They are calcium aluminum silicate ($CaAl_2Si_2O_8$) and calcium silicate hydrate ($Ca_2SiO_4.H_2O$) in sorbent A8 and A16 respectively. Calcium silicate and/or aluminum compounds have also been reported in sorbents prepared from coal fly ash [8,9]. Based on these finding, it is possible to conclude that the phases present in the sorbent (calcium silicate and/or aluminum compounds) are key factors in determining the SSC of the sorbent. In addition, the amount of RHA and CaO used in the preparation mixture could be the controlling factor influencing the formation of calcium silicate and/or aluminum compounds in the sorbent. Another conclusion is that apart from calcium silicate and/or aluminum compounds, silica and vaterite, all the other phases detected in the sorbent were generally different from the phases detected in sorbent prepared using coal fly ash [8-10] and oil palm ash [7] as the siliceous materials. This is probably due to the different composition of coal fly ash and oil palm ash as compared to RHA. This result indirectly described the difference in the correlation between sorbent surface area and the SSC for sorbent prepared from coal fly ash, oil palm ash and RHA.

(a)

(b)

(c)

(d)
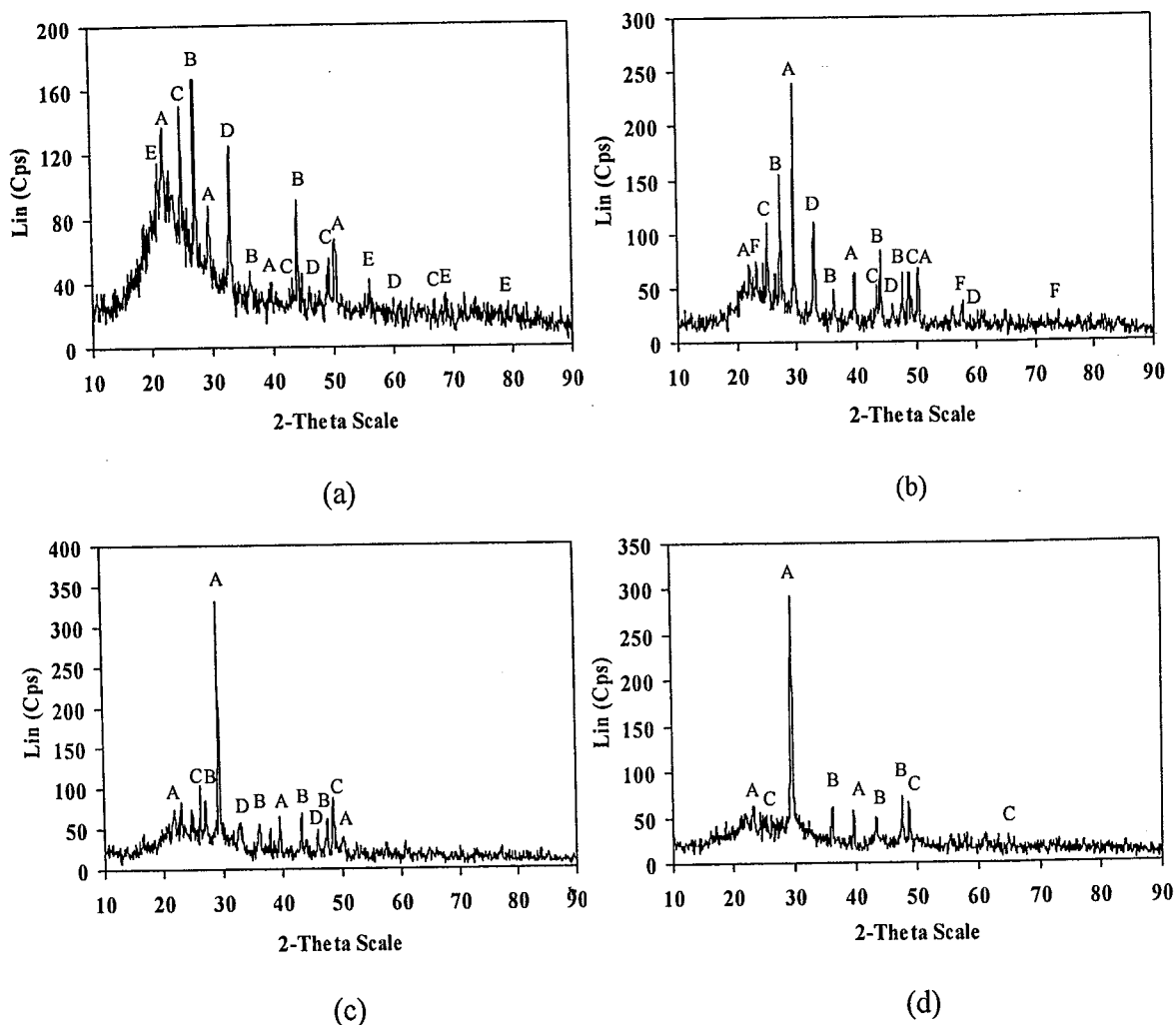
Figure 5. XRD spectrum of sorbent (a) A8; (b) A16; (c)A1; and (d) A21.
XRD label: (A) vaterite ($CaCO_3$); (B) silica (SiO_2); (C) mountainite ((Ca, Na_2, K_2)$_2$ $Si_4O_{10}.3H_2O$); (D) iron oxide (Fe_2O_3); (E) calcium aluminum silicate ($CaAl_2Si_2O_8$); (F) calcium silicate hydrate ($Ca_2SiO_4.H_2O$)

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Sorbents A1, A8, A16 and A21 were also subjected to other physical analysis to determine whether the sorbent with significantly high and low desulfurization activity exhibited any distinctive physical properties or otherwise. Based on the pore size distribution analysis, all sorbents had similar pore size distribution with an average pore size between 9 and 13 nm (Figure 6).
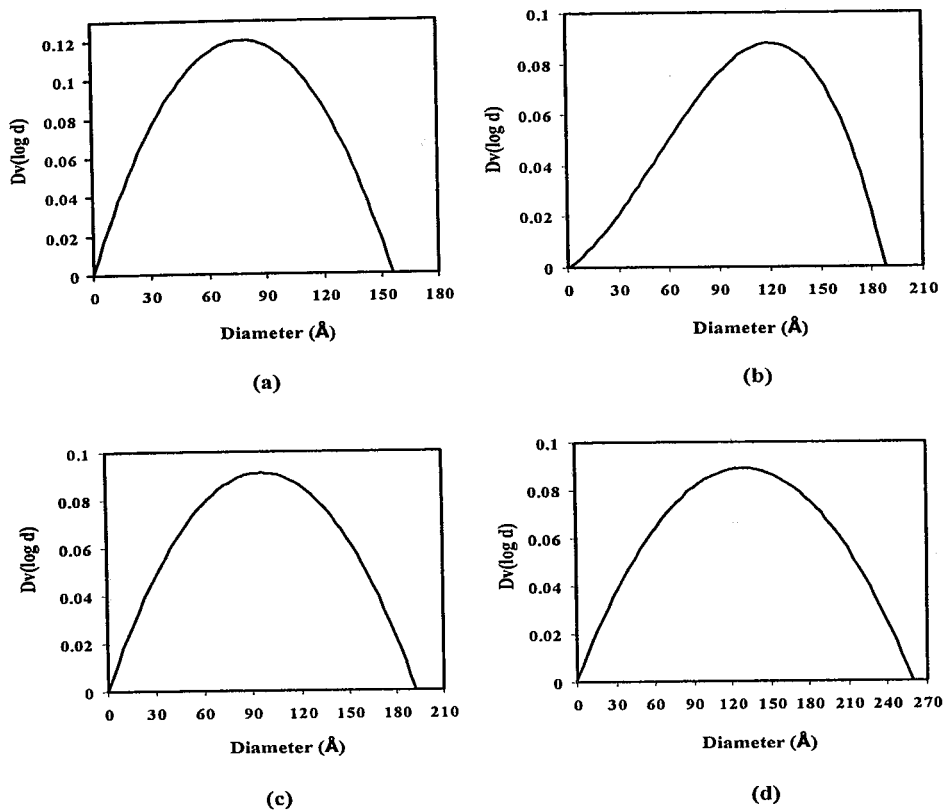
(a)

(b)

(c)

(d)

Figure 6. Particle size distributions of sorbent (a) A8; (b) A16; (c) A1 and (d) A21

Scanning Electron Micrograph (SEM) analysis on the sorbents indicated that the surface morphology of the sorbents consist of irregular rough particles with different shapes and sizes that agglomerate together (Figure 7). It was concluded that there are no significant differences between the pore size distribution and surface morphology of these four sorbents indicating that sorbent pore size and surface morphology is not a key factor in determining the SSC of the sorbent prepared from RHA.
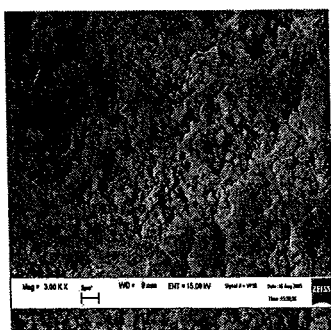
(a)
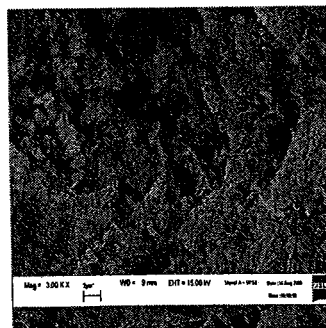
(b)
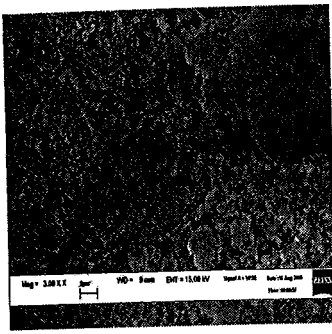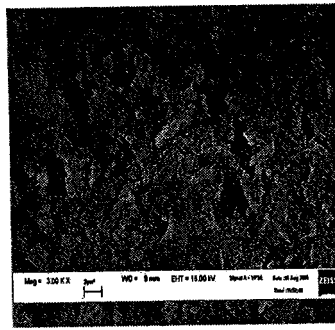
(c)   (d)

Figure 7. SEM micrographs of sorbent (a) A8; (b) A16; (c) A1 and (d) A21

2.1.5. Breakthrough Curves of the Desulfurization Activity.

The desulfurization breakthrough curves of sorbents with the highest activity (A16) and lowest activity (A21) as well as the starting materials (RHA and CaO) are shown in Figure 8. The two starting materials (RHA and CaO) had very low SSC as they could maintain 100% removal of SO_2 from the feed gas for only 2 min and 4 min, respectively. Sorbent A21 showed similar low SSC. Conversely, sorbent A16 exhibited very high SSC as it could completely remove SO_2 from the feed gas for the first 20 min. Beyond 20 min of reaction time, the concentration of SO_2 gradually increases until there is no more SO_2 sorption activity in the sorbent (when the outlet concentration of SO_2 from the reactor is the same as the inlet concentration). As discussed above, this is due to the reactive species form in sorbent A16.
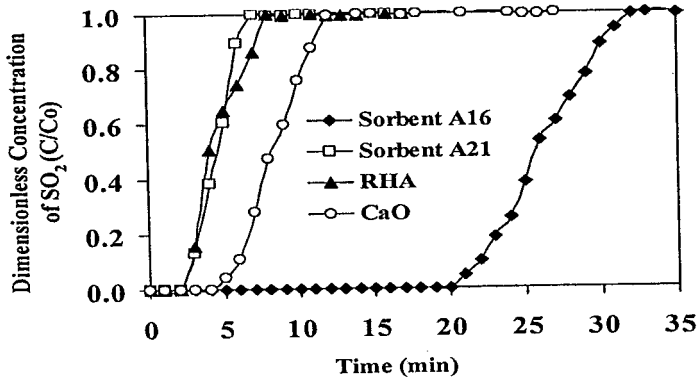
Figure 8. Breakthrough curves of the sorbent for highest and lowest desulfurization activity and its raw materials.

2.2. Improvement of RHA/CaO sorbent toward SO₂/NO removal.

2.2.1 Effect of different type of additives

As has been revealed that higher SSC did not show any correlation with specific surface area, on the other hand, many studies indicate that relative humidity has the greatest impact on the SSC of dry Ca-based sorbents at low temperature [10-15]. The relative humidity is consecutively connected to moisture content of the solids. In addition, some additives have been employed to alter the moisture content on the prepared sorbent surface in equilibrium with a gas phase of a given relative humidity [4, 16-20]. Thus, the use of additive would then be expected to improve the sorbent SSC in desulfurization processes in the way of altering the sorbent particle's physical/chemical properties. Therefore, the scope of this work is to evaluate the effectiveness of various additives in the preparation of RHA-based sorbent for desulfurization process at low temperature.

Figure 9 shows the effect of different type of additives used in the preparation of RHA/CaO sorbent. With an additives concentration of 0.25 mol/l, most of the sorbents were successful in increasing the sorption capacities of RHA/CaO sorbent toward SO_2 as compared to sorbent without additive. However, some of additives do not perform well such as $NaHCO_3$ and $NaBr$ whereby SSC are about the same as sorbent prepared without additive. Apart from that, instead of giving negative effect on SSC of sorbent, the addition of $BaCl_2$ does

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not have any beneficial effect at all. As the concentration of additive increase to about 0.5 mol/l, the SSC of the sorbent prepared with the addition of $CaCl_2$, LiCl, $NaHCO_3$, $BaCl_2$, K_2HPO_4 and $FeCl_3$ also increases significantly. Nevertheless, for some additives such as NaOH, NaBr, KOH and $MgCl_2$, the results were different. At higher concentration (above 0.25 mol/l), these additives cause the SSC of RHA/CaO sorbent to decrease. This result reflects that there is an optimum additive concentration during the sorbent preparation that favors high sorbent SSC. From the viewpoint of additive addition to RHA/CaO sorbent SSC, NaOH gave better enhancement effect. Sorbent prepared with NaOH addition exhibited the highest SSC (30 mg SO_2/g sorbent) at optimum concentration (0.25 mol/l) compared to other additives examined.
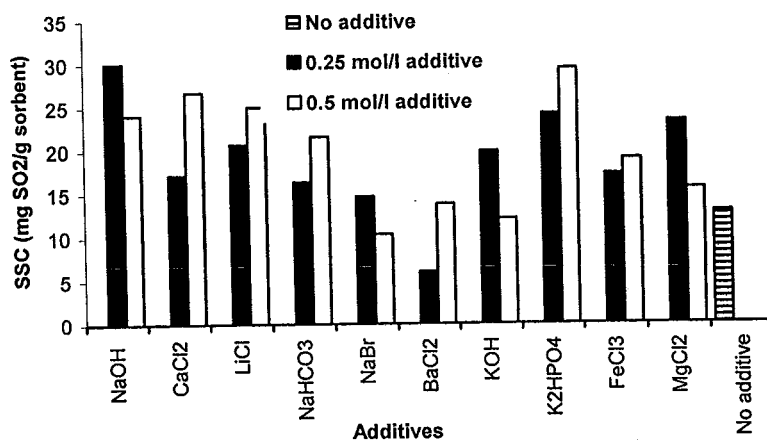
Figure 9. Effect of various additives on SSC of RHA-based sorbent during 100% SO_2 removal

In the addition of additive to RHA/CaO sorbent, the hydroxide of the cation plays a crucial role. The cation of additive should be very soluble for the sorbent to be effective [21]. Apart from that, the beneficial effect of additive addition is supposedly due to the presence of additive that might increase the dissolution rate of silica from RHA The increase in the dissolution of silica will ultimately increase the formation of Si-Ca complex that has a high SSC[1,7,22-25]. However, the X-ray diffraction (XRD) pattern of sorbents prepared with the addition of NaOH (shown in Figure 10) exhibited different results when compared with RHA/CaO sorbent without NaOH addition. Only characteristic peak of calcium carbonate ($CaCO_3$) was detected at $2\theta = 29.39°$ and $39.39°$. Apart from that, a weak peak corresponding to unreacted amorphous silica was also observed at $2\theta = 35.96°$ and $48.60°$ for sorbent prepared with NaOH. On the other hand, more phases were detected in the sorbent prepared without the addition of additive, such as $Ca_2SiO_4 \cdot H_2O$ ($2\theta = 25.16°/27.32°$), $Ca_3Si_2O_7$ ($2\theta = 38.01°/46.09°/50.42°$) and $Ca_3Al_2Si_3O_{12}$ ($2\theta = 37.22°/47.46°/57.70°/60°$). This result indicates that both sorbents prepared with NaOH contained much less of these Si-Ca complex phases. In addition, the reaction between silica and CaO during the hydration process has somehow been inhibited by the existence of additive. This might be due to the fact that NaOH is a strong alkaline and the dissolution of CaO was limited by the common ion effect [4].
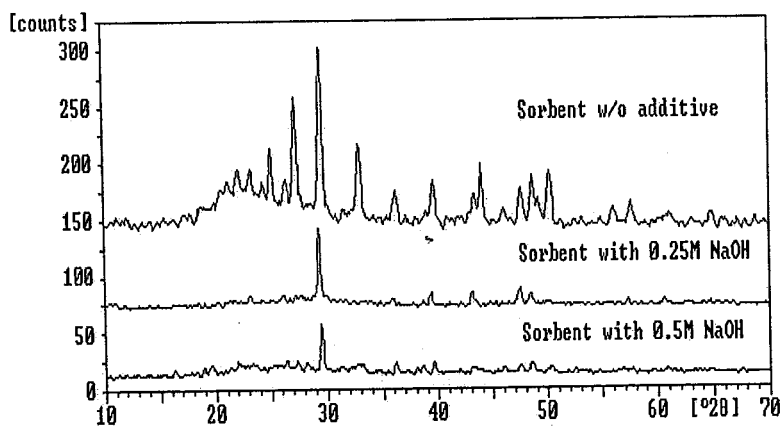

Figure 10. XRD pattern of RHA/CaO sorbent with and without NaOH

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The sorbents prepared with NaOH addition was further subjected to FTIR analysis to characterize specific functional group. It was observed from Fig. 3 that there was no distinct FTIR spectrum pattern for both sorbents prepared before subjected to humidified flue gas. The spectrums (Fig. 11.a & b) showed the prepared sorbents were mainly composed of carbonate (CO_3^{2-}) due to a broad band near 1450 cm^{-1} and a sharp band near 875 and 712 cm^{-1} [26,27]. A sharp vibration band approximately at 3640 cm^{-1} usually caused by the stretching of CaO-H [25]. The bands around 460-470 cm^{-1} (Si-O-Si band) and 795 cm^{-1} (Si-O-Si symmetric strength) are observed for amorphous silica. However, Si-O-Si asymmetric bands which usually near 1100 cm^{-1} is not detected [28-32]. A broad band situated around 1050 cm^{-1} is assigned to Si-O-C stretch [33]. Moreover, the band around 3450 cm^{-1} is typically caused by hydroxyl groups or adsorbed water due to O-H stretches. Since the sorbent was prepared from RHA, this also can be caused by silanol groups [30,32]. In contrast, after both sorbents subjected to feed gas (Fig. 11.c & d), the vibration peaks of CO_3^{2-} become weaker, which indicated the amount of carbonate decreased. Furthermore, the products of the desulfurization reaction, mainly sulfate (SO_4^{2-}) species, is characterized by a broad bands due to S-O stretching near 1050-1100 cm^{-1}, S-O bending at 670 cm^{-1} and a single peak close to 1640 cm^{-1} related to hydroxyl groups (O-H bending) [30,34]. The relative intensity of hydroxyl groups displayed an obvious increase due to hygroscopic properties of prepared sorbent, which adsorb more water from humidified flue gas and thus enhance SSC. These O-H bands also exhibited a different degree of hydration for the water molecules in the crystal lattice structure. Additionally, a slight/weak band around 970 cm^{-1} is detected for sulfite (SO_3^{2-}) species [33,35].
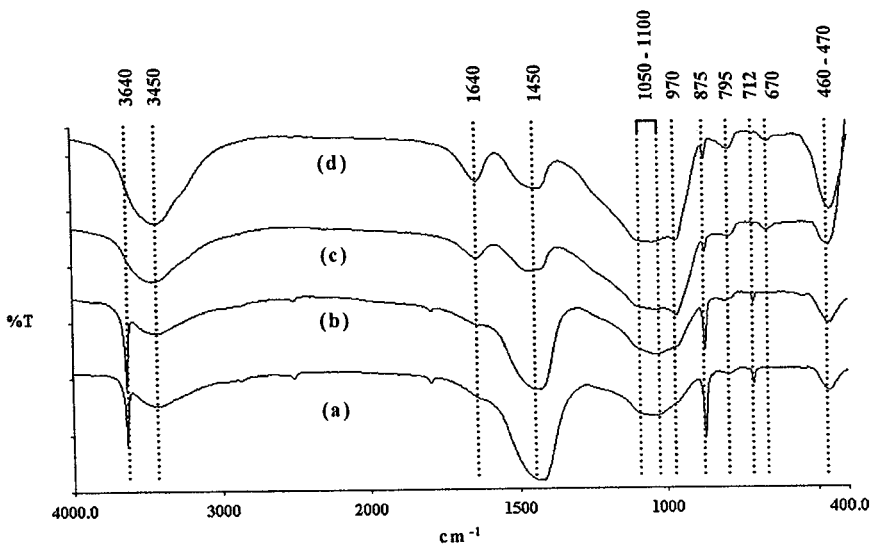

Figure 11. Transmittance IR spectra of prepared sorbent with (a) 0.25 mol/l NaOH; (b) 0.5 mol/l NaOH; and sorbents after subjected to humidified flue gas for (c) 0.25 mol/l NaOH and (d) 0.5 mol/l NaOH addition.

