Carbon Monoliths from Victorian Brown Coal for Electrical Swing Adsorption Process for CO_2 Capture

Final Report

BCIA Funded Project

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Contents

Summary

In this final report, we report on the testing of the Victorian brown coal monolith and prediction of the performance in an ESA system. We were not able to obtain experimental data on the Victorian Brown Coal monolith due to insufficiency of sample but we were able to obtain adsorption data and physical properties which, together with our validate model, allowed us to predict the performance of the brown coal monolith. However, we have validated our model of the ESA apparatus using commercial carbon monoliths (provided by MAST carbon) and we have measured the properties of small pieces of the Victorian Brown Coal monolith – this has allowed us to calculate what the expected performance would be.

Our initial data showed that the MAST carbon performance was superior to the Victoria brown coal performance (recovery and purity) but this may be attributed to the physical geometric parameters of the sample rather than any intrinsic deficiency of the brown coal itself. In addition, there is considerable scope to improve the synthesis and application of the brown coal samples, especially given the very low base cost of the material and the relatively low synthesis cost.

1. Introduction and Background

This project concerns the development and testing of Carbon Capture technology utilizing Victorian Brown Coal as the capture agent. The project is a collaboration of Monash University and The University of Melbourne as part of a consortium of international partners including industry and research organisations through the European Framework 7 Project MATESA (http://www.sintef.no/projectweb/matesa/).

The project includes two aspects: (a) materials synthesis of the Victorian Brown Coal Monoliths (conducted at Monash University) and (b) development of an experimental testing platform and simulation tools for assessing the performance of the monoliths in an electrical swing adsorption (ESA) mode. In an ESA process, the energy for desorption of the adsorbed component of flue gas (CO_2) is provided by the Joule (ohmic) heating of the monolith which must be conductive. This approach efficiently delivers the required energy directly to the point at which it is required, thereby minimising (for example, radiative and conductive) losses. This final report covers progress made in the final year at The University of Melbourne in delivering the third component of the project; namely, testing of Victorian Brown Coal Monoliths in the ESA system.

2. Victorian Brown Coal Monoliths - Characterisation

As indicated in the second year report, an experimental ESA system was constructed to test the performance of carbon monoliths and to generate proof of concept and engineering data to allow evaluation of the ESA process. The ESA system was then tested on a MAST carbon sample. The results were reported in the second progress report and published[1]. An example of the results obtained are shown below in Figure 1. In this figure, we show the carbon dioxide collected from the monolith on application of the electric current – two different current levels were used (8.5 and 12 A) and N2 purge gas was used to sweep the CO_2 from the sample. Isotherms of CO_2 and N_2 on the brown coal monoliths were measured by the group of Chaffee and reported in their final report. The measurements were made on small fragments of monolith which are taken to be representative of larger pieces. Figure 1 shows the adsorption isotherms at 293, 303 and 313K for CO_2 on the brown coal monolith.

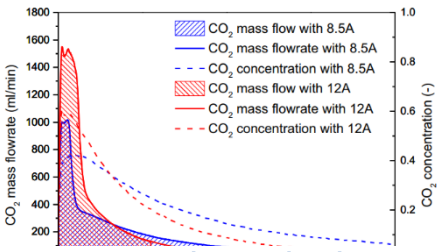
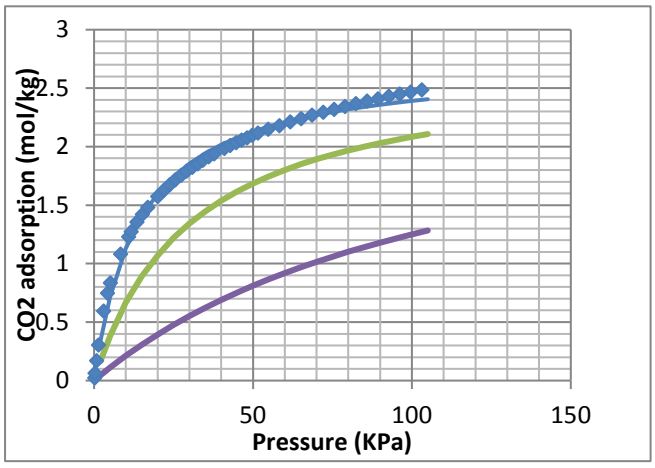


Figure 1 Harvest time at electric current 12 A and 8.5 A



From these measurements, we used the Clausius equation to estimate the isosteric heat of adsorption for use in the single site Langmuir equation. The adsorption heat (Q) was found to be 18,000 J/mol.