2.2.2 Effect of relative humidity

It was well-known that the reaction which involves SO_2 and dry-type sorbent at low temperature proceeds under the presence of appreciable amount of water vapor. The effect of water vapor (relative humidity, RH) on the SSC of RHA/CaO sorbent with various type of additive addition is shown in Figure 12. Form experimental results obtained, it was found that RH exerted significant influence on the sorbent SSC. When the reaction was carried out under dry condition (0% RH), the maximum sorbent SSC was only found to be capable of achieving 20 min of 100% SO_2 removal (SSC = 17.2 mg SO_2/g sorbent), i.e using NaOH as an additive. However, after introducing water vapor (RH) from humidified flue gas, most the sorbent SSC increases drastically with relative humidity. In contrast, the addition of NaBr and K_2HPO_4 showed only slightly increase in SSC, while $NaHCO_3$ is the only additive that caused the sorbent SSC to decrease when the RH of the activity test was increase from 50% to 80%.
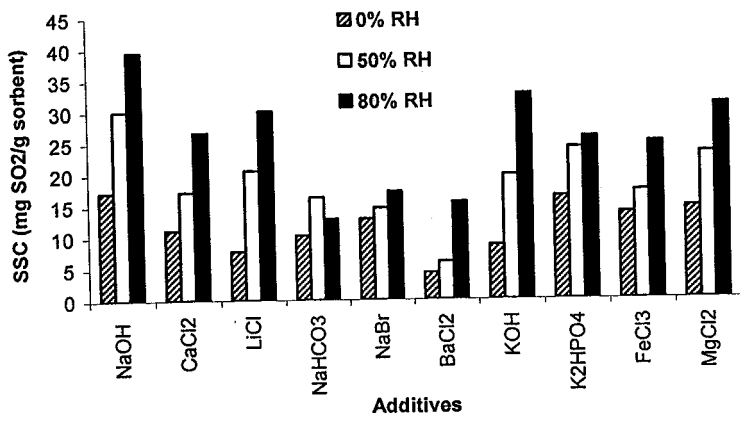
Figure 12. Effect of relative humidity on SSC of RHA-based sorbent with different type of additives during 100% SO₂ removal

In all cases, the addition of NaOH still gave the maximum SSC. The SSC of RHA/CaO sorbent prepared with NaOH addition increases from 30 to 39.5 mg SO₂/g sorbent as the water vapor increases from 50% RH to 80% RH. The positive effect of RH on the SSC of the sorbent was due to the water adsorbed and/or collected on the sorbent surface which played an important role in the reaction between the dry-type sorbent and SO₂. Furthermore, with the presence of additives the water sorption capacities of sorbents also increase since most of additives tested act as deliquescent material (*i.e* highly hygroscopic substances). At the same time the Ca-based compound in the interior of the RHA particle become more accessible to SO₂. As can be seen from scanning electron micrograph (SEM) analysis (Figure 13), after subjected to humidified flue gas, particle size of the sorbents significantly increase (at the same magnification, 100 X). The larger particle size of the sorbent could be due to the agglomerating of smaller particles during the desulfurization reaction. It was also observed that the particles of sorbents containing additive have a wet-look as compared with sorbent prepared without additive which have a dry-look and the particles are more loose. Furthermore, it has been reported by Ho et al. [13] and Liu et al. [10] that the reaction of SO₂ with Ca-containing sorbents at low temperature requires the presence of water on the surface of sorbent particles and the extent of reaction increases with an increasing amount of water adsorbed.

(a)

(b)

14
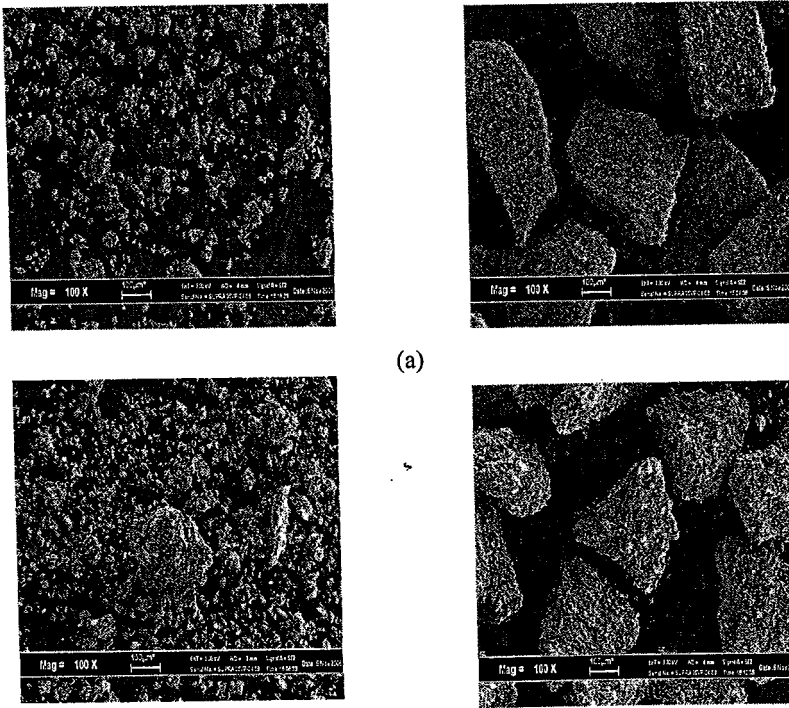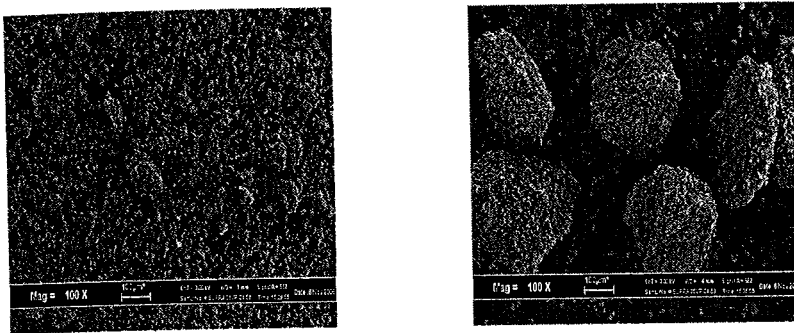
(c)

Figure 13. SEM micrograph of RHA/CaO sorbents prepared with the addition of (a) NaOH (b) KOH and (c) CaCl₂ before and after subjected to humidified flue gas at 80% RH.

## 2.2.3 Analysis of SSC of RHA (un-treated & pre-treated)/CaO/NaOH Sorbents

Sodium hydroxide (NaOH) has been found to be the best additive among all the other additives studied and the results also reflected that there is an optimum additive concentration during the sorbent preparation that favors high SSC, and this needs further study. Apart from that, the characteristics of amorphous silica in RHA was further investigated by pre-treating RHA with heating at 600 °C with the aim to remove the organic matter and leaving behind a silica-rich residue that can be used to synthesize the sorbent. The un-treated and pre-treated RHA hereinafter is referred to as $RHA_{300\ °C}$ and $RHA_{600\ °C}$, respectively.

2.2.3.1 Characteristics of Un-treated and Pre-treated RHA.

Figure 14 shows the surface morphologies of $RHA_{300\ °C}$ and $RHA_{600\ °C}$, respectively. Both the samples were found to have uniform structure, the former with a dome-shaped structure and the latter with a skeletal structure. Nevertheless, $RHA_{600\ °C}$ was found to have a more porous structure compared to $RHA_{300\ °C}$.
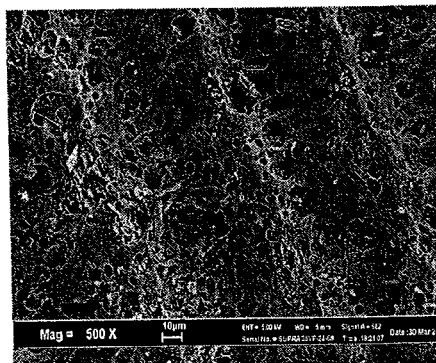
(a)   (b)

Figure 14. Morphological details of RHA: (a) $RHA_{300\ °C}$ (b) $RHA_{600\ °C}$

The presence of amorphous silica in both RHA was confirmed from the X-ray diffraction patterns shown in Figure 15. It was observed that there are no defined peaks, only a broad "hump" between (2θ) 15 and 30° diffraction angle. However, an indistinct peak corresponding to α-cristobalite silica was detected at $2\theta = 22°$, a similar trend reported elsewhere [36-39]. Moreover, these patterns are similar to X-ray spectra of silicic acid reported in the literature [40] and are characteristics of amorphous substances. On the other hand, the crystalline structure was detected when rice husk was heated at 1000 °C as shown in the inset of Figure 15. Although, the results indicated that heating RHA at 600 °C did not change the structure of silica from amorphous to crystalline, however $RHA_{600\ °C}$ exhibited less crystalline intensity (Figure 15) indicating a higher content of amorphous silica as compared to $RHA_{300\ °C}$. Apart from that, heating RHA at 600 °C also change the color of the ash from black to whitish-grey, an indication of higher content of silica. Nevertheless, both RHA present an adequate characteristic profile that can be useful in the preparation of sorbent from siliceous materials.
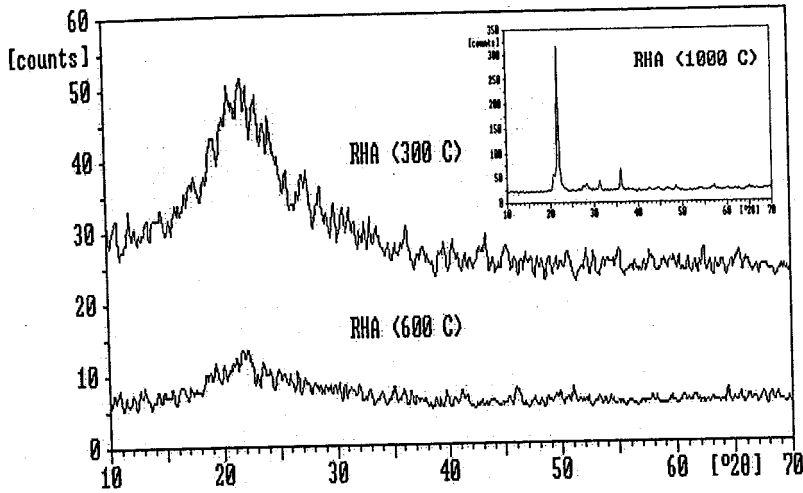
15

Figure 15. XRD pattern of rice husk heated at 300 °C and 600 °C

2.2.3.2. Effect of sorbent preparation variables on the sorbent sorption capacity toward SO_2.

The effects of sorbent preparation variables on the sorbent SSC were evaluated using a CCFCD to determine the optimal sorbent preparation variable that results in maximum SSC. All the sorbents prepared were tested for the SSC based on the method described earlier and the values were tabulated in Table 4. The data in Table 4 were then fitted to Eq. (1) using multiple regression analysis technique. The resulting empirical mathematical models of the SSCs (Y_3 and Y_6) are given in Eq. (3) and (4) in term of actual factor, respectively.

$$Y_3 = 11.614 - 0.985\ x_1 + 0.714\ x_2 + 67.58\ x_3 - 0.039\ x_4 + 0.0159\ x_1^2 + 0.325\ x_2^2$$
$$- 114.068\ x_3^2 - 0.000106\ x_4^2 - 0.0496\ x_1 x_2 - 0.697\ x_1 x_3 + 0.00563\ x_1 x_4$$
$$+ 1.589\ x_2 x_3 + 0.00477\ x_2 x_4 + 0.0257\ x_3 x_4 \tag{3}$$

$$Y_6 = 11.266 - 0.273\ x_1 - 6.325\ x_2 + 70.192\ x_3 + 0.0319\ x_4 + 0.0148\ x_1^2 + 0.0509\ x_2^2$$
$$- 149.526\ x_3^2 - 0.000306\ x_4^2 - 0.00993\ x_1 x_2 + 0.161\ x_1 x_3 + 0.00134\ x_1 x_4$$
$$+ 2.2245\ x_2 x_3 + 0.0334\ x_2 x_4 + 0.0429\ x_3 x_4 \tag{4}$$

The predicted values for SSC responses (Y_3 and Y_6) were calculated using these models and the resulting values are also tabulated in Table 4.

The significance of each model was assessed from the coefficient of determination (R^2) which was found to be 0.997 and 0.995 for Y_3 and Y_6 responses, respectively. These values imply that only 0.3% and 0.5% of the variation in Y_3 and Y_6 responses can not be explain by the models. The models were also verified by using analysis of variance (ANOVA) as summarized in Table 6 for each response. The calculated F-value corresponding to SSC for each model are 170.25 and 91.03, respectively and both of this value exceeds the tabulated F-value ($F_{0.05\ (14,6)} = 3.96$) based on 95% confidence level. The significance of each term in the model was also evaluated by looking at the P value (Prob > F). P value lower than 0.05 indicates that the term is significant at 95% confidence level. Referring to Table 6, it was observed that most of the terms in the model were significant with $P < 0.05$. In usual cases, the term with $P > 0.05$ can be omitted from the model. However, in this study, the insignificant terms were still maintained to support the hierarchical nature of this model. Apart from that, both the models were also found to have in-significant lack of fit. Based on these statistical tests, both the models were found to be adequate in representing the actual correlation between the SSC and the sorbent preparation variables.

Based on Table 6, all the linear terms of the sorbent preparation variables studied except for x_4 (hydration temperature) have significant effect on the SSCs for both types of sorbents prepared (using un-treated and pre-treated RHA).

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**Table 6. Analysis of Variance (ANOVA) for response surface quadratic model**

Term	Degree of freedom	F value Y_3	F value Y_6	Prob > F Y_3	Prob > F Y_6	Coefficient Y_3	Coefficient Y_6	Standard error Y_3	Standard error Y_6
Model	14	170.25	91.03	< 0.0001[*]	< 0.0001[*]				
x_1	1	59.91	42.51	0.0002[*]	0.0006[*]	2.145	3.003	0.277	0.461
x_2	1	153.37	7.81	< 0.0001[*]	0.0314[*]	3.432	1.287	0.277	0.461
x_3	1	403.06	136.02	< 0.0001[*]	< 0.0001[*]	2.488	2.402	0.124	0.206
x_4	1	0.00	0.87	1.0000	0.3876	0.000	-0.429	0.277	0.461
x_1^2	1	17.36	5.44	0.0059[*]	0.0584	1.022	0.951	0.245	0.408
x_2^2	1	5.84	0.05	0.0521	0.8273	0.593	0.093	0.245	0.408
x_3^2	1	844.68	525.42	< 0.0001[*]	< 0.0001[*]	-7.129	-9.345	0.245	0.408
x_4^2	1	1.17	3.52	0.3214	0.1097	-0.265	-0.765	0.245	0.408
x_1x_2	1	3.00	0.04	0.1342	0.8419	-0.536	-0.107	0.310	0.515
x_1x_3	1	101.25	1.95	< 0.0001[*]	0.2119	-1.394	0.322	0.139	0.230
x_1x_4	1	52.84	1.08	0.0003[*]	0.3379	2.252	0.536	0.310	0.515
x_2x_3	1	14.98	10.63	0.0083[*]	0.0173[*]	0.536	0.751	0.139	0.230
x_2x_4	1	1.08	19.13	0.3391	0.0047[*]	0.322	2.252	0.310	0.515
x_3x_4	1	5.39	5.42	0.0593	0.0588	0.322	0.536	0.139	0.230
Residual	6								
Lack of fit	2	0.087	3.76	0.9188	0.1204				

Y_3 = sorbent prepared from RHA$_{300\,°C}$; Y_6 = sorbent prepared from RHA$_{600\,°C}$; [*] significant at $p < 0.05$.

This finding is in agreement with the result reported before (Section 2.1), whereby hydration period and the amount of RHA/CaO were found to be the most important variables that effect the preparation of sorbent that is highly reactive towards SO_2. The insignificant effect of hydration temperature indicates that neither increasing nor decreasing the slurrying temperature will produce sorbent with higher SSC. This finding is clearly supported by the data trend shown in Table 4, whereby the sorbents prepared with the same preparation variables but at different hydration temperature (D15-D17) had almost similar SSC for both types of sorbents prepared. Apart from that, the data in Table 6 also showed that the amount of additive (x_3) used in the preparation mixture had the largest effect on the SSC (highest F-value). The effect of this variable will be discussed in detail in the subsequent section. For the quadratic term, only variable x_1 and x_3 in model Y_3 and variable x_3 in model Y_6 shows significant effect. On the other hand, for the effect of interaction between variables, only the interaction between variables x_2 (RHA/CaO ratio) and x_3 (NaOH amount) was found to give significant effect for both the models. Figure 16 shows the effect of varying RHA/CaO ratio and amount of NaOH on SSC at constant hydration period (12 h) and hydration temperature (200 °C) for sorbents prepared using the un-treated and pre-treated RHA, respectively. The interaction characteristic for both types of sorbent appears to be similar with a elongated U-shaped plots, i.e. in one axis, there is a linear increase in SSC, however, on the other axis, the SSC increase up to only a certain point, then decreases thereafter. To be specific, when the amount of NaOH was held constant, an increase in the RHA/CaO ratio significantly increases the SSC of both types of sorbents prepared. Conversely, when the RHA/CaO ratio was maintained constant, the SSC of both types of sorbent prepared increase with increasing amount of NaOH up to about 0.25 mol/l. At higher concentration of NaOH, the SSC gradually decreases. This result reflects that the optimum concentration of NaOH to be used in the preparation mixture that favors high sorbent SSC is about 0.25 mol/l. At this optimum value, the maximum SSC of sorbents prepared using RHA$_{300\,°C}$ and RHA$_{600\,°C}$ was obtained at 19.73 and 24.02 mg SO_2/g sorbent respectively (Table 4). This result is in concurrence with the work reported by previous researcher [4, 20].
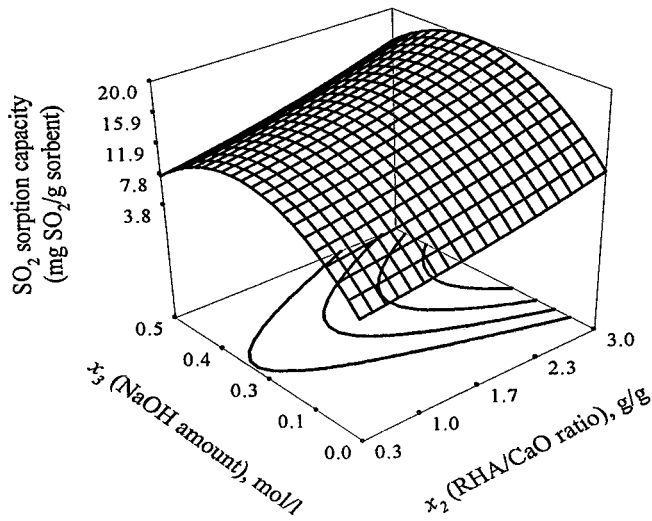
(a)
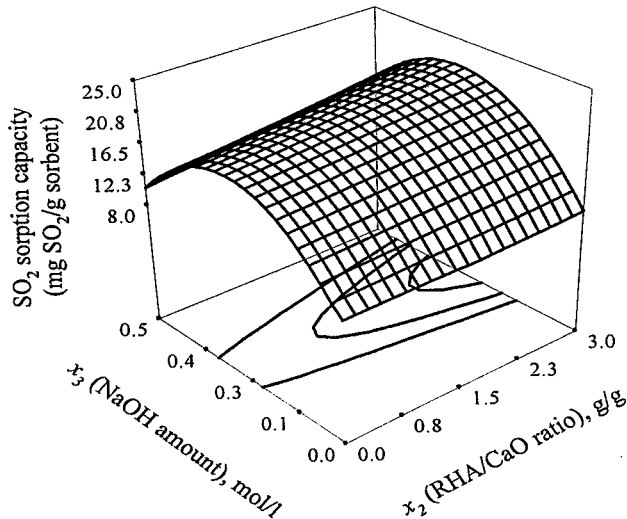
(b)

Figure 16. Surface plot of SSC as a function of RHA/CaO ratio and additive amount: (a) sorbent prepared from $RHA_{300 °C}$, (b) sorbent prepared from $RHA_{600 °C}$.

2.2.3.3. Effect of the addition of NaOH as additive.

Based on the data tabulated in Table 4, the inclusion of NaOH as additive in the preparation mixture resulted in sorbents with significantly higher SSC as compared to sorbents prepared without the addition of NaOH. For sorbents prepared without the addition of NaOH, the SSC obtained ranges from 3.43 to 11.15 mg SO_2/g sorbent while for sorbents prepared with the addition of NaOH, the SSC obtained ranges from 9.44 to 24.02 mg SO_2/g sorbent. This results clearly indicates that the addition of NaOH in the sorbent significantly increases the SSC of the resulting sorbent with an optimum NaOH concentration of about 0.25 mol/l. In order to study the role of NaOH, we have attempted to test the desulfurization capacity of using NaOH alone, but with no success as NaOH liquefied easily at high reaction temperature. Nevertheless, we could conclude that the increase in the sorbent SSC with the addition of NaOH is not significantly due to the direct reaction between NaOH

(strong base) and SO_2 (acidic gas) because if this were to be the case, higher concentration of NaOH would have resulted in even higher sorbent SSC. However, as mentioned earlier, the addition of NaOH with concentration higher than 0.25 mol/l resulted in a decrease in the sorbent SSC. Nevertheless, a small amount of NaOH could still directly react with SO_2 to form Na_2SO_3.

Previously, it was reported that the presence of NaOH as additive at optimum value might increase the dissolution rate of silica from the ash (the rate-limiting step of the reaction between ash and Ca-based compouns) [4]. The increase in the dissolution of silica will eventually increase the formation of Si-Ca complex that has a high SSC [1,7,24,25]. Nevertheless in this study, the X-ray diffraction pattern of sorbents prepared with the addition of NaOH as shown in Figure 17 exhibited different results as compared with our earlier examination of RHA sorbent without NaOH addition. In our previous discussion, the key factor for high SSC for sorbents prepared from RHA without the addition of NaOH is the formation of specific Ca-Si complex in the sorbent. However, the XRD pattern of sorbent prepared from RHA_{300} °C and RHA_{600} °C with the addition of NaOH (Figure 17) exhibited otherwise. Only a weak peak corresponding to calcium magnesium silicate hydroxide is detected in sorbent D12 prepared from RHA_{300} °C, while the main phases were identified as $CaCO_3$ and $Ca(OH)_2$. For sorbent D10 prepared using RHA_{600} °C, only weak peaks of $CaCO_3$ was detected. Nevertheless, the peak intensity of amorphous silica was found to reduce in both the sorbents indicating that it has reacted with silica to form highly amorphous compounds that cannot be detected by XRD. The absence of Ca-Si complex in the sorbent indicates that the reaction between CaO and silica during the hydration process has somehow been inhibited by the presence of NaOH. One possible reason is due to the fact that NaOH is a strong alkaline and thus the addition of NaOH limits the dissolution of CaO as both are basic compounds (common ion effect) [4]. Since we can now rule out that the high SSC of sorbents prepared with the addition of NaOH is not due to the formation of Ca-Si complex, thus the next step to further understand the role of NaOH in increasing the sorbent SSC is by studying the surface morphology of the sorbent.
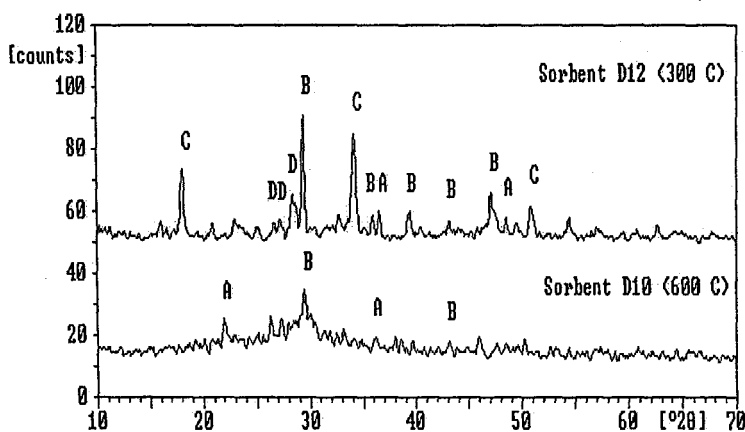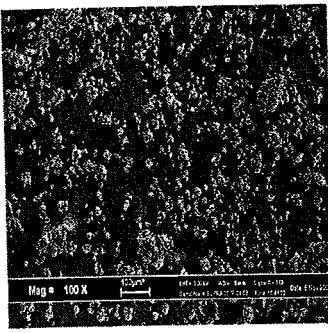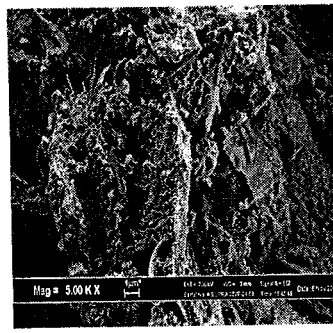

Figure 17. XRD pattern of sorbent D10 (prepared from RHA_{600} °C) and D12 (prepared from RHA_{300} °C). XRD label: (A) SiO_2; (B) $CaCO_3$; (C) $Ca(OH)_2$; (D) $Ca_2Mg_5Si_8O_{22}(OH)_2$.

Figure 18 and 19 show the SEM Micrograph of sorbents prepared using RHA_{300} °C and RHA_{600} °C respectively before and after reacting with SO_2 at various magnification. Based on Figure 18(b) and 19(b), it was observed that the skeletal structure of RHA was no longer visible after the hydration process. Instead, the sorbents were found to have needle like appearance structure. The extend of reaction between the sorbent and SO_2 can be evaluated by comparing Figure 18(a) and 18(c) or Figure 19(a) and 19(c). Looking at Figure 18(a) and 18(c), it was observed that the particle size of the sorbent significantly increase after the reaction with SO_2. Similar results can be obtained by looking at Figure 19(a) and 19(c). The larger particle size of the sorbent could be due to the agglomerating of smaller particles during the desulfurization reaction. The extensive agglomeration could also be because of higher content of water vapor present on the surface of the sorbent during the desulfurization reaction. This has been discussed in Section 2.2.2. Thus, with the addition of NaOH in the sorbent that can act as a deliquescent material, more water vapor are presence on the surface of the sorbent leading to higher SSC. However, the addition of NaOH higher than 0.25 mol/l caused the SSC to decrease. As described earlier, addition of higher concentration of NaOH limits the dissolution of CaO as both are basic compounds (common ion effect). Closer scrutiny at higher magnification (5000X) reveals coarse surface protuberances on the sorbent after reacting with SO_2 for both types of sorbents (Figure 18(d) and 19(d)). The surface of the sorbent was covered by lumps of uneven shapes particles, which is most probably the products of the desulfurization reaction.
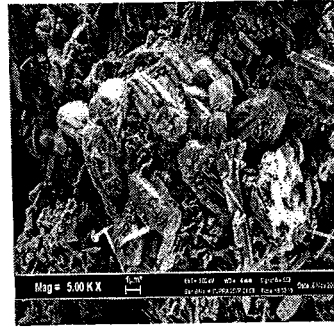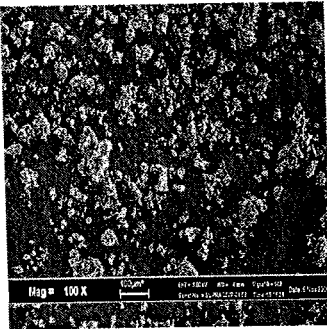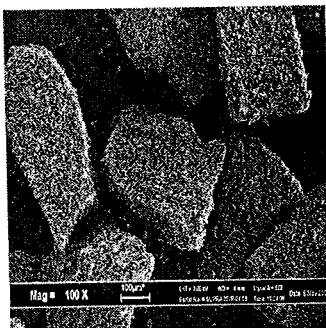
(a)

(b)
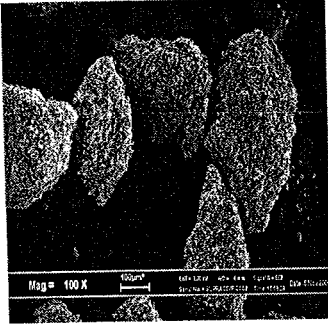
(c)

(d)

Figure 18. SEM Micrograph of sorbent D12 prepared from $RHA_{300\,°C}$: (a) at 100X (b) at 5000X (c) after reaction with SO_2 at 100X and (d) after reaction with SO_2 at 5000X
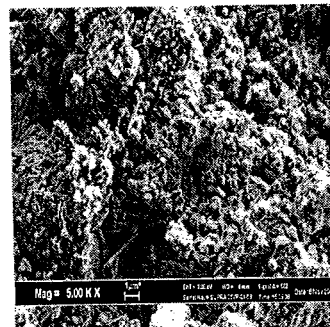
(a)

(b)

(c)

(d)

Figure 19. SEM Micrograph of sorbent D10 prepared from $RHA_{600\,°C}$: (a) at 100X (b) at 5000X (c) after reaction with SO_2 at 100X and (d) after reaction with SO_2 at 5000X

2.2.3.4 Effect of un-treated vs. pre-treated RHA and optimization.

The results on sorbent preparation variables appraised by central composite face centered design until this point has demonstrated that both the sorbents prepared from un-treated and pre-treated RHA shows higher sorbent SSC as compared to previous study using sorbent prepared from coal fly ash and oil palm ash. However, as mentioned earlier, one of the aims of this study is to determine if the un-treated RHA or pre-treated RHA is more favorable in producing sorbent with a higher SSC. One way of doing this is first by optimizing the sorbent preparation variables to obtain sorbent with the highest SSC. Again, this optimization process is carried out by using the optimization point prediction function in Design Expert Software, whereby 3 different combinations of sorbent preparation variables that can result in sorbent with the highest SSC were obtained for both types of sorbent. The prediction is given in Table 7 along with their optimization criteria, predicted and experimental values of SSC. Based on the data presented in Table 7, it was found that the software gave a very accurate prediction as the error between predicted and experimental value is less than 10%. Apart from that, the results also show that the sorbents prepared from RHA $_{600\ °C}$ resulted in sorbent with a higher SSC possibility due to higher content of amorphous silica as confirmed by the XRD analysis. However, a lengthy hydration time of 20 h is needed for the preparation of the sorbent. The reason for the elongated hydration period required for the preparation of RHA$_{600\ °C}$ sorbents might be due to the presence of NaOH which reduces the dissolution of CaO. Since RHA$_{600\ °C}$ already contains a very high amount of reactive silica, the positive effect of NaOH on the sorbent SSC is no longer significant.

Table 7. Sorbent preparation with optimum condition for the highest (three) desirability solutions

x_1	x_2	x_3	x_4	Desirability	SSC (mg SO$_2$/g sorbent)		Error (%)
					Predicted	Experimental	
$x_1 / x_2 / x_3$ (in range value), x_4 (minimum value) with maximum response*							
5.67	2.91	0.31	150	1.00	20.50	19.73	-3.72
RHA$_{300\ °C}$ 8.63	2.94	0.32	150	1.00	19.79	18.02	-8.94
7.11	2.94	0.29	150	1.00	20.13	18.88	-6.24
20	0.40	0.27	150	1.00	23.98	23.17	-3.39
RHA$_{600\ °C}$ 20	0.30	0.24	150	1.00	23.91	24.88	4.06
20	0.53	0.31	150	0.99	23.68	24.02	1.47
x_2 / x_3 (in range value), x_1 / x_4 (minimum value) with maximum response*							
4	2.76	0.40	150	1.00	19.81	18.88	-4.70
RHA$_{300\ °C}$ 4	2.71	0.27	150	1.00	20.09	19.73	-1.77
4	2.64	0.31	150	1.00	20.15	18.88	-6.32
4	0.33	0.26	150	0.89	18.85	19.73	4.67
RHA$_{600\ °C}$ 4	0.58	0.25	150	0.88	18.64	17.16	-7.95
4	0.85	0.24	150	0.87	18.37	19.73	-7.41

* Optimization criteria

This result indirectly depicted that the presence of additive (NaOH) will only give significant positive effect on the sorbent SSC when the availability of raw reactive species, in this case amorphous silica, is less/limited. Nevertheless, such a long hydration period is unlikely to be used in the industry due to practical constraints and unfavorable economic concerns. Thus, we attempt to optimize the system again by now fixing the hydration period at 4 h. Based on the results also tabulated in Table 7, it was observed that both the different types of sorbents now shows almost similar sorbent SSC. Therefore, for practical and cost-effective considerations, sorbents prepared from un-treated RHA (RHA$_{300\ °C}$) is more favorable than sorbents prepared using pre-treated RHA (RHA$_{600\ °C}$).

2.2.4 Removal of SO$_2$/NO Over Rice Husk Ash (RHA)/CaO-Supported Metal Oxides

The sorption characteristics of SO$_2$ over the RHA/CaO sorbent with or without additive has been discussed However, this sorbent was unable to remove NO gases. In this section, RHA/CaO sorbent was prepared by employing impregnation method with various metal oxides. This sorbent was then tested for SO$_2$ and NO removal activity.

The X-ray diffraction patterns of the raw RHA and as well as prepared RHA/CaO sorbent supported with ZnO, MnO, Fe$_2$O$_3$ and CeO$_2$, respectively, are shown in Figure 20. The X-ray reflections of amorphous silica from raw RHA are observed with a broad peak around $2\theta \sim 22°$ diffraction angle [36,39]. Whereas, the prepared

RHA/CaO sorbents supported with various metal oxides displayed poor crystallinity with the diffraction lines due to only silica ($2\theta \sim 22°$) and calcite ($2\theta \sim 29.4°$) [41] are visible. No diffraction lines attributed to ZnO, MnO, Fe_2O_3 and CeO_2 crystal phases obviously appeared in the prepared RHA/CaO sorbents, indicating that these metal oxides were highly dispersed on the RHA/CaO surface.
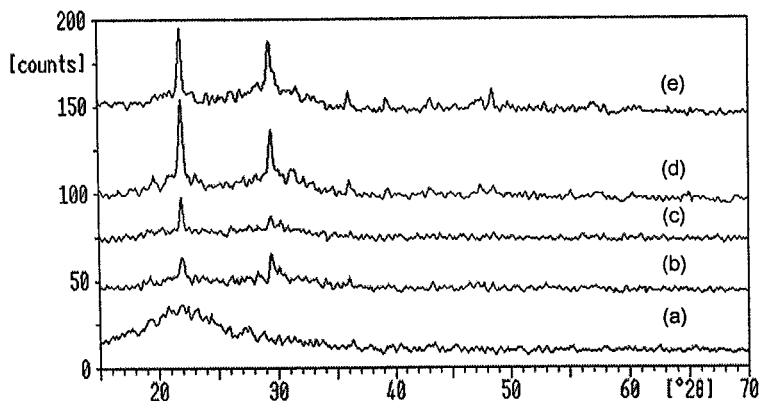

Figure 20. X-ray diffraction patterns for: (a) raw RHA and RHA/CaO sorbent supported with (b) ZnO, (c) MnO, (d) Fe_2O_3, (e) CeO_2.

In order to compare the performance of these prepared sorbents, activity tests were carried out. Table 8 shows the sorption capacity for simultaneous removal of SO_2 and NO for RHA/CaO-supported metal oxide sorbents in terms of the time for sorbent can maintain 100% removal and the amount of SO_2 and NO being absorbed. It was observed that sorption capacity of each sorbent in removal of SO_2 and NO are different. The longer the time of the sorbent can maintain 100% removal of SO_2 and NO, the higher the amount of SO_2 and NO were removed from simulated flue gas. It was found that most of the supported metal oxides exhibit good result in simultaneous removal of SO_2/NO. However, there were no significant differences in the sorption capacity during 100% SO_2 removal over RHA/CaO sorbent-supported with MgO, CoO, ZnO and Al_2O_3 indicating that reaction rate for SO_2 removal was almost similar under the operating conditions used. A significant improvement in the SO_2 sorption capacity was achieved when RHA/CaO sorbent were impregnated with MnO, Fe_2O_3 and CeO_2. On the other hand, RHA/CaO sorbent supported with ZnO, Al_2O_3, Fe_2O_3 and CeO_2 shows maximum NO removal during 60 min operation time. Nevertheless, only a small amount of NO was removed when MgO was impregnated to RHA/CaO sorbent. The different of SO_2/NO sorption capacities between the active phases may be due to the characteristic nature and the reaction mechanism of these sorbents. RHA/CaO-supported CeO_2 exhibit a higher sorption capacity than other supported metal oxide for removing SO_2 and NO simultaneously.

Table 8. Sorption capacity of different RHA/CaO-supported metal oxide sorbents for simultaneous removal of SO_2 and NO

RHA/CaO-supported metal oxide	Time during 100% removal (min)		Sorption capacity (mg pollutant/g sorbent)	
	SO_2	NO	SO_2	NO
MgO	13	3	10.218	0.138
MnO	20	16	15.720	0.736
CoO	16	35	12.576	1.610
ZnO	9	60	7.074	2.761
Al_2O_3	11	60	8.646	2.761
Fe_2O_3	23	60	18.078	2.761
CeO_2	36	60	28.296	2.761

The RHA/CaO-supported CeO_2 sorbent was further subjected to FTIR analysis to characterize specific functional group. The corresponding FTIR spectrums of raw RHA, RHA/CaO-supported CeO_2 sorbent before and after subjected to SO_2/NO are plotted in Figure 21. The spectrums showed the raw RHA and prepared sorbents were mainly composed of amorphous silica due to a band situated around 460-470 cm^{-1} (Si-O-Si band),

795 cm^{-1} (Si-O-Si symmetric) and 1100 cm^{-1} (Si-O-Si asymmetric) [29-32]. Moreover, the band around 3450 cm^{-1} is typically caused by hydroxyl groups or adsorbed water due to O-H stretches. Since the sorbent was prepared from RHA, this also can be caused by silanol groups [30,32]. On the other hand, after RHA/CaO-supported CeO$_2$ sorbent was subjected to SO$_2$/NO gases, the products of the reaction were detected, mainly sulfate (SO$_4^{2-}$) and nitrate (NO$_3^-$) species. These species are characterized by S-O bending near 600 cm^{-1}, a single peak close to 657 cm^{-1} and a broad band due to S-O stretching at around 1050-1100 cm^{-1}. Furthermore, a single peak close to 1640 cm^{-1} related to hydroxyl groups (O-H bending) was also appeared [30,34]. Additionally, a slight/weak band around 853 cm^{-1} and 1384 cm^{-1} are detected for nitrate (NO$_3^-$) species [33,34].
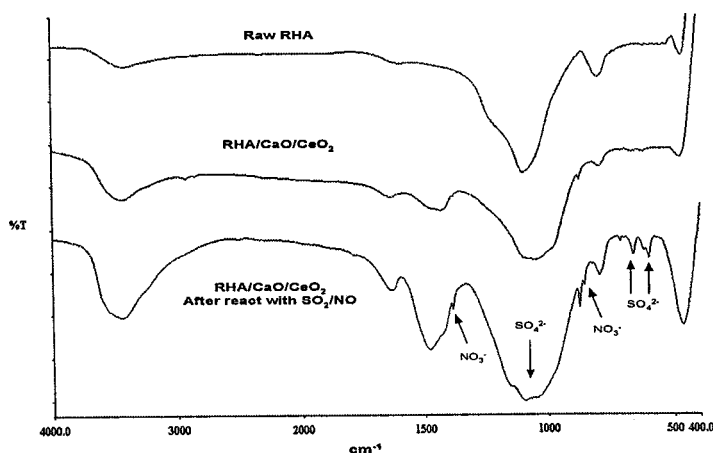

Figure 21. FTIR spectra of the raw RHA, RHA/CaO-supported with CeO$_2$ and after react with simulated flue gas

As many authors have shown that the presence of NO together with SO$_2$ can enhance the sorption capacity of calcium-based sorbents [42-45], whereby the existence of SO$_2$ and NO accelerated the removal of each other, respectively. In this study, it was also assumed that metal oxide, particularly CeO$_2$ plays a catalytic role in simultaneous removal of SO$_2$ and NO. CeO$_2$ has been reported to have sufficient oxidation activity at active centers to promote oxidation of SO$_2$ to SO$_3$ and allow the sorption of SO$_2$/SO$_3$ (at basic sites) with formation of sulfates [46]. At the same time, oxidation and sorption of NO to form nitrates would also take place.