Fig. 2 Isotherms of CO_2 on brown coal monolith; symbol - experiment, lines – simulations

According to the single site Langmuir model, the adsorption amount (q) can be calculated as:

$$q = \frac{MB_0 \exp\left(\frac{Q}{RT}\right)P}{1+B_0 \exp\left(\frac{Q}{RT}\right)P} \qquad (1)$$

where M, B_0, are Langmuir parameters (M = 2.73 kg/mol; and B_0 = 2.55 x 10^{-05} 1/kPa), and T and P are temperature and pressure respectively. R is the ideal gas constant. The isotherms for

[1] Zhao, Q., *et.al*, "Impact of operating parameters on CO2 capture using carbon monolith by Electrical Swing Adsorption technology (ESA)" *Chemical Engineering Journal*, 327, 441, 2017.

nitrogen on the monolith were also determined by the Chaffee group and reported in their final report.

In addition to the adsorption isotherms, we also determined the physical properties and electrical resistance of the small sample of monolith provided. These data are shown in the Table below:

Table 1: Physical Properties of the Victorian Brown Coal Monolith

Physical properties	Parameters	Units	Value
Density	$\boldsymbol{\rho}$	kg/m3	534
Porosity	$\boldsymbol{\varepsilon}$	1	0.32
Heat capacity	$\boldsymbol{c_p}$	J/(kg·K)	$6.58T_s - 1410$
Length	$\mathbf{l}$	cm	6.5
Diameter	$\mathbf{d}$	cm	1.5
Channel width	$\boldsymbol{l_{ch}}$	mm	0.9
Wall thickness	$\mathbf{w}$	mm	0.3
Resistance	$\boldsymbol{\Omega}$	ohm	0.604

3. Victorian Brown Coal Monolith – Testing in ESA apparatus

A small section of extruded brown coal monolith was provided for ESA testing. The brown coal monolith (resistance of 0.604Ω) – ID 15mm x L 63mm was sealed with Teflon tape and located in our ESA system where several solenoid valves were provided for maintaining a breakthrough process with data logged with LabVIEW software. Figure 3 is a schematic of the apparatus.

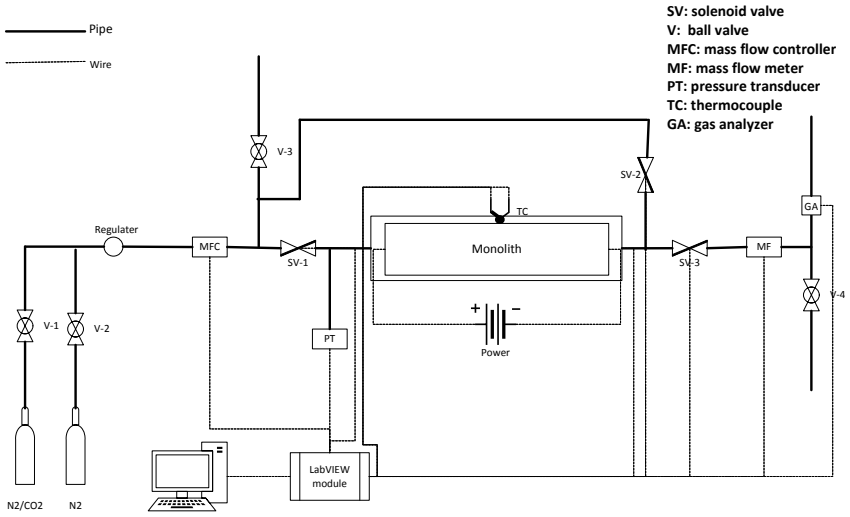


Fig. 3 Schematic of ESA apparatus

Breakthrough experiments were performed to determine the adsorption kinetics of the monolith. In this experiment, a stream containing 15% CO_2 in nitrogen is introduced into the column and the exit concentration of CO_2 is measured as a function of time. Measurement of this dynamic curve and its analysis in the context of a model provides values of the overall mass transfer coefficient. We have performed breakthrough experiments at flowrates of 100 and 300 ml/min, at room temperature and an atmosphere pressure. A typical set of results are shown in Figure 4. Once the breakthrough experiment was completed, the monolith was placed in an oven at 100°C for ½ an hour to release the CO_2 adsorbed and then cooled under an N_2 environment prior to a new experiment. Each breakthrough run was repeated in triplicate.

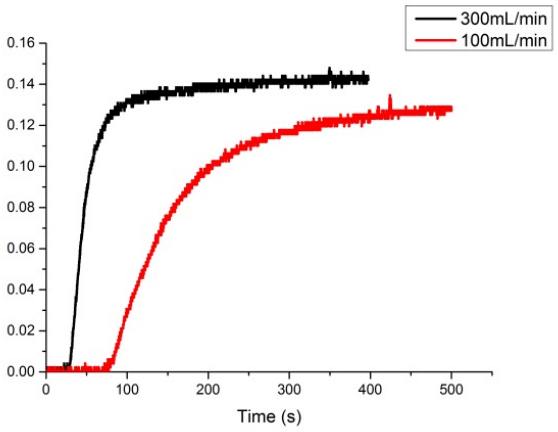


Figure 4. Breakthrough experiment with the brown coal monolith at room temperature and ambient pressure. The feed is 15% CO2 in nitrogen.