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3. CONCLUSIONS

The removal of SO_2 and NO from simulated flue gas were investigated utilizing rice husk ash (RHA)-based sorbent In the preliminary study, sorbents were prepared from RHA and CaO using water hydration method and tested for SO_2 sorption capacities (SSC) using fixed bed reactor. The effect of various sorbent preparation variables were examined using response surface methodology (RSM). Based on the model developed, the amount of RHA, amount of CaO and hydration period used in the preparation of sorbent significantly influenced the SSC of the sorbent. To further increase the SSC of these kind of sorbents, different type of additives have been employed (i.e. NaOH, $CaCl_2$, LiCl, $NaHCO_3$, NaBr, $BaCl_2$, KOH, K_2HPO_4, $FeCl_3$ and $MgCl_2$). Most of the additives tested increased the SSC of RHA/CaO sorbent, because it allows for a higher degree of SO_2 removal, whereby NaOH has been found to be the best additive among all the other additives studied. However, this sorbent was unable to remove NO gases. Therefore, modification has been made for this kind of sorbent by employing impregnation method with various metal oxides. The results showed that RHA/CaO sorbents impregnated with CeO_2 displayed the highest sorption capacity among other impregnated metal oxides for the simultaneous removal of SO_2 and NO. Infrared spectroscopic results indicate the formation of both sulfate (SO_4^{2-}) and nitrate (NO_3^-) species due to a catalytic role played by CeO_2.

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Key Factor in Rice Husk Ash/CaO Sorbent for High Flue Gas Desulfurization Activity

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Siliceous materials such as rice husk ash (RHA) have potential to be utilized as high performance sorbents for the flue gas desulfurization process in small-scale industrial boilers. This study presents findings on identifying the key factor for high desulfurization activity in sorbents prepared from RHA. Initially, a systematic approach using central composite rotatable design was used to develop a mathematical model that correlates the sorbent preparation variables to the desulfurization activity of the sorbent. The sorbent preparation variables studied are hydration period, x_1 (6–16 h), amount of RHA, x_2 (5–15 g), amount of CaO, x_3 (2–6 g), amount of water, x_4 (90–110 mL), and hydration temperature, x_5 (150–250 °C). The mathematical model developed was subjected to statistical tests and the model is adequate for predicting the SO_2 desulfurization activity of the sorbent within the range of the sorbent preparation variables studied. Based on the model, the amount of RHA, amount of CaO, and hydration period used in the preparation step significantly influenced the desulfurization activity of the sorbent. The ratio of RHA and CaO used in the preparation mixture was also a significant factor that influenced the desulfurization activity of the sorbent. A RHA to CaO ratio of 2.5 leads to the formation of specific reactive species in the sorbent that are believed to be the key factor responsible for high desulfurization activity in the sorbent. Other physical properties of the sorbent such as pore size distribution and surface morphology were found to have insignificant influence on the desulfurization activity of the sorbent.

Introduction

Combustion of fossil fuels, such as coal and oil, generates gaseous pollutants, especially sulfur dioxide (SO_2). It is believed that SO_2 emissions can cause various adverse effects on human health (respiratory) and on the environment (acid rain) (1, 2). Therefore, control of SO_2 emissions has become increasingly stringent all over the world and has resulted in national and regional initiatives to reduce its emissions. Presently, SO_2 is being removed using various types of flue gas desulfurization (FGD) units. A wet-type FGD unit based on a limestone slurry scrubbing is most widely used and suitable for large scale boilers such as those installed in coal- or oil-fired power plants. Although the wet process has a

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high efficiency in removing SO_2, it has a number of disadvantages, mainly the large space required for installation, the large volume of water required, and high capital and operating expenses. In contrast, dry-type FGD offers a simpler alternative method to the wet-type FGD, and is suitable for small-scale boilers. Basically, dry-type FGD utilizes solid alkaline sorbents to adsorb SO_2 via the neutralization process (3, 4). Recent research in dry-type FGD has focused on synthesizing different types of dry calcium-based sorbents that have a high capacity for SO_2 sorption.

In order to synthesize calcium-based sorbents that have a high activity for SO_2 sorption, siliceous starting materials need to be activated with CaO or Ca(OH)$_2$ (5). Most of the siliceous materials reported in the literature are coal fly ash (3, 6–10), oil palm ash (11), diatomaceous earth (12), and silica fume (4, 13). Recently, rice husk ash (RHA) was reported to have a better potential as the source of siliceous material due to its high content of silica which ranges from 60 to 90% (14). RHA is an agricultural waste material that is abundantly available through the rice milling process in rice-producing countries like Malaysia and Thailand. In Malaysia alone, it is estimated that 78 thousand tons of RHA is produced annually (15). At the moment, RHA is used as a cement substitute (16–18), as an alternative source for active silica production (19–21), for vulcanizing rubber (22), and as an oil adsorbent (23–24). However, most of the utilization of RHA still remains at a laboratory scale. Therefore, a huge amount of RHA has to be disposed, either in landfills or ash ponds. This method of ash disposal is a waste of valuable land area which is not easily available in urban areas. Since the utilization of RHA is still limited, the synthesis of sorbent from this agricultural waste material would offer an attractive use of RHA to capture SO_2 from the flue gases of small-scale boilers running on sulfur-containing fossil fuel. This would help to reduce the problem of ash disposal faced by the rice milling industry. At the same time, converting a waste into a value-added product would also bring economic benefits to the rice millers.

In our previous study, we reported the optimum conditions to prepare high surface area sorbent from RHA (25). However, our further study revealed that surface area is not the key factor for high desulfurization activity in sorbents prepared from RHA. Little information is thus available for synthesizing RHA sorbents that have a high desulfurization activity. Furthermore, the key factor for high desulfurization activity in sorbents prepared from other siliceous materials has been inconclusive. Some studies report high surface area is the key factor in having sorbent with a high desulfurization activity (9, 10, 13), while others report it is the amount of Ca ions present in the preparation mixture (4, 6). These previous results suggest further study is warranted to identify the key factor in sorbent synthesized from siliceous material that could lead to having high desulfurization activity.

The objective of this work is to identify the key factor for high desulfurization activity in sorbents prepared from RHA. Simultaneously, this work also intends to identify the sorbent preparation variables that could lead to producing sorbent with a high desulfurization activity.

Experimental Section

Sorbent Preparation. The sorbents were prepared from lime (CaO) and rice husk ash (RHA). The CaO was obtained from BDH Laboratories, England while the RHA was provided by Kilang Beras & Minyak Sin Guan Hup Sdn.Bhd., Nibong Tebal, Malaysia. The RHA used was collected directly after the burning of rice husk without any pretreatment. However, it
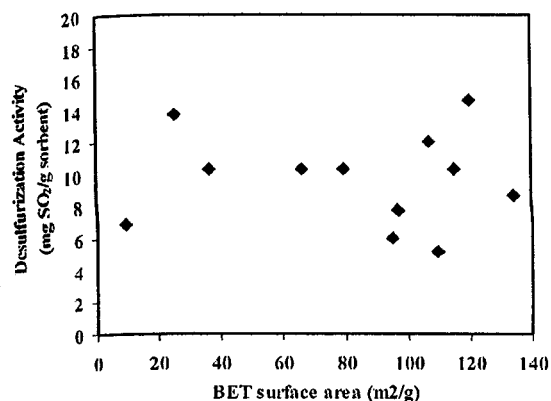
FIGURE 1. Desulfurization activity as a function of the BET specific surface area.

(XRD) spectra were recorded on a Siemens D5000 X-ray diffractometer for the powdered samples with Cu Kα radiation in the range of diffraction angle (2θ) 10–90° at a sweep rate of 1°/min to determine the phases present in the sorbent.

Results and Discussion

Effect of Specific Surface Area. To elucidate the role of specific surface area on the desulfurization activity of the sorbents prepared from RHA, sorbents with surface areas ranging from 9.52 to 134 m^2/g were subjected to activity study. Figure 1 shows the desulfurization activity of the sorbents versus their specific surface area. The desulfurization activity of the sorbent did not correlate with the specific surface area of the sorbent. This indicates surface area may not be the key factor that influences the desulfurization activity of sorbents prepared from RHA. Other factors in sorbents prepared from RHA are thus more important to having a high desulfurization activity.

Correlation Between Sorbent Preparation Variables to Desulfurization Activity. To identify the key factor in sorbents prepared from RHA involved in high desulfurization activity, a statistically designed set of experiments was conducted to study the effect of five sorbent preparation variables and their interactions on the desulfurization activity of the sorbent. From the data presented (Table 2), sorbent A16 exhibited the highest desulfurization activity at 17.2 mg SO_2 captured/g sorbent. Sorbent A21 exhibited the lowest desulfurization activity at 1.72 mg SO_2 captured/g sorbent. Visual inspection of the data tabulated in Table 2 also reveal that sorbent preparation variables have a significant effect on the desulfurization activity of the sorbent. Since there are five sorbent preparation variables that were studied simultaneously, a more systematic method to study the influence of the various sorbent preparation variables on the desulfurization activity would be to develop a mathematical model that correlates the sorbent preparation variables to the desulfurization activity of the sorbent.

Using multiple regression analysis, the response (desulfurization activity) obtained in Table 2 was correlated with the five sorbent preparation variables using the mathematical model as shown in eq 1. The coefficients of the full regression model equation and their statistical significance were determined and evaluated using Design-Expert software. The final regression model equation obtained in terms of coded value after discarding the insignificant effects (identified using the Fisher Ftest) is given as

$$Y = 7.11 + 1.72\,x_1 + 1.86\,x_2 + 1.72x_3 + 1.20\,x_1^2 + 0.980\,x_2^2 + 0.970\,x_2x_3 \quad (2)$$

TABLE 3. Anova for the Regression Model Equation and Coefficients

source	sum of squares	degree of freedom	mean of square	F test	prob > F
model	313	20	15.7	20.8	<0.0001*[a]
x_1	70.7	1	70.7	93.8	<0.0001
x_2	82.9	1	82.9	110	<0.0001*
x_3	70.7	1	70.7	93.8	<0.0001*
x_4	0.490	1	0.490	0.650	0.437
x_5	0.00	1	0.00	0.00	1.00
x_1^2	42.9	1	42.9	56.9	<0.0001*
x_2^2	29.0	1	29.0	38.5	<0.0001*
x_3^2	1.01	1	1.01	1.34	0.272
x_4^2	0.550	1	0.550	0.730	0.413
x_5^2	1.74	1	1.74	2.31	0.157
x_1x_2	0.00	1	0.00	0.00	1.00
x_1x_3	1.66	1	1.66	2.20	0.166
x_1x_4	0.00	1	0.00	0.00	1.00
x_1x_5	0.180	1	0.180	0.240	0.631
x_2x_3	14.9	1	14.9	19.8	0.001*
x_2x_4	0.00	1	0.00	0.00	1.00
x_2x_5	0.180	1	0.180	0.240	0.631
x_3x_4	0.180	1	0.180	0.240	0.631
x_3x_5	0.740	1	0.740	0.980	0.344
x_4x_5	0.180	1	0.180	0.240	0.631
residual	8.29	11	0.750		

[a] Asterisk (*) indicates significant term.

A positive sign in front of a term indicates a synergistic effect. The statistical significance of eq 2 was verified by the Fisher test (F test) using analysis of variance (ANOVA) as shown in Table 3.

Based on a 95% confidence level, the mathematical model developed was found to be significant in predicting the desulfurization activity of the sorbent, as the computed F value (20.8) is higher than the theoretical $F_{0.05\,(20,11)}$ value (2.65). Furthermore, the probability value (P value) of the model was less than 0.0001, indicating the model is highly reliable. Each significant term in the model was also found to be significant at a 95% confidence level, as the computed F values for the respective terms are higher than the theoretical $F_{0.05\,(1,11)}$ value (4.84). The validity of the mathematical model was also checked using the lack-of-fit test and the coefficient of determination (R^2). The P value of lack-of-fit test demonstrates that considerable improvement was achieved after the exclusion of the statistically insignificant terms. The P value of lack-of-fit for the model after excluding the insignificant terms is 0.0769 (an increase from 0.0319 when all the terms were included in the model). This value is greater than 0.05 indicating that the lack-of-fit for the mathematical model is insignificant. Insignificant lack-of-fit is good because the model fit the data well. Apart from that, the coefficient of determination (R^2) of the model is 0.952 indicating that 95.2% of the variability in the response (desulfurization activity) could be explained by the mathematical model. When all the terms (significant and insignificant) are included in the mathematical model, the R^2 value is increased by only 0.0221. This result justifies dropping the insignificant terms from the mathematical model as the insignificant terms only contribute 2.21% to the variability in the response (desulfurization activity).

The mathematical model developed was also inspected for its validity using visual inspection by plotting the experimental versus the predicted sorbent desulfurization activity (Figure 2). The predicted values of the desulfurization activity of the 32 sorbents synthesized are also given in Table 2. The results demonstrated that the model provided a very accurate description of the experimental data, indicating that

TABLE 1. Coded and Actual Values of the Variables Used in the Design of Experiment

			levels of variables				
variable	units	coding	−2	−1	0	1	2
hydration period	h	x_1	1	6	11	16	21
amount of RHA	g	x_2	0	5	10	15	20
amount of CaO	g	x_3	0	2	4	6	8
amount of water	mL	x_4	80	90	100	110	120
hydration temperature	°C	x_5	100	150	200	250	300

was sieved prior to use to obtain ash with a particle size of 125 μm. The BET specific surface areas of RHA and CaO are 56.3 and 5.62 m^2/g, respectively. The chemical composition of RHA is 73.0% SiO_2, 1.40% P_2O_5, 0.350% Al_2O_3, 0.250% Fe_2O_3, 0.620% CaO, 2.20% K_2O, 0.890% MgO, 0.290% others, and 21.0% ignition loss.

The sorbents were prepared using the water hydration method. Two grams of CaO was added to 90 mL of distilled water at 80 °C. Upon stirring, the temperature of the slurry rose up to 90 °C and, simultaneously, 5 g of RHA was added into the slurry. The resulting slurry was heated at about 100 °C for 16 h with stirring. The slurry was filtered and dried at 150 °C for 2 h. The sorbents in powder form were pelletized, crushed, and sieved to obtain the required particle size range of 250–300 μm. The sorbent preparation variables of hydration period, amount of RHA, amount of CaO, amount of water, and hydration temperature were varied according to the experimental design described below.

Experimental Design. Response surface methodology was used to study the individual and interaction effects of various sorbent preparation variables (independent variables) toward the desulfurization activity of the sorbent (dependent variables). In this study, a half-fraction five-variable central composite rotatable design (CCRD) with replicate in each point and α = 2 was adopted (26). Table 1 presents the range and levels of the five sorbent preparation variables studied.

In order to use CCRD to study the five sorbent preparation variables, 16 factorial points (A1–A16), 10 axial points (A17–A26), and 6 replicates at the center point (A27–A32) are required for a total of 32 experiments. Table 2 shows the complete experiment design matrix. Six replicate runs at the center of the design were performed to allow the estimation of pure error. All experiments were carried out in a randomized order to minimize the effect of unexplained variability in the observed responses due to extraneous factors. The data from Table 2 were utilized to develop a correlation between the sorbent preparation variables and its desulfurization activity by fitting it to a second-order polynomial equation as shown below:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \quad (1)$$

where Y is the predicted desulfurization activity (mg SO_2 captured/g sorbent), b_0 is the offset term (constant), b_i is the linear coefficients, b_{ii} is the quadratic coefficients, b_{ij} is the interaction coefficients, x_i and x_j are the coded values of the various sorbent preparation variables, and n is the number of sorbent preparation variables.

Statistical Analysis and Model Fitting. Design Expert software version 6.0.6 (STAT-EASE Inc., Minneapolis, MN) was used to develop the mathematical model (as shown in eq 1) that correlates the sorbent preparation variables with its desulfurization activity based on the data presented in Table 2. The accuracy of the model was evaluated by the

TABLE 2. Experimental Design Matrix and Result of the Ccrd

run (solid code)	x_1	x_2	x_3	x_4	x_5	experimental desulfurization activity (mg/g)	predicted desulfurization activity (mg/g)
A1	−1	−1	−1	−1	1	5.15	4.77
A2	1	−1	−1	−1	−1	8.58	8.41
A3	−1	1	−1	−1	−1	7.72	7.41
A4	1	1	−1	−1	1	10.3	9.77
A5	−1	−1	1	−1	−1	6.01	6.05
A6	1	−1	1	−1	1	10.3	10.1
A7	−1	1	1	−1	1	12.0	11.7
A8	1	1	1	−1	−1	15.4	15.3
A9	−1	−1	−1	1	−1	6.01	5.69
A10	1	−1	−1	1	1	8.58	8.05
A11	−1	1	−1	1	1	7.72	7.05
A12	1	1	−1	1	−1	10.3	9.84
A13	−1	−1	1	1	1	6.86	6.55
A14	1	−1	1	1	−1	10.3	10.2
A15	−1	1	1	1	−1	12.0	11.8
A16	1	1	1	1	1	17.2	16.7
A17	−2	0	0	0	0	7.72	8.35
A18	2	0	0	0	0	14.6	15.2
A19	0	−2	0	0	0	6.86	7.20
A20	0	2	0	0	0	13.7	14.6
A21	0	0	−2	0	0	1.72	2.77
A22	0	0	2	0	0	9.44	9.63
A23	0	0	0	−2	0	6.86	7.20
A24	0	0	0	2	0	6.86	7.77
A25	0	0	0	0	−2	7.72	7.92
A26	0	0	0	0	2	6.86	7.92
A27	0	0	0	0	0	6.86	6.94
A28	0	0	0	0	0	6.86	6.94
A29	0	0	0	0	0	7.72	6.94
A30	0	0	0	0	0	6.86	6.94
A31	0	0	0	0	0	6.86	6.94
A32	0	0	0	0	0	7.72	6.94

coefficient of determination (R^2), lack-of-fit test, and analysis of variance (ANOVA), all performed using the Design Expert software.

Activity Study. The activity of the sorbents was tested in a fixed-bed reactor attached to an experimental rig. A stream of gaseous mixture containing SO_2 (2000 ppm), NO (500 ppm), O_2 (10%), water vapor, and N_2 as the balance was subsequently passed through the sorbent at a reaction temperature of 100 °C. The concentration of the SO_2 in the flue gas was measured using a portable flue gas analyzer (IMR 2800P) before and after the sorption process. The schematic diagram and details of the activity study are presented elsewhere (9, 25). The desulfurization activity of the sorbent is expressed by the weight of SO_2 captured from the flue gas per gram of sorbent (27). The amount of SO_2 captured by the sorbent was evaluated from the time the sorbent could maintain 100% removal of SO_2 until it showed negligible activity (when the outlet SO_2 concentration became the same as the inlet SO_2 concentration). The weight of SO_2 captured by the sorbent was measured by integrating the difference between the inlet and outlet concentrations. The desulfurization activity in this work is also reported as the breakthrough curves of the desulfurization reaction (C/C_0 versus t), where C is the outlet concentration of SO_2 (ppm) from the reactor and C_0 is the initial concentration of SO_2 (ppm).

Chemical and Physical Analysis. The chemical composition of RHA was determined using a Rigaku RIX 3000 X-ray fluorescence (XRF) spectrometer. The specific surface area and pore size distribution of the sorbents and raw materials were determined using the BET and BJH methods, respectively, on an Autosorb-1 Quantachrome analyzer. A Leo Supra 35 VP scanning electron microscope (SEM) was used to examine the sorbent surface morphologies. X-ray diffraction
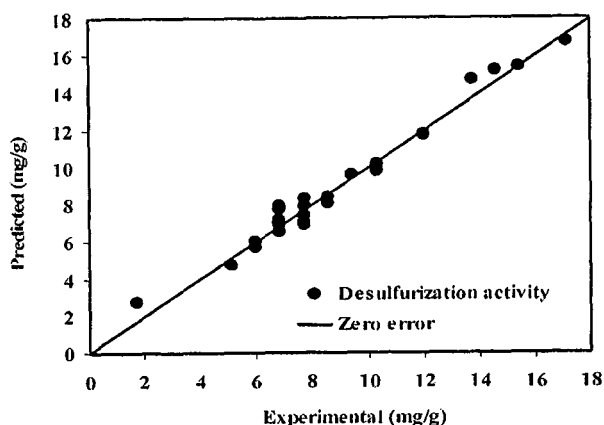
FIGURE 2. Experimental versus predicted desulfurization activity.

it was successful in capturing the correlation between the five sorbent preparation variables to the desulfurization activity of the sorbent. In addition, the R value (multiple correlation coefficient) for the plot was found to be 0.974, indicating a very good correlation between the experimental and predicted values. From all these validity tests, the model was found to be adequate for predicting the desulfurization activity of the sorbent within the range of the sorbent preparation variables studied.

Effects of Sorbent Preparation Variables. Based on the mathematical model, it was observed that the linear terms of hydration period (x_1), amount of RHA (x_2), and amount of CaO (x_3) were found to have significant positive effect (P values <0.05) on the desulfurization activity of the sorbent. In contrast, amount of water (x_4) and hydration temperature (x_5) did not have significant effects on the desulfurization activity. The quadratic terms of x_1 and x_2 also effect the desulfurization activity, but are less pronounced than the linear terms. The interaction between variables, amount of RHA (x_2) and amount of CaO (x_3) was also found to have significant effect on the desulfurization activity. Among all the significant variables that affect the desulfurization activity, amount of RHA (x_2) was found to have the largest effect (due to the highest F value). Hydration period (x_1) and amount of CaO (x_3) have almost similar effect, while the interaction between x_2 and x_3 has the least significant effect on the desulfurization activity. In our previous study (25), hydration temperature had the largest effect on the sorbent surface area prepared from RHA. However, as indicated in the discussion earlier, hydration temperature was found to have negligible effect on the desulfurization activity. Therefore, this result further supports the conclusion that high surface area may not be the key factor for sorbents having high desulfurization activity.

To facilitate a straightforward examination of the effect of amount of RHA (x_2) and amount of CaO (x_3) and their interaction, the mathematical model developed was utilized to construct three-dimensional response surfaces. Figure 3 a and b shows the desulfurization activity response surface and contour plot, respectively, with varying amount of RHA (x_2) and amount of CaO (x_3) at constant hydration period (11 h), amount of water (100 mL), and hydration temperature (200 °C). A significant interaction was observed between amount of RHA (x_2) and amount of CaO (x_3) (Figure 3). This observation is in agreement with the ANOVA results presented in Table 3 where the interaction term between x_2 and x_3 was found to have a prominent effect on the sorbent desulfurization activity (high F test value). When the amount of CaO was held constant at 2 g, an increase in the amount of RHA did not significantly affect the desulfurization activity of the sorbent. However, when the CaO was held fixed at a higher

(b)   Desulfurization Activity (mg SO₂/g sorbent)
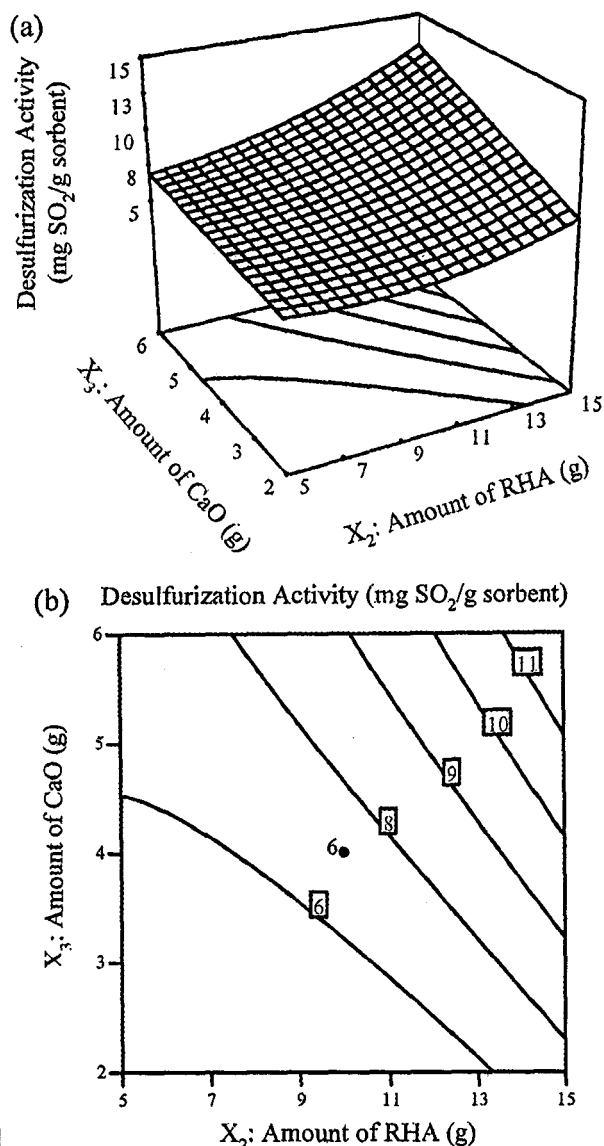
FIGURE 3. Effect of amount of RHA and amount of CaO on the desulfurization activity: (a) response surface plot and (b) contour plot.

amount (6 g), an increase in the amount of RHA increased the desulfurization activity of the sorbent significantly. Thus, the ratio of the amount of RHA to the amount of CaO used in the preparation mixture significantly influenced the desulfurization activity of the resulting sorbent. A similar result can also be obtained by observing the data trend tabulated in Table 2. Among the 32 different types of sorbent that were tested for its respective desulfurization activity, only sorbent A8 and A16 exhibited significantly high desulfurization activity. Comparing the sorbent preparation variables that were used to synthesize these two sorbents, the only similarity between them is the ratio of amount of RHA to CaO, which was 2.5. This observation indicates that the ratio of RHA to CaO used in the preparation mixture is an important factor that could lead to the synthesis of sorbent with a high desulfurization activity. Although sorbents A7 and A15 were also prepared using the same ratio, the desulfurization activity was found to be significantly lower. This is most probably due to the low hydration period used in the preparation step that limits the formation of the reactive species in the sorbent.
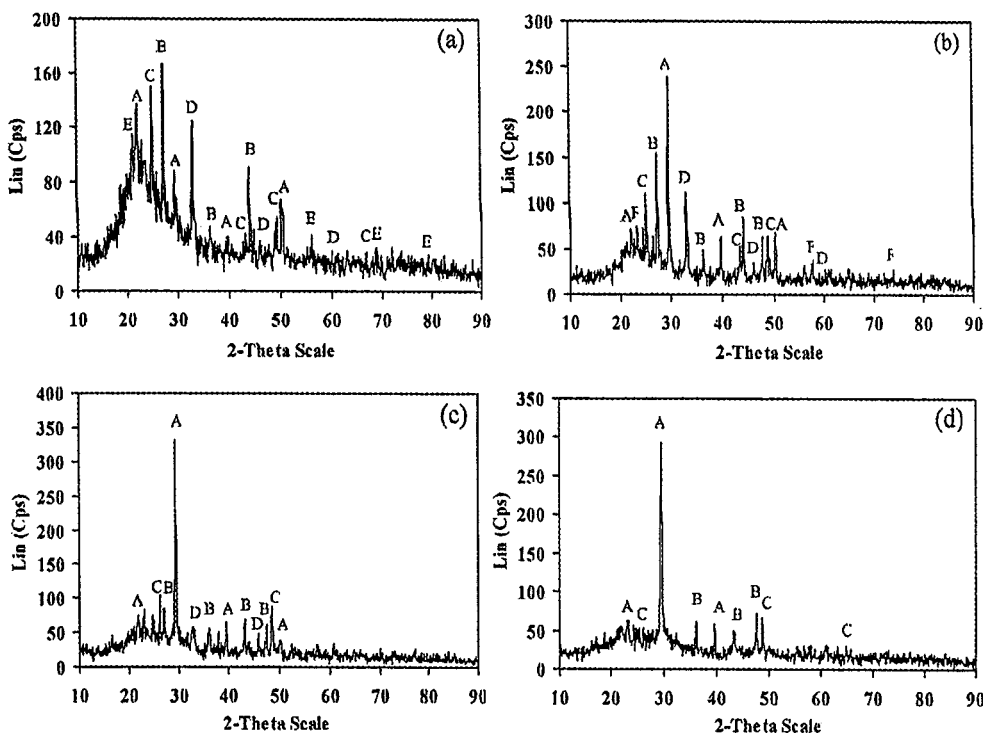
FIGURE 4. XRD spectrum of sorbent (a) A8; (b) A16; (c) A1; and (d) A21. XRD label: (A) vaterite ($CaCO_3$); (B) silica (SiO_2); (C) mountainite ((Ca, Na_2, K_2)$_2$ $Si_4O_{10}\cdot 3H_2O$); (D) iron oxide (Fe_2O_3); (E) calcium aluminum silicate ($CaAl_2Si_2O_8$); and (F) calcium silicate hydrate ($Ca_2SiO_4\cdot H_2O$).

The effect of hydration period on the desulfurization activity can be obtained directly by observing the data in Table 2. An increase in hydration period always increased the desulfurization activity of the sorbent. It has been reported that the reaction between calcium based materials and siliceous material involves a pozzolanic reaction that is very slow (28). Thus, a longer hydration period is required for the dissolution of silica from RHA to react with CaO to form the reactive species that is responsible for SO_2 sorption. Consequently, hydration period becomes the limiting factor for the formation of the reactive species in the sorbent. The desulfurization activity of the sorbent could be influenced by either the amount or type of reactive species formed in the sorbent. The total amount of raw materials used in the preparation mixture is not crucial in determining the total amount of reactive species formed in the sorbent, but it is the hydration period that is more crucial. Sufficient hydration period is required to ensure that the pozzolanic reaction between the starting materials can proceed to completeness (11).

Physical and Chemical Characterization. Up to this point, the results have indicated that the significant sorbent preparation variables that affect the desulfurization activity of the sorbent are somehow related to the formation of specific reactive species in the sorbent. Therefore, sorbents that exhibited significantly high and low desulfurization activity were subjected to X-ray diffraction (XRD) analysis to identify the various phases present in the sorbent. Figure 4 a and b shows the XRD spectra of sorbent A8 and A16, respectively (high desulfurization activity), while Figure 4 c and d show the same for sorbent A1 and A21, respectively (low desulfurization activity). The peak characteristics of vaterite ($CaCO_3$), silica (SiO_2), mountainite ((Ca, Na_2, K_2)$_2$ $Si_4O_{10}\cdot 3H_2O$) and iron oxide (Fe_2O_3) were detected in all the four sorbents except in sorbent A21 where iron oxide was not detected (Figure 4d). Other than the four phases that were detected, additional phases were also detected in sorbents A8 and A16 which exhibited high desulfurization activity. They are calcium aluminum silicate ($CaAl_2Si_2O_8$) and

calcium silicate hydrate ($Ca_2SiO_4\cdot H_2O$) in sorbent A8 and A16, respectively. Calcium silicate and/or aluminum compounds have also been reported in sorbents prepared from coal fly ash (29, 30). Based on these findings, it is possible to conclude that the phases present in the sorbent (calcium silicate and/or aluminum compounds) are key factors in determining the desulfurization activity of the sorbent. In addition, the amount of RHA and CaO used in the preparation mixture could be the controlling factor influencing the formation of calcium silicate and/or aluminum compounds in the sorbent. Another conclusion is that apart from calcium silicate and/or aluminum compounds, silica and vaterite, all the other phases detected in the sorbent were generally different from the phases detected in sorbent prepared using coal fly ash (29–31) and oil palm ash (11) as the siliceous materials. This is probably due to the different composition of coal fly ash and oil palm ash as compared to RHA. This result indirectly described the difference in the correlation between sorbent surface area and the desulfurization activity for sorbent prepared from coal fly ash, oil palm ash, and RHA.

Sorbents A1, A8, A16, and A21 were also subjected to other physical analyses to determine whether the sorbents with significantly high and low desulfurization activity exhibited any distinctive physical properties or otherwise. Based on the pore size distribution analysis, all sorbents had similar pore size distribution with an average pore size between 9 and 13 nm (See Figure K, Supporting Information). Scanning electron micrograph (SEM) analysis on the sorbents indicated that the surface morphology of the sorbents consisted of irregular rough particles with different shapes and sizes that agglomerated together (See Figure L, Supporting Information). It was concluded that there are no significant differences between the pore size distribution and surface morphology of these four sorbents indicating that sorbent pore size and surface morphology is not a key factor in determining the desulfurization activity of the sorbent prepared from RHA.

Breakthrough Curves of the Desulfurization Activity. The desulfurization breakthrough curves of sorbents with
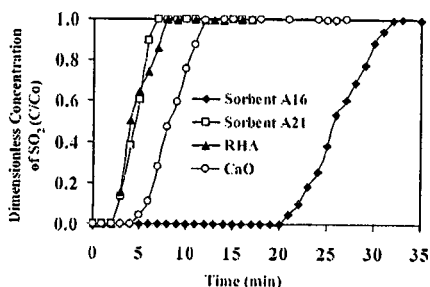
FIGURE 5. Breakthrough curves of the sorbent for highest and lowest desulfurization activity and its raw materials.

the highest activity (A16) and lowest activity (A21) as well as the starting materials (RHA and CaO) are shown in Figure 5. The two starting materials (RHA and CaO) had very low desulfurization activity as they could maintain 100% removal of SO_2 from the feed gas for only 2 and 4 min, respectively. Sorbent A21 showed similar low desulfurization activity. Conversely, sorbent A16 exhibited very high desulfurization activity as it could completely remove SO_2 from the feed gas for the first 20 min. Beyond 20 min of reaction time, the concentration of SO_2 gradually increased until there was no more SO_2 sorption activity in the sorbent (when the outlet concentration of SO_2 from the reactor is the same as the inlet concentration). As discussed above, this is due to the reactive species form in sorbent A16.

Acknowledgments

Supporting Information Available

Figure K a to d show the pore size distributions of sorbents A8, A16, A1, and A21 respectively, while Figure L a to d shows the SEM micrographs of sorbents A8, A16, A1, and A21 respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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Communication

Dry SO_2 Removal Process Using Calcium/Siliceous-Based Sorbents: Deactivation Kinetics Based on Breakthrough Curves

The removal of sulfur dioxide (SO_2) from simulated flue gas was investigated in a laboratory-scale stainless steel fixed-bed reactor using sorbents prepared from various siliceous materials, i.e., coal fly ash (CFA), oil palm ash (OPA) and rice husk ash (RHA) mixed with lime (CaO) by means of the water hydration method. Experiments were carried out with a flue gas flow rate of 150 mL/min, reaction temperature of 100 °C, and SO_2 concentration of 1000 ppm. It was found that sorbents prepared from RHA have high BET surface areas and high SO_2 sorption capacities, based on breakthrough curve analysis. In addition, the SO_2 breakthrough curves were also described in terms of a simple first-order deactivation model containing only two rate constants, one of which, k_s, describes the surface reaction rate constant while the other, k_d, describes the deactivation rate constant. The values of k_s and k_d obtained from the deactivation kinetics model were in good agreement with the experimental breakthrough curves and were also compared with those available in the literature.

1 Introduction

Sulfur dioxide (SO_2), emitted in flue gases resulting from the combustion process using sulfur-containing fuels is a major air pollutant whose emissions has been linked to the formation of acid rain, urban smog and many other undesirable environmental hazards. A number of SO_2 removal processes have been developed and applied in various industries to reduce the emission of SO_2. One of these processes is the dry-type desulfurization process operating at low temperature and which utilizes dry sorbent. The dry-type method for flue gas desulfurization (FGD) has recently attracted considerable research interest due to the drawbacks of wet-type methods [1, 2].

The extent of research of SO_2 removal using dry-type sorbent prepared from calcium-based waste-derived siliceous materials has proliferated in the past two decades. Sorbents obtained by hydrating a mixture of calcium-based sorbent

containing different sources of silica have led to significantly higher SO_2 sorption capacity as compared to calcium-based ($CaO/Ca(OH)_2/CaCO_3$) sorbent alone. Previously, the preparation of high SO_2 sorption sorbents from various waste-derived siliceous materials has been studied, i.e., coal fly ash (CFA) [3–6], oil palm ash (OPA) [7, 8] and rice husk ash (RHA) [9–11] with calcium-based sorbents, for dry-type FGD processes.

Many gas-solid reaction kinetic models have been employed to describe the desulfurization reaction between calcium-based sorbent with SO_2, e.g., the shrinking unreacted core model [12, 13], changing grain size model [14], single pore model [15], and random pore model [16–18]. However, these kinetic model equations are generally nonlinear and it is difficult to incorporate them without having to perform lengthy computer programs. As a result, a number of simpler, semi-empirical models have been developed by investigators. Moreover, the availability of kinetic models for the reaction between calcium-based and siliceous materials with SO_2 is still very limited in the literature. Recently, Suyadal et al. [19] compared limestone sulfation and deactivation of sorbent particles by coke formation, both of which can be described in terms of an exponential decrease in available surface area with time. This

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deactivation model has been able to successfully describe the experimental breakthrough curves for the sorption of SO_2 from simulated flue gases using calcined limestone in a fluidized-bed reactor.

Accordingly, in many applications and process settings, the analysis of sorbent deactivation is one of the important steps in the design and evaluation of fixed-bed reactor performance under dry-type desulfurization conditions. This is especially true when long term use of the sorbent in a continuous flow reactor is considered. In such situations, the economic feasibility of the process may hinge on the useful lifetime of the sorbent. In the present work, an analysis of the performance of sorbents prepared from a previous study (calcium-based CFA, OPA and RHA) was carried out using the deactivation model based on breakthrough curves.

2   Experimental

2.1   Sorbent Preparation

The sorbents were prepared by water hydration of a mixture of coal fly ash (CFA)/oil palm ash (OPA)/rice husk ash (RHA) with a calcium base (CaO/CaSO₄) from a previous study [5, 8, 9]. The preparation method is described as follows. A certain amount of calcium base was added to 100 mL of deionized water at 80 °C. Upon stirring, the temperature of the slurry rose to 90 °C and simultaneously, a specific amount of CFA/OPA/RHA was added into the slurry. The resulting slurry was heated at ca. 100 °C for a period of time with stirring in order to allow the hydration process to occur. The slurry was filtered and dried at 150 °C for 2 h. The sorbents in powder form were pelletized, crushed and sieved to obtain the required particle size range of 250–300 µm. The preparation conditions and specific surface areas of the sorbents are shown in Tab. 1. The prepared sorbents were then tested for desulfurization activity.

2.2   Activity Study

The activity of the sorbent was tested in a laboratory-scale stainless steel fixed-bed reactor that was fitted in a furnace. A stream of mixed gases containing SO_2 (1000 ppm), NO (500 ppm), CO_2 (12 %), O_2 (5 %), water vapor and N_2 (as the remainder) was subsequently passed through the sorbent, at a

reaction temperature of 100 °C. The concentration of the in the flue gas was measured using a Portable Flue Analyzer (IMR 2800P), before and after the sorption pro The schematic diagram and details of the activity study presented elsewhere [3–5]. The desulfurization activity of sorbent reported in this study is presented as the breakthr curves (C/C_o vs time) where C is the outlet concentration SO_2 (ppm) from the reactor and C_o is the initial concentra of SO_2 (ppm)[1]. The desulfurization activity of the sorb also expressed by the weight of SO_2 captured from the flu per g of sorbent, where the amount of SO_2 captured b sorbent was evaluated from the time the sorbent was ab maintain 100 % removal of SO_2, until it showed negligibl tivity (when the outlet SO_2 concentration became the sam the inlet SO_2 concentration).

2.3   Deactivation Model Assumptions

The deactivation model of SO_2 sorption by sorbent pre from a calcium base and siliceous materials in a fixed-bed tor was formulated using the following assumptions [20] the system is isothermal, (2) the external mass transfer li tions are neglected, (3) deactivation is slow, and therefor fixed-bed reactor can be assumed to behave like a batch reactor with plug constant flow of fluid, (4) the system is do steady-state; and (5) sorbent deactivation is first-orde respect to the solid surface, and is assumed to decrease nentially with time. The simple form of the first-order d vation term can be expressed by the following equation:

$$\ln\left(\ln\left(\frac{C_o}{C}\right)\right) = \ln(k_s\tau) - k_d t$$

where C_o and C are the inlet and outlet concentrations o k_s, k_d and t are the surface reaction rate constant, first-o deactivation rate constant and reaction time, respectivel surface-time term [21], τ, is similar to the weight-time by Levenspiel [20] for a batch of solid particles under first-order deactivation with a plug constant flow of Consequently, a straight line should be obtained if th hand side of Eq. (1) is plotted versus reaction time. The represents the k_d value, and k_s can be derived from the cept.

3   Results and Discussion

In order to examine the proposed deactivation mode value of $\ln[\ln(C_o/C)]$ from Eq. (1) was plotted as a funct time for each prepared sorbent, for SO_2 removal activi fixed-bed reactor. As can be seen in Fig. 1, the linearity data points for each sorbent was obtained. From the grap estimated values of the deactivation rate constants fo sorbent prepared from CFA, OPA and RHA have corr coefficients (R^2) of 0.93; 0.96; and 0.94, respectively

Table 1. Preparation conditions and BET specific surface areas of the sorbents at optimum conditions.

Sorbents	Hydration Process Variable				Specific BET Surface Area (m^2/g)	Ref.
	Period (h)	CaO (g)	CaSO₄ (g)	Ash (g)		
CFA/CaO/CaSO₄	10	5	5.5	13.1	62.2	[5]
OPA/CaO/CaSO₄	24	5	1	15	88.3	[8]
RHA/CaO	16	2	–	15	106.10	[9]

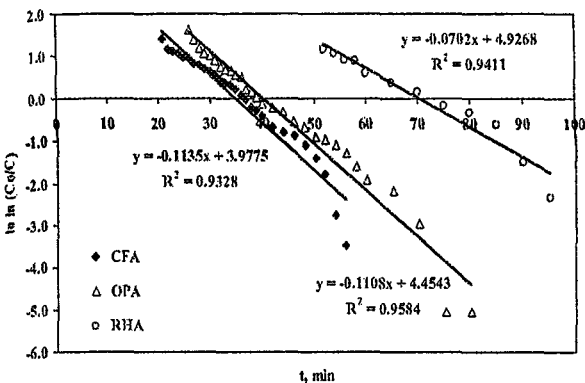1)   List of symbols at the end of the paper.

Figure 1. Deactivation kinetics of SO_2 sorption by various sorbents prepared from calcium/siliceous-based materials in fixed-bed reactor.

shows that the proposed deactivation model, Eq. (1), gives an adequate representation of the experimental breakthrough curves of SO_2 sorption, and can be used to find rate constants for fixed-bed reactors. The calculations of the rate constants for each prepared sorbent, are summarized in Tab. 2.

The deactivation rate constant, k_d, was found to be higher for sorbents prepared from CFA and OPA, respectively, compared to sorbents prepared from RHA. This means that the SO_2 sorption capacity of sorbents prepared from CFA and OPA was lower, which can be observed from the low surface reaction rate constant, k_s. The observed surface reaction rate constants of sorbents prepared from RHA were higher. This may be due to the important role played by silica and specific surface area. The higher silica content in RHA (88 %) [10], compared to CFA/OPA (40–60 %) [3,7], might be related to the formation of various calcium silicate hydrate compounds

(during the hydration process) [7, 11]. These pozzolanic products are usually almost amorphous and have very high surface areas, which can enhance SO_2 sorption capacity [22–24].

The validity of the proposed deactivation model was also confirmed by comparing the simulated breakthrough curves with experimental data at 2000 ppm SO_2, as shown in Fig. 2, for each prepared sorbent. It is seen that the model gave very good predictions of the experimental data. The SO_2 sorption capacities obtained in this study (for 100 % SO_2 removal) were calculated to be 10.72; 5.36; and 4.29 mg SO_2/g sorbent for sorbents prepared from RHA, OPA and CFA, respectively.

The values of the rate constants were also compared with those contained in the literature, as shown in Tab. 2. The deactivation rate constant values from this study are almost the same order of magnitude as those reported in the literature. However, the surface reaction rate constants are much
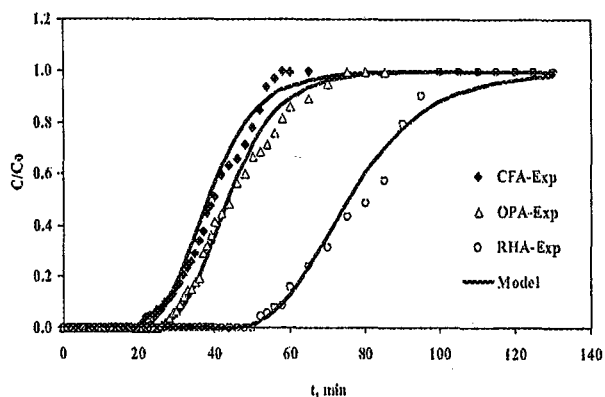
Figure 2. Comparison between experimental SO_2 breakthrough curves (at 2000 ppm SO_2) of various prepared sorbents and those predicted by the model.

Table 2. Comparison of deactivation model parameters.

Sorbents	Reactor	Gas stream	Condition	$k_s\tau$	k_s (m s^{-1})	$K_d \cdot 10^3$ (s^{-1})	Ref.
Activated Carbon	Packed Bed	Air-TCE[a] Vapor (VOC)	TCE = 6350 ppm	8.428		1.18	[21]
			TCE = 6750 ppm	8.711		1.33	
			TCE = 7300 ppm	9.634		1.71	
Calcined Limestone (CaO)	Fluidized Bed	$SO_2/CO_2/O_2/H_2O/N_2$	SO_2 = 3000 ppm		$0.17 \cdot 10^{-4}$	1.40	[19]
			SO_2 = 2000 ppm		$0.09 \cdot 10^{-4}$	1.15	
			SO_2 = 1000 ppm		$0.06 \cdot 10^{-4}$	0.97	
CFA/CaO/CaSO$_4$	Fixed Bed	$SO_2/NO/CO_2/O_2/H_2O/N_2$	SO_2 = 1000 ppm		$4.29 \cdot 10^{-6}$	1.89	This study
OPA/CaO/CaSO$_4$					$4.87 \cdot 10^{-6}$	1.85	
RHA/CaO					$6.50 \cdot 10^{-6}$	1.17	

[a] TCE=Trichloroethylene
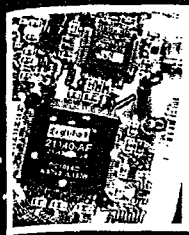
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Jurnal Ilmu Pengetahuan dan Teknologi Terapan

Daftar Isi

CALCIUM-BASED WITH WASTE-DERIVED SILICEOUS MATERIALS AS A SORBENT FOR DRY-FGD TECHNOLOGY: REACTIVITY AND CHARACTERISTIC

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Abstract

The emission of sulfur dioxide (SO_2) to the atmosphere causes severe air pollution and formation of acid rain which are known to give detrimental impacts on human health and the environment. The removal of SO_2, which mainly come from the combustion of fossil fuel, is an increasingly important environmental challenge. Among the technologies that show promise for SO_2 reduction is dry flue gas desulfurization (FGD) technology. One new development of dry FGD technology is the use of calcium/siliceous-based sorbents, which has gained a lot of attention in the last few years. Several studies have reported the preparation of sorbents from calcium-based (lime, limestone and hydrated lime) by reacting it with siliceous materials, such as fly ash, diatomaceous earth and silica. This sorbents show remarkable SO_2 scavenging abilities, due to high surface area. Furthermore, the use of dry calcium/siliceous-based sorbents for FGD process offers a more economical and retrofits technology. This short review attempts to present the basic understanding and overview of SO_2 emissions and characteristic/reactivity of sorbents used.

Keywords: SO_2 emissions, sorbent, siliceous materials, flue gas desulfurization (FGD)

1. Introduction

Sulfur dioxide (SO_2) is arguably the most important pollutant on EPA's list of six criteria pollutants and the reduction of SO_2 emissions remains the main focus in industrial regions

around the world. There are two primary adverse affects of SO_2, its adverse respiratory affects on human and its contribution to acid rain, which damages the environment (Srivastava, 2001). Anthropogenic SO_2 emission is mainly caused by combustion of sulfur-containing fossil fuels such as coal (0.5% to 10%) and oil (0.5% to 3%) (Citepa, 2004). Electricity generating plants account for nearly 70 % of all SO_2 emissions. The second major source of sulfur dioxide is industrial combustion processes, such as boilers, process heaters, metallurgical operations,

roasting and sintering, coke oven plants, processing of titanium dioxide, pulp production, and the thermal treatment of municipal and industrial wastes (Baukal, 2004., Goorissen, 2002).

There has been a constant effort to research and determine not only economical but more effective technologies for the control of the criteria pollutants, especially SO_2. General options for removing of sulfur emissions include (1) energy management measures, (2) increasing the proportion of non-combustion renewable energy sources (i.e. hydro, wind, etc.), (3) fuel switching (e.g. from high- to low-sulfur coals, from coal to gas and/or liquid fuels), (4) fuels can be purified from sulfur compounds, (5) the burning process can be organised in a way where the SO_2 formed is bound by the mineral part of the fuel or by special additives injected into the burner, and (6) exhaust gases can be purified before their

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outlet into the atmosphere (Baukai, 2004., Coorissen, 2002). The methods used in the last case can be referred to as Flue Gas Desulfurization (FGD) processes. A large number of FGD processes have been developed and are expected to play an important role in reducing SO_2 emission from power plants. FGD methods can be classified according to the end product formed in the process. The methods are divided into regenerable and non-regenerable processes, where in the former case the removed sulfur dioxide is recovered as sulfur, sulfur dioxide or sulfuric acid. In the latter case the end product is mainly a waste material which has to be dumped. Presently, regenerable FGD process was used less compared to non-regenerable process. This might be due to relatively high capital and operating expenses compared with other FGD processes (Srivastava, 2001). These processes can further be divided into subgroups depending on the reactive phase where SO_2 is removed (dry, semi-dry or wet processes).

Wet FGD processes are currently most widely used in the industries using limestone slurry ($CaCO_3$) as sorbent. These methods are highly efficient in removing SO_2 (92 - 96 %), however they require a large space for installation and produce a huge amount of wet sludges which must be disposed of (Ishizuka,200). Hence, in order to overcome this limitation, researches have shifted their attention on the dry FGD methods because of their potential simplicity and lower cost. Most of the non-regenerable dry FGD methods utilize calcium-based chemicals (limestone, lime & hydrated lime) because they produce relatively safe and stable end product, viz. calcium sulfate hydrate (gypsum) (Galos, 2003).

2. Properties and Formation of Sulfur Dioxide (SO_2)

SO_2 is a colorless nonflammable acidic gas with a pungent odor. SO_2 has a boiling point of -10 °C and is a melting point of -75.5 °C. SO_2 can be very corrosive in the presence of water and is highly soluble in water with density of 2.618 g/l at 25 °C and 1 atm. At room temperature, the solubility of SO_2 is approximately 200 g SO_2/l (Baukal, 2004.,Brady, 2000., Chiang, 1998). Thus, 1 ml of water could dissolve 76 mL SO_2. SO_2 dissolves in water by forming hydrates, $SO_2.nH_2O$, where n varies with concentration of

SO_2 and temperature. The hydrates are in equilibrium with hydrogen ion and hydrogen sulfite ion as shown by the following reaction

$$SO_2 + H_2O \leftrightarrow H^+ + HSO_3^- \qquad [1]$$
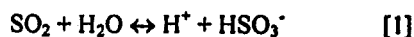
The source of SO_2 is resulted naturally from, for example, volcanic eruption (estimated to be roughly 13×10^6 tons/year, which is 5 to 10% of the quantity released by human activities). The largest source is from industrial combustion processes (Brady, 2000). SO_2 represents 98% of the sulfur oxide (SO_x) pollutants generated by combustion process. The oxidation of SO_2 could also take place to form sulfur trioxide (SO_3) (Probstein, 1985). SO_2 tends to preferred at higher temperature, while SO_3 is more preferred at lower temperature (Baukal, 2004). The oxidation steps of these reactions are as follow

$$S + O_2 \rightarrow SO_2 \qquad [2]$$

$$SO_2 + 1/2\ O_2 \rightarrow SO_3 \qquad [3]$$

The problem in the atmosphere is that SO_3 reacts with water (rain) to form sulfuric acid (H_2SO_4)

$$SO_3 + H_2O \rightarrow H_2SO_4 \qquad [4]$$

3. Requirement Characteristics of Sorbents

Sorption is the common term used for both absorption and adsorption. The main difference is that solute are attracted (clings) to the outer surface of the particle sorbent, in other word molecules accumulate in the interfacial layer/bulk phase (adsorption/dissolution), while another has been actually incorporated into the particle's structure of the sorbent (absorption i.e. solute diffuses into a porous solid and clings to interior surfaces). Absorbent typically experience a physical/chemical change. In most applications, adsorbents are regenerable (can be reactivated via removal of the contaminants/fluids) (Dabrowski, 2001). Many materials can be used as sorbents in gas-solid processes. In general, cost effective sorbents are needed. A sorbent can be assumed as low cost if it requires little processing, is abundant in nature, or is a by-product or waste material from another industry. And of course, improving the sorption capacity may

compensate the cost of additional processing (Bailey, 1999).

Although there are many processes available for the SO₂ removal, dry flue gas desulfurization (FGD) remain as the most economical process. Now, the problem is how to choose and prepare the solid sorbents. Generally, SO₂ sorbents based on its ability to neutralize bases is used. A base suitable for use as a sorbent must meet a number of requirements (Chiang, 1998., Bailey, 1999., Yang, 1999). For example:

- Highly porous
- It must react rapidly with SO₂ in the presence of water vapor
- It must have a high capacity for SO₂
- The base must be low cost
- It must react with flue gas to give an environmentally acceptable product, if not, can be disposed of in a landfill
- It must not contain appreciable concentrations of toxic ion
- Beyond all this, the sorbent should have good handling characteristic (i.e. should flow readily in handling system, and it should not form wall deposits in ducts.
-

4. Reactivity of Calcium/Siliceous-Based Sorbents with SO₂

Among the previously considered sorbents for SO₂ removal are sodium-based sorbents (i.e. NaHCO₃); metal oxide-based sorbents (i.e MgO with CeO₂, Al₂O₃); zeolite; activated carbon; and calcium-based sorbents (i.e CaCO₃, CaO, Ca(OH)₂). The options that are present advantages both economically and environmentally sorbent is the use of calcium-based absorbents. In order to increase the SO₂ removal activity, these calcium-based materials must be activated. Jozewicz & Rochelle [14] found that calcium-based materials can be activated by reacting it with siliceous material (i.e. fly ash). They postulated that the rate-limiting step of the reaction of fly ash with Ca(OH)₂ was the dissolution of silica from the fly ash. They found that silica was the most reactive component of the fly ash and the solids reactivity (toward SO₂) increased with slurry time and slurry temperature. After that, many researchers have shown that calcium-based sorbents can be activated by reacting it with siliceous materials, such as coal fly ash, diatomaceous earth and silica fume. From those

studies. it was shown that higher SO₂ removal activity correlates with higher specific surface area and the content of silica used to prepare the sorbent. During the activation process, the acid components of the fly ash (or other siliceous materials) are first dissolved, reacting with the basic Ca^{2+} and OH⁻ ions from the calcium-based solution. As a result, calcium silicate hydrates (CSH), calcium aluminate hydrates, calcium aluminate silicate hydrates, ettringite, tobermorite and other reactive species can be obtained, and this reaction is called pozzolanic reaction (Taylor, 1964., Goni, 2003). These pozzolanic products are high surface area foil-like materials, and this products would be depend on the absorbent preparations such ash type of ash, water solid ratio, weight ratios of starting materials, hydration temperature and hydration period. It is believed that the formations of CHS (and other reactive species) are responsible for the enhancement of the absorbent reactivity toward SO₂ absorption.

Currently, we did the experiment on the utilization of rice husk ash (RHA) as a source of siliceous materials for the synthesis of sorbent for dry FGD process. RHA is among the materials that contain high amount of silica (60–90%) produced from rice husk burning (Chaudhary, 2004). In this study, the removal of SO₂ from simulated flue gas was investigated using RHA-calcium based sorbent. It was found that this sorbent does have higher BET surface area and have a high capacity in SO₂ adsorption in comparison with coal fly ash/calcium- and oil palm ash/calcium-based sorbents (Dahlan, 2005).

5. Conclusion

In this paper, the basic understanding of sorbent characteristic and reactivity toward SO₂ has been reviewed. Many materials can be used as sorbents in gas-solid processes. However, the most promising one is the use of calcium/siliceous-based sorbents. Pozzolanic reaction taking place during the activation process of silica and calcium materials to form reactive species which is result in a highly porous sorbents. Due to highly porous and high silica content, rice husk ash (RHA) has the potential as a sorbent for flue gas desulfurization (FGD) process.

Acknowledgments

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IMPROVED INDUSTRIAL GAS SEQUESTRATION BY ADSORPTION ON THIN FILM COMPOSITES

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ABSTRACT

The worldwide market for industrial gases is ever increasing in demand. In the U.S.A, "gas business" is on the order of $4.9 billion annually. The global market for industrial gases (value of the gas alone, capital costs i.e., equipment and operation excluded) is anticipated to encroach $52 billion by 2008, attesting to massive global demand for industrial gas. It is imperative that industrial gases are managed in a sustainable manner during the production and recovery processes, for an industry that emancipates gas needlessly to the atmosphere, may be construed as unfathomably cost frivolous in one hand, and utter oblivion, on the other. Conventional practices in the gas industries to manufacture purified gases are through adsorption processes (PSA/TSA) and cryogenic separation technology. Additionally, membrane technology has been introduced and recently it begins to gain popularity due to its positive impact on economics and practicality. This article recapitulates recent finding and development of thin film composites for improved gas enrichment facilitated by adsorption mechanism.

Keywords: Membrane, Industrial Gases, Adsorption, Thin Film, Non-Cryogenic.

EFFECT OF NaOH ON PREPARATION AND SORPTION CAPACITY OF RICE HUSK ASH (RHA)/CaO-BASED SORBENTS FOR FLUE GAS DESULFURIZATION (FGD) AT LOW TEMPERATURE

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ABSTRACT

Previous studies have reported the preparation of sorbents from various types of siliceous materials for dry-type flue gas desulfurization (FGD) process. Since the content of silica in the siliceous materials is an important parameter affecting the sorption capacity of the sorbents, rice husk ash (RHA) has a potential to be utilized for the synthesis of sorbent as RHA has high content of silica. In an attempt to further increase the sorbent sorption capacity, the present study was carried out to investigate the impact of NaOH addition on preparation of RHA/CaO-based sorbents for the removal of sulfur dioxide (SO_2) from simulated flue gas using fixed bed reactor. For sorbent prepared with NaOH, higher SO_2 sorption capacity was obtained compared with sorbent prepared without the addition of NaOH. This is probably due to the ability of a sorbent to retain water layers on the surfaces of sorbent particles at low temperature reaction, due to role played by NaOH as a deliquescent material. The highest SO_2 sorption capacity (22.31 mg SO_2/g Ca^{2+}) of sorbent was obtained at hydration period of 20 h, RHA to CaO ratio of 3 and the addition of 0.5 mol/l NaOH. Apart from that, SO_2 sorption capacity was also affected by ratio of RHA/CaO, hydration time and the concentration of NaOH.

Keywords: Flue Gas Desulfurization (FGD); Sorbent; SO_2 Sorption Capacity; Rice Husk Ash (RHA); Additive

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Keywords: Flue Gas Desulfurization (FGD); Sorbent; SO_2 Sorption Capacity; Rice Husk Ash (RHA); Additive

INTRODUCTION

Power stations that burn sulfur-containing fossil fuels (coal and oil) constitute the major source of sulfur dioxide (SO_2) emission. Some industrial processes also produce SO_2, although the amount of their emissions is lower than that in power stations. The evolution of SO_2 emissions varies from different world regions. The SO_2 emissions have been reduced in the USA and Europe in the last decades (by 45% from 1975 to 2002 and 60% from 1980 to 1997, respectively) and tend to level out at present time. In the meantime those in developing countries are steadily going up (mainly in the Asian Pacific countries, including Malaysia) as much as triple from 1990 levels by 2010 if current trends continue [1,2]. Therefore, different methods have been developed in the past to remove SO_2 from combustion gases before they are realesed to atmosphere.

Nowadays, a great number of scrubbing systems, referred in the literature as flue gas desulfurization processes (FGD), are well-established technologies, either wet- or dry-type methods. In comparison to wet method, dry technologies have fewer problems of corrosion and scaling-up. Furthermore, it produces dry solid waste which is easier to handle and require no wastewater treatment [3,4]. Nevertheless, acid gas sorption capacities are generally lower than those achieved with wet technologies. In dry-type systems to remove SO_2 from flue gases take advantage of the acid character of these compounds to retain them. All of them are based on the addition of alkaline solid sorbents, so that neutralization of the acid compounds takes place with the formation of solids as reaction products.

Since the pioneer work by Jozewicz and Rochelle in 1986 [5], the content of silica in the siliceous materials become an important parameter affecting the SO_2 sorption capacity of the sorbents prepared from calcium-based materials. Then, many researchers have shown that calcium-based sorbents can be prepared with various types of siliceous materials, such as coal fly ash, oil palm ash, diatomaceous earth and silica fume. Apart from that, rice husk ash (RHA), which has a high content of silica (60–90 %) [6], has a potential to be utilized as a sorbent for dry-type FGD process. RHA is one of the waste materials available abundantly in Malaysia that is produced from rice husk burning. In Malaysia, it was estimated that more than 80 thousand metric tons of RHA is produced annually [7]. RHA contains both crystalline and amorphous silica. The amorphous silica is more active than the crystalline [4], therefore it predominates in participating in the pozzolanic reaction.

In our previous study, we have reported the preparation of high SO_2 sorption sorbents from coal fly ash [8,9], oil palm ash [10,11] and RHA [12] for dry-type FGD process at low temperature. Among those sorbents prepared, RHA/CaO-based sorbent shows highest SO_2 sorption capacity. However, in order to further increase the SO_2 sorption capacity of sorbent prepared from calcium/siliceous-based materials, previous researchers have been attempting to use additive in the preparation of the sorbent such as NaOH [13-16]. The scope of this work was to examine SO_2 sorption capacity by RHA/CaO-based sorbent for FGD process at low temperature, whereby the effect of NaOH as an additive was investigated.

MATERIALS AND METHOD

Sorbent Preparation. The sorbent was prepared from $CaO/Ca(OH)_2$, NaOH and rice husk ash (RHA). The RHA was collected from Kilang Beras & Minyak Sin Guan Hup Sdn.Bhd., Nibong Tebal, Malaysia. Prior to use, RHA was combusted in a furnace at temperature 600 °C to make sure that amorphous silica was formed. The chemical composition of RHA is shown in Table 1.

The sorbents were prepared using water hydration method [4] and is described as follows. The CaO or $Ca(OH)_2$ and RHA with/without NaOH in 100 ml distilled water were placed into 250 ml erlenmeyer flask, sealed with parafilm tape. The weight ratio (R) of RHA/Ca-based, hydration period and additive (NaOH) amount of 1/3 – 3, 4 – 20 hours and 0 – 1 mol/l, respectively, were studied. The slurry was inserted to water bath shaker at temperature of 65 °C under constant shaking rate of 150 rpm for a cetain hydration period. Afterward, the slurry was then filtered and dried at 150 °C for 2 h. The sorbents were then palletized, crushed and sieved to obtain the required particle size range of 250-300 μm. The sorbent prepared was then tested for SO_2 sorption capacity.

Table 1: X-RF Analysis of RHA

Composition (Oxides)	Percentage (wt %)
SiO_2	89
K_2O	2.6
P_2O_5	1.2
MgO	0.86
CaO	0.68
Cl_2O	0.32
Al_2O_3	0.21
Trace	0.93
LOI	4.2

SO$_2$ Sorption Study. The SO_2 sorption capacity of the sorbents was tested in a laboratory-scale stainless steel fixed-bed reactor (0.8 cm ID) fitted in a furnace for isothermal operation. During the study, 0.5 g of sorbent was packed in the center of the reactor supported by 0.05 g of borosilicate glass wool. A stream of gaseous mixture containing SO_2 (2000 ppm), NO (500 ppm), O_2 (10 %), water vapor (50 % humidity) and N_2 as the balance was subsequently passed through the sorbent at a reaction temperature of 87 °C. The total flow rate of the gas stream was controlled at 150 ml/min using mass flow controller. The concentration of the SO_2 in the flue gas was measured using Portable Flue Gas Analyzer IMR 2800P before and after the sorption process. The schematic diagram and details of the experimental rig is presented elsewhere [8-12]. The desulfurization activity of the sorbent is expressed by the weight of SO_2 captured from the flue gas per gram sorbent [13]. The amount of SO_2 captured by the sorbent was evaluated from the time the sorbent could maintain 100% removal of SO_2 until it shows negligible activity (when the outlet SO_2 concentration becomes the same as the inlet SO_2 concentration). The weight of SO_2 captured by the sorbent was measured by integrating the difference between the inlet and outlet concentration.

RESULTS AND DISCUSSION

Effect of Different Ca-Based Sorbent. In the preliminary study, the usage of different Ca-based materials (CaO or Ca(OH)$_2$) in the preparation of sorbent form RHA were done comparatively in order to obtain a better sorbent towards achieving higher SO_2 sorption capacity. The different between the sorbents prepared from CaO and Ca(OH)$_2$ is shown in Fig. 1.

The SO_2 sorption capacity of sorbents prepared increased with hydration period. However, the sorbent prepared from CaO showed high SO_2 sorption capacity (7.72 mg/g), which was twice as much as that of the sorbent prepared from Ca(OH)$_2$ (3.43 mg/g) at hydration period of 4 h. These results suggest that when CaO is used as Ca-based material in the preparation of sorbent with RHA, a highly SO_2 sorption capacity of sorbent can be prepared within a short hydration period. Apart from that, according to Ishizuka *et al* [3] when CaO is used as a Ca-based material in water hydration process, the following exotermic reaction takes place:

$$CaO + H_2O \leftrightarrow Ca(OH)_2 \quad \Delta H = -104.1 \text{ kJ/mol} \tag{1}$$
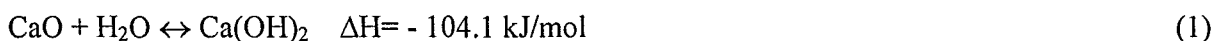
The conversion of CaO to $Ca(OH)_2$ will release a huge amount of heat, creating a temporary heat storage that will exaggerate the formation of active species within the sorbent surface. The formation of more reactive species will subsequently increase the SO_2 sorption capacity of sorbent.
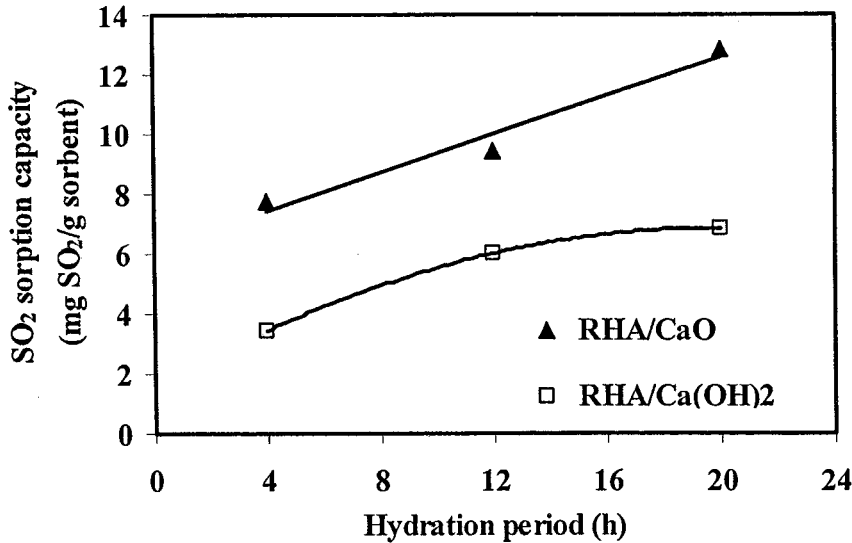

Figure 1: Effect of CaO or $Ca(OH)_2$ Toward SO_2 Sorption Capacity in the Preparation of Sorbent with R = 3 as a Function of Hydration Period.
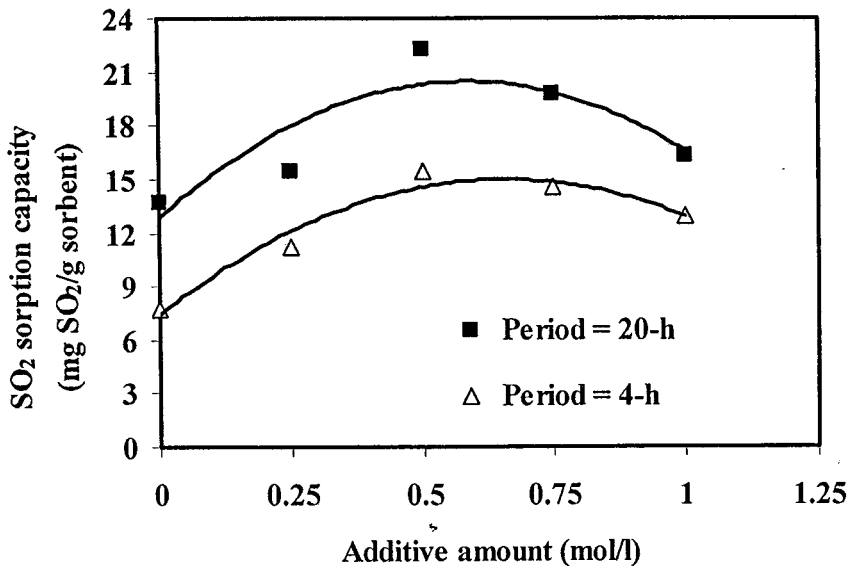

Figure 2: Effect of NaOH Addition on RHA/CaO-Based Sorbent with R = 3

Effect of Additive (NaOH). A further increase in SO_2 sorption capacity was observed when RHA and CaO were mixed with NaOH during the preparation of sorbent. Fig. 2 shows the effect

of NaOH as an additive in the range of 0 to 1 mol/l in the preparation of sorbent with hydration period of 4 h and 20 h, respectively.

The addition of 0.25 and 0.5 mol/l NaOH brought about 20-50% increment in the SO_2 sorption capacity for both hydration period used in the preparation of sorbent. This can be explained that the presence of NaOH might increase the dissolution rate of silica from the RHA. This will eventually increase the formation of Si-Ca complex that has a high SO_2 sorption capacity. Apart from that, the enhancement effect of NaOH addition on the SO_2 sorption capacity mainly due to the deliquescent property of NaOH. This can be explained by measuring the amount of water adsorbed by comparing the weight of sorbent before and after sulfation test. The amount of water adsorbed on the sorbents with addition of 0; 0.25; and 0.5 mol/l NaOH were measured to be 184.1; 230.4; and 379.2 g H_2O/kg sorbent, respectively, at a reaction temperature of 87 °C and 50% relative humidity. These results indicate that more water was collected when NaOH was present. It also has been shown by Liu *et al* [17] and Ho *et al* [18] that the reaction of SO_2 with Ca-containing sorbents at low temperature requires the presence of water in several molecular layers thick on the surface of sorbent particles, and the extent of reaction increases with an increasing amount of water adsorbed. However, the addition of NaOH above 0.5 mol/l caused the SO_2 sorption capacity decrease. The reason for the decreased SO_2 sorption capacity might result from the very low concentration of dissolved Ca-based present in the sorbent prepared because the NaOH increases the solubility of the silica in the RHA. The silica precipitates the dissolved calcium as calcium silicate hydrate (CHS) [19,20]. Consequently, there is a substitution effect in this case, which has been suggested by Peterson and Rochelle [13]. This also explains that there is an optimum NaOH concentration during the sorbent preparation, as shown in Fig. 2. The optimum NaOH concentration of 0.5 mol/l was found in this study for both hydration periods used (4 h and 20 h) in the preparation of sorbents, which gave SO_2 sorption capacity of 15.44 and 22.31 mg/g, respectively. It was also observed from the sorbents prepared that sorbents not containing NaOH are dry and loose before and after the reaction test, however, the sorbents containing NaOH tend to stick together and have wet appearance due to deliquescence of NaOH.
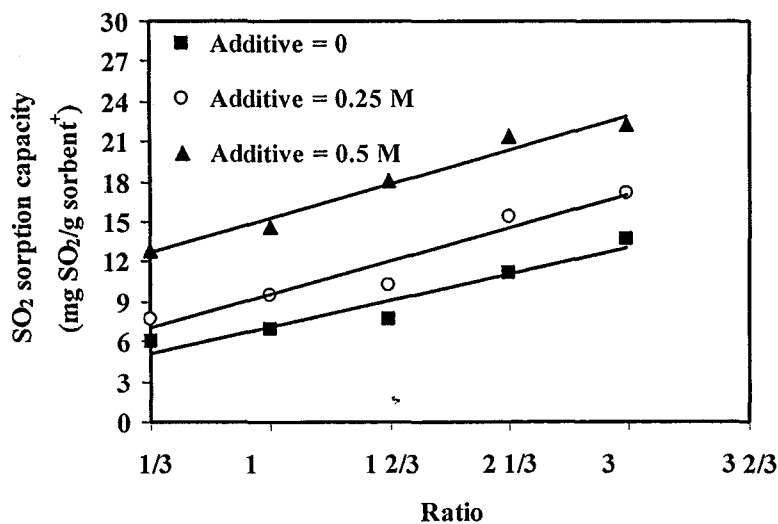

Figure 3: Effect of RHA/CaO Ratio on the Preparation of Sorbent at Various NaOH Amount

Effect of RHA/CaO Ratio. The effect of RHA/CaO ratio on SO_2 sorption capacity was investigated in this research in the range of 1/3 to 3 as observed in Fig. 3. SO_2 sorption capacities of sorbent prepared using 20 h hydration period were increases as the initial raw material ratio increases. This behavior can be explained by considering that the rate-limiting step of the pozzolanic reaction of RHA with CaO during the sorbent preparation is the dissolution of silica from the RHA, whereby, the reaction rate will increase with the concentration of silica in the reaction mixture. This behavior has previously been explained [5,13,21]. Furthermore, with the addition of NaOH, the dissolution rate of silica from the RHA might also increase as the increasing SO_2 sorption capacity, as has been discussed on the effect of additive. The maximum SO_2 sorption capacities obtained in this study at RHA/CaO ratio of 3 were 13.73; 17.16; and 22.31 mg/g with the addition of 0; 0.25; and 0.5 mol/l NaOH, respectively.

Compared to our previous work, the SO_2 sorption capacity of the sorbent prepared in this work was still higher. Table 2 shows the comparison of the SO_2 sorption capacity of various calcium/siliceous-based sorbents. Higher SO_2 sorption capacity of the sorbent prepared from RHA/CaO/NaOH might be due to role played by silica, which is higher compared to coal fly ash and oil palm ash, and additive (NaOH) content.

TABLE 2: Comparison of the SO_2 Sorption Capacity

Calcium/Siliceous-based materials	SO_2 Sorption Capacity (mg SO_2/g sorbent)	Reference
Coal fly ash/ CaO/CaSO$_4$	4.60	[8]
Oil palm ash/ Ca(OH)$_2$/CaSO$_4$	7.36	[10]
RHA/CaO/CaSO$_4$	17.14	[12]
RHA/CaO/NaOH	22.31	Present work

CONCLUSIONS

The present study has investigated the preparation of sorbents from RHA/Ca-material with or without the addition of additive *i.e.* NaOH. Sorbent prepared from CaO in place of Ca(OH)$_2$ exhibited higher SO_2 sorption capacity. The SO_2 sorption capacity of sorbent prepared from RHA/CaO was higher due to the important role played by silica and additive content. The enhancement effect of NaOH addition mainly resulted from the fact that NaOH is deliquescent material and its presence increases the amount of water collected by a sorbent, which is required for the SO_2 reaction at low temperature.

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12TH ASIAN CHEMICAL CONGRESS (12ACC)

August 23 – 25, 2007
Putra World Trade Centre, Kuala Lumpur, Malaysia

BOOK OF ABSTRACTS

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12TH ASIAN CHEMICAL CONGRESS (12ACC)

August 23 – 25, 2007
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BOOK OF ABSTRACTS

Preface

The **12th Asian Chemical Congress (12ACC)** is the flagship scientific meeting of the Federation of Asian Chemical Societies (FACS). Held every two years by a member society of FACS, the Asian Chemical Congress has become a major international meeting of both eminent and upcoming scientists and researchers from all over the world. 12ACC is hosted by Institut Kimia Malaysia (IKM) in Kuala Lumpur, Malaysia from August 23-25, 2007. It has attracted more than 1,500 delegates from over 50 countries. With 1,292 titles being presented, 12ACC ranks among the biggest ACCs ever held.

The **Scientific Programme** of 12ACC comprises the following:

Plenary Sessions comprising six (6) Plenary Lectures
Four (4) FACS Awardee Lectures
Four (4) Scientific Sessions:
  ➢ Inorganic, Organometallic and Bioinorganic Chemistry (IOB)
  ➢ Organic Chemistry: Mechanism and Syntheses (ORC)
  ➢ Physical and Theoretical Chemistry (PTC)
  ➢ Oils and Fats Chemistry and Technology (OCT)
Seven (7) International/Regional Symposia:
  ➢ International Symposium on Environmental and Green Chemistry (EGC)
  ➢ International Symposium on Food Analysis, Chemistry and Technology (FACT)
  ➢ International Symposium on Innovation in Chemistry Education (ICE)
  ➢ International Symposium on Natural Products and Medicinal Chemistry (NPMC)
  ➢ International Symposium on Polymer and Materials Chemistry (PMC)
  ➢ Third Regional Symposium on Total Laboratory Management (QSEL) 2007
  ➢ Malaysian International Symposium on Analytical Sciences (SKAM-20) 2007

A total of 1,293 presentations, comprising 6 plenary lectures, 4 FACS Awardee Lectures, 113 keynotes, 418 orals and 749 posters would be made at 12ACC. The breakdown of the presentations is as follows:

Session / Symposium	Special	Keynote	Oral	Poster	Total
Plenary Lectures	6				6
FACS Award Lectures	4				4
IOB		5	32	93	130
ORC		7	41	108	156
PTC		8	42	55	105
OCT		5	19	15	39
EGC		31	63	71	165
FACT		6	26	31	63
ICE		6	25	11	42
MPNC		8	18	165	191
PMC		20	62	81	163
QSEL		5	20	-	25
SKAM-20		12	70	121	203
TOTAL	10	113	418	752	1293

195 – 328 mg/L; BOD$_5$ 243 – 307 mg/L and COD 1120 – 1400 mg/L respectively. After adding 10 mg/L Cu (II) into tap water, BOD$_5$ and COD of the effluent show a decrease in early stage, but after a while, it gradually increase and return to the same level as before adding Cu)II). Continuous washing on the oil palm fiber and kernel will reduce the percentage of COD effectively. In conclusion, oil palm fiber and kernel which used as media were found to contribute to a higher value of BOD$_5$ and COD. Adding in Cu(II) into the water sample did not affect the BOD$_5$ and COD significantly except in the early stage

ECC 054 (Oral)

SAWDUST—A GREEN AND ECONOMICAL SORBENT FOR THE REMOVAL OF CADMIUM (II) IONS

Saima Q. Memon
Interface Analysis Center, University of Bristol, Bristol

The ability of sawdust (treated and untreated) waste, a waste material derived from the commercial processing of cedrus deodar wood for furniture production, to remove Cd(II) ions from aqueous solution was determined. Sorption was found to be rapid (~97% within 8 min). The binding of metal ions was found to be pH dependent, optimal sorption accruing at around pH 4–8. Potentiometric titrations of sawdust revealed two distinct pKa values, the first having the value similar to carboxylic groups (3.3–4.8) and second comparable with that of amines (8.53–10.2). Retained Cd(II) ions were eluted with 5ml of 0.1 mol l^{-1} gml□HCl. Detection limit of 0.016 $^{-1}$ was achieved with enrichment factors of 120. Recovery was quantitative using sample volume of 600 ml. The Langmuir and D–R isotherm equations were used to describe partitioning behaviour for the system at different temperatures. Kinetic and thermodynamic behaviour of sawdust for Cd(II) ions removal was also studied.

EGC 055 (Oral)

EFFECT OF VARIOUS ADDITIVES ON THE SO$_2$ SORPTION CAPACITIES OF RICE HUSK ASH/LIME SORBENTS FOR DRY-TYPE FLUE GAS DESULFURIZATION AT LOW TEMPERATURE

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In this study, the effectiveness of 10 additives towards improving SO$_2$ sorption capacities (SSC) of rice husk ash (RHA)/lime (CaO) sorbent were investigated. The sorbents were prepared using water hydration method by slurrying RHA, CaO and different type of additives. The additives studied are NaOH, CaCl$_2$, LiCl, NaHCO$_3$, NaBr, BaCl$_2$, KOH, K$_2$HPO$_4$, FeCl$_3$ and MgCl$_2$. The experiments were conducted under humidified flue gas using a laboratory-scale stainless steel fixed-bed reactor to simulate the conditions encountered in the bag filters during spray drying flue gas desulfurization process. Most of the additives tested increased the SSC of RHA/CaO sorbent, because it allows for a higher degree of SO$_2$ removal, whereby sodium hydroxide (NaOH) has been found to be the best additive among all the other additives studied. The beneficial effect of the additives might be due to its alkaline and hygroscopic (deliquescent) properties that promote SSC of RHA/CaO sorbent. However, the effectiveness of these additives was found to be also dependent on the relative humidity of the flue gas. Although most of the additives were show to have positive effect on the SSC of the RHA/CaO sorbent, some was found to have negative or insignificant effect. Thus, this study demonstrates that proper selection of additives can improve the SSC of RHA/CaO sorbent significantly

EGC 056 (Oral)

DESIGN MODEL FOR PHENOL REMOVAL IN CONSTRUCTED WETLAND INCORPORATING BIOFILM PROCESS

Vanitha Gopalkrishnan [1], Lim Poh Eng [1], Md. Sani Ibrahim [1] and Koh Hock Lye [2]
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Penang, Malaysia

Constructed wetland is considered as an environmentally friendly waste treatment system as it fully utilized emergent plants and microorganisms for the removal of pollutants. Existing design models for constructed wetland are based on first-order kinetics using input/output data without distinguishing the respective role of the microorganisms attached to the wetland media (biofilms) and those suspended in the aqueous phase. The objective of this study was to illustrate the significance of both the biofilms and suspended microorganisms in the removal of phenol in

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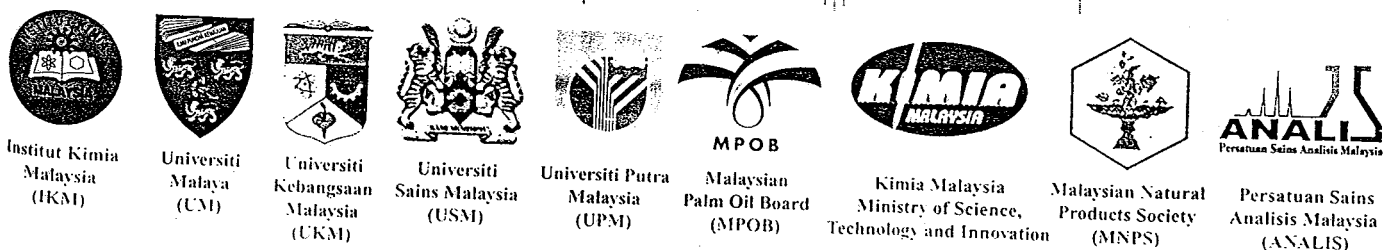
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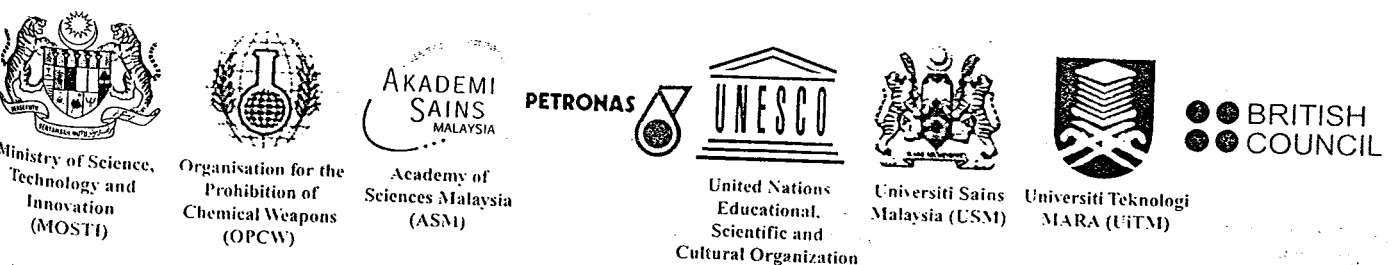
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Datuk Dr Soon Ting Kueh
on behalf of the 12ACC Abstract Committee
Institut Kimia Malaysia

Date: July 31, 2007

Preface

The **12th Asian Chemical Congress (12ACC)** is the flagship scientific meeting of the Federation of Asian Chemical Societies (FACS). Held every two years by a member society of FACS, the Asian Chemical Congress has become a major international meeting of both eminent and upcoming scientists and researchers from all over the world. 12ACC is hosted by Institut Kimia Malaysia (IKM) in Kuala Lumpur, Malaysia from August 23-25, 2007. It has attracted more than 1,500 delegates from over 50 countries. With 1,292 titles being presented, 12ACC ranks among the biggest ACCs ever held.

The **Scientific Programme** of 12ACC comprises the following:

Plenary Sessions comprising six (6) Plenary Lectures
Four (4) FACS Awardee Lectures
Four (4) Scientific Sessions:
  ➤ Inorganic, Organometallic and Bioinorganic Chemistry (IOB)
  ➤ Organic Chemistry: Mechanism and Syntheses (ORC)
  ➤ Physical and Theoretical Chemistry (PTC)
  ➤ Oils and Fats Chemistry and Technology (OCT)
Seven (7) International/Regional Symposia:
  ➤ International Symposium on Environmental and Green Chemistry (EGC)
  ➤ International Symposium on Food Analysis, Chemistry and Technology (FACT)
  ➤ International Symposium on Innovation in Chemistry Education (ICE)
  ➤ International Symposium on Natural Products and Medicinal Chemistry (NPMC)
  ➤ International Symposium on Polymer and Materials Chemistry (PMC)
  ➤ Third Regional Symposium on Total Laboratory Management (QSEL) 2007
  ➤ Malaysian International Symposium on Analytical Sciences (SKAM-20) 2007

A total of 1,293 presentations, comprising 6 plenary lectures, 4 FACS Awardee Lectures, 113 keynotes, 418 orals and 749 posters would be made at 12ACC. The breakdown of the presentations is as follows:

Session / Symposium	Special	Keynote	Oral	Poster	Total
Plenary Lectures	6				6
FACS Award Lectures	4				4
IOB		5	32	93	130
ORC		7	41	108	156
PTC		8	42	55	105
OCT		5	19	15	39
EGC		31	63	71	165
FACT		6	26	31	63
ICE		6	25	11	42
MPNC		8	18	165	191
PMC		20	62	81	163
QSEL		5	20	-	25
SKAM-20		12	70	121	203
TOTAL	10	113	418	752	1293

EGC 115 (Poster)

REMOVAL OF SO₂/NOₓ FROM FLUE GAS OVER DRY-TYPE SORBENT INCORPORATED WITH METAL OXIDE CATALYSTS – A REVIEW

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The global emission of SO_2 and NO_x has increased rapidly in the line with the increase in energy consumption as a result of economic and population growth worldwide. This phenomenon has resulted in significant negative impact to both the environment and human health as SO_2 and NO_x are toxic and acidic gases that causes human respiratory problem, acid rain and impair visibility. Consequently, for the past few decades, researchers has been developing new technologies for removing SO_2 and NO_x from flue gases generated, especially in power plants, using various sorbents/catalyst. Nevertheless, most of the technologies developed are for the removal of SO_2 and NO_x using separate individual processes. Since SO_2 and NO_x are normally present together, thus it would be beneficial if there is a process that can remove both pollutants simultaneously. However, developing a simultaneous process is very challenging as both pollutants have contradictory properties especially in term of solubility. Therefore, more study need to be carried out in developing this simultaneous process. This paper aims to review briefly the typical de-SO_2 and de-NO_x technology currently being implemented in the industries. Based on some fundamental research results, sorbents/catalyst incorporated with metal oxide, especially rare earth metal shows promising results in reduction SO_2/NO_x. This paper will also highlight some of the promising technology currently being developed for simultaneous removal of SO_2 and NO_x from flue gas using various sorbents/catalyst integrated with metal oxide.

EGC 116 (Poster)

EQUILIBRIUM STUDY ON THE ADSORPTION OF CR(III), NI(II), AND ZN (II) IONS FROM WASTEWATER BY POWDERED POMELO (*Citrus maxima*) PEELINGS

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The pomelo is the largest member of the citrus fruits. Pomelo has thick fibrous skin, which makes it a good adsorbent for heavy metal ions in water. In this study, we evaluated the capability of powdered pomelo peelings to remove Cr(III), Ni(II), and Zn(II) from wastewater. Five adsorption models (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Flory-Huggins isotherms) were used to evaluate the influence of the type of ions on the adsorption process. The data shows that Langmuir and Freundlich isotherms described the adsorption process more appropriable than the other isotherm models. The nature of the heavy metal ion affects the adsorption capacity of the sorbent. The results showed that the powdered pomelo peelings could be used for the removal of Cr(III), Ni(II) and Zn(II) from wastewater.

EGC 117 (Poster)

MAGNETOCALORIC EFFECT IN ZINC FERRITE NANOPARTICLES

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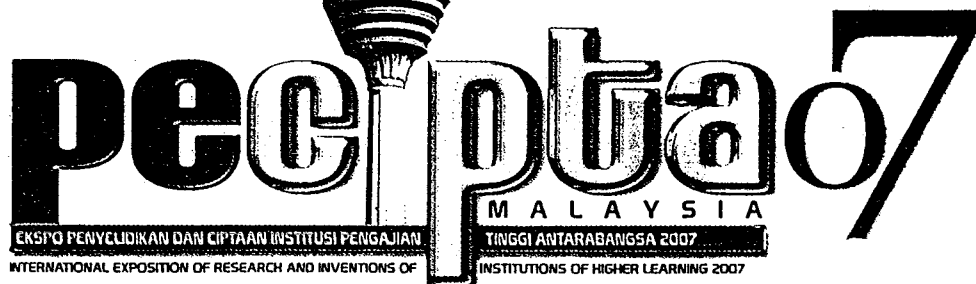[2] Department of Opthalmic Optics Konyang University, Daejeon, Korea 320-718
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Magnetic nanoparticles provide an attractive alternative to conventional bulk magnetocaloric effect (MCE) materials because of their ease of assembly in thin film form and other desirable features such as control over the entropy change across the superparamagnetic-blocking transition usually determined by the particle size. We have synthesized zinc ferrite nanoparticles using chemical co-precipitation technique through a sonochemical method with surfactant such as oleic acid. The average size of the zinc ferrite particles can be controlled by the ratio R = [H₂O]/[surfactant] with mean size about 11.2 nm and 13.4 nm. Powder X-ray diffraction measurements show the spinel structure

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EXHIBITOR(S)

Dr. Lee Keat Teong, Prof. Dr. Abdul Rahman Mohamed,
Assoc. Prof. Dr. Azlina Harun@Kamaruddin, Irvan Dahlan

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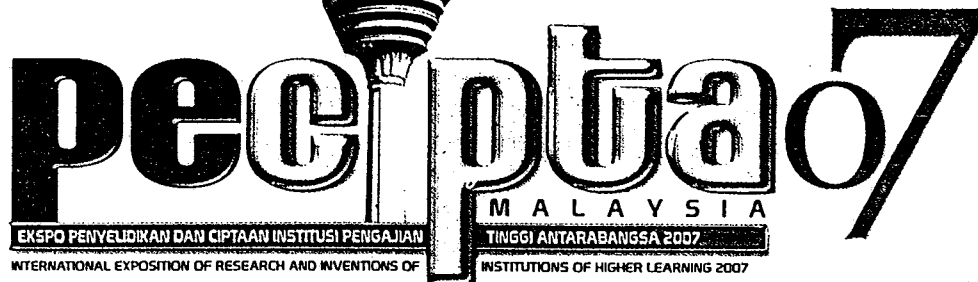
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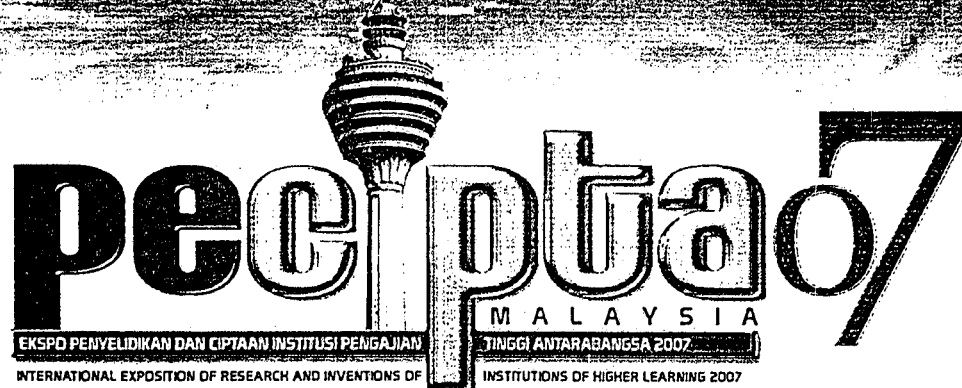
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REKAAN / CIPTAAN

Rice Husk Ash-Based Sorbent/ Catalyst As A Novel Industrial Gas Cleaning Technology

PEREKA / PENCIPTA

Dr. Lee Keat Teong , Prof. Dr. Abdul Rahman Mohamed ,
Assoc. Prof. Dr. Azlina Harun@Kamaruddin , Irvan Dahlan

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SIMULATANEOUS REMOVAL OF SO_2 AND NO
USING IMPREGNATED C_aO/RICE HUSK ASH
SORBENT WITH METAL OXIDE

GUI MEEI MEI
Matric No.: 73121

April 2007

ACKNOWLEDGEMENT

ABSTRACT

Rice Husk Ash (RHA) with high silica content is believed can be used to synthesis sorbent for simultaneous removal of sulfur dioxide (SO_2) and nitrogen oxide (NO_x). According to previous studies, reaction between rice husk ash and calcium oxide (CaO) or calcium hydroxide ($Ca(OH)_2$) gives calcium-silicate-hydrates gels (C-S-H); $(xCaO \cdot SiO_2 \cdot yH_2O)$ that has higher porosity structure and larger surface area than silica. Besides, studies has proved that C-S-H is a highly reactive sorbent that can be used to remove SO_2 from flue gas effectively.

The main objective of this thesis is to synthesis sorbents that can remove SO_2 and NO_x from flue gas simultaneously. It is believed that the sorption activity of CaO/rice husk ash sorbent can be improved to achieve NO_x removal by adding metal oxide on the surface of the sorbent via impregnation method. The impregnation method being used in this thesis is wet impregnation method and few metal oxides that is believed has adsorptive activity on NO_x has been chosen. The effect of various sorbent preparation variables such as types of metal oxides, metal solution precursors, metal loading, and pretreatment of RHA on sorption activity are also investigated.

Sorption activity test on the sorbents has revealed that there is improvement of sorption capacity of the impregnated CaO/RHA sorbent compared to the non impregnated sorbent. Among of all of the sorbents being synthesized, the CaO/RHA sorbent impregnated with Ce_2O_3 has the highest capacity for removal of SO_2 and NO simultaneously.

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STUDY OF FLUE GAS DESULFURIZATION
USING ADSORBENT MADE FROM RICE HUSK
ASH /Ca O/Na OH

JIBRAIL B KANSEDO
Matric No : 70495

April 2006

ACKNOWLEDGEMENT

STUDY OF FLUE GAS DESULFURIZATION USING ADSORBENT PREPARED FROM RICE HUSK ASH/CaO/NaOH

ABSTRACT

Adsorbents for dry-type flue gas desulfurization (FGD) were prepared from rice husk ash (RHA), calcium oxide and NaOH as additive by water hydration method. Two types of RHA were used in the experiment, one was obtained directly from the mill (black colored), and the other was obtained after pre-treatment of the black colored RHA with temperature at 600 °C. The chemical compositions of the RHAs were determined using X-ray Fluorescence (XRF) spectrometer. It was found out that the weight percentage of SiO_2 in the white colored RHA is higher (89.0 wt %) than in the black colored RHA (68.0 wt %). Response surface methodology (RSM) based on four-variable central composite face centered design (CCFCD) was used to determine the effect of hydration period (4 - 20 h), RHA/Ca ratio (0.3 – 3 g), amount of additive (0 – 0.5 g NaOH) and hydration temperature (150 – 250 °C) on the SO_2 removal activity. It was found that the most important variables affecting the SO_2 removal activity were the RHA/Ca ratio and the amount of additive. For experiment model set D1 (using RHA with pretreatment) under optimal conditions, the best values for hydration period, RHA/Ca ratio, amount of additive and hydration temperature were 10.08 hr, 2.86 g/g, 0.5 mol/L and 150 °C respectively. Whereas for experiment model set D2 (using black colored RHA) under optimal conditions, the best values were hydration period of 13.37 hr, RHA/Ca ratio of 3 g/g, additive amount of 0.5 mol/L and hydration temperature at 150 °C. At these conditions, the maximum SO_2 removal activity for experiment model set D1 is 135.403 mg SO_2 absorbed/g Ca^{2+} while for experiment model

set D2, the value is 129.047 mg SO_2 absorbed/g Ca^{2+}. The results of this study have clearly showed that by pre-treating RHA, the SO_2 removal activity is much better.