A mathematical model of the adsorption process was developed in the COMSOL™ platform. was constructed to simulate the performance of the brown coal monolith and allow simulation of a full ESA cycle.

4. Mathematical Model of the ESA process

In order to simplify model complexity and reduce computation time, every channel in the monolith was assumed to have identical geometry and condition. Thus, the behaviour in one channel can represent those in the overall monolith. The one channel model is further simplified to 1D.

A mass balance of component i in the gas phase in a monolith channel is shown in Equation 2:

$$\frac{\partial C_i}{\partial t} + \rho_w \frac{1-\varepsilon_m}{\varepsilon_m}\frac{\partial q_i}{\partial t} + \frac{\partial (v_{ch} C_i)}{\partial z} = D_{ax,i}\frac{\partial^2 C_i}{\partial z^2} \qquad (2)$$

where, C_i (mol/m3) is the gas concentration in the monolith channel, and v_{ch} (m/s) is the gas velocity. The gas adsorption kinetics can be described successfully using a Linear Driving Force (LDF) model, which is simple, analytic, and physically consistent. The mass balance in the monolith wall is described by the LDF model, which is shown in Equation 3.

$$\frac{\partial q_i}{\partial t} = k_{LDF}(q_i^* - q_i) \qquad (3)$$

Where, q_i (mol/kg) is the quantity of component i adsorbed by activated carbon, k_{LDF} (1/s) is the kinetic coefficient, q_i^* (mol/kg) is the quantity of component i absorbed by activated carbon at equilibrium. The pressure drop in the monolith channel is described by Darcy law:

$$\frac{\partial P}{\partial z} = -150\frac{\mu_g(1-\varepsilon_m)^2}{\varepsilon_m^3 l_{ch}^2} v_{ch} \qquad (4)$$

Where, μ_g (Pa*s) is the mixture gas viscosity.

The energy balance of gas mixture is described by:

$$\varepsilon_m \rho_g c_v \frac{\partial T_g}{\partial t} - \varepsilon_m R_g T_g \frac{\partial C_t}{\partial t} = \lambda \frac{\partial^2 T_g}{\partial z^2} - \varepsilon_m \rho_g c_p v_{ch} \frac{\partial T_g}{\partial z} - a'(1-\varepsilon_m) h_f (T_g - T_s) \quad (5)$$

Where, ρ_g (kg/m3) is the gas mixture density, c_v (J/(kg·K)) is the heat capacity of the gas mixture at constant volume, λ_g (W/(m·K)) is the thermal conductivity of the gas, c_p (J/(kg·K)) is the heat capacity of the gas at constant pressure, a' (1/m) is the area to volume ratio, and h_f (W/(m2·K)) is the surface heat conduction coefficient.

The energy balance of the solid phase is described by

$$\rho_w c_{ps} \frac{\partial T_s}{\partial t} = h_f(T_g - T_s) + \frac{h_w(T_w - T_s)}{1 - \varepsilon_m} + \rho_w \sum_{i=1}^{n} -\Delta H_i \frac{\partial q_i}{\partial t} + \frac{\phi I^2 R}{1 - \varepsilon_m} \quad (6)$$

Where, ρ_w (kg/m3) is the density of the monolith wall, c_{ps} (J/(kg·K)) is the heat capacity of the monolith wall, T_w (K) is the surrounding temperature, h_w (W/(m2·K)) is the surface heat conduction coefficient of wall, ϕ is the energy efficiency of the Joule effect, and I (A) is the electric power applied to the monolith. ϕ value is determined in the simulation and then verified by experiment.

The average purity and CO2 recovery are determined by the following equations:

$$\text{Purity} = \frac{\int_0^t w_{CO_2} V_{out} dt}{\int_0^t V_{out} dt} \quad (7)$$

$$\text{Recovery} = \frac{\int_0^t w_{CO_2} V_{out} dt}{\int_0^{t_0} (w_{CO_2,in} V_{in,ads} - w_{CO_2,out} V_{out,ads}) dt} \quad (8)$$

Where, w_{CO_2} is the CO2 mole fraction of exiting gas in the desorption step, V_{out} (ml/s) is the flow rate of exiting gas in the desorption step, t (s) is the desorption time, $w_{CO_2,in}$ is the CO2 mole fraction of feed gas in the adsorption step, $V_{in,ads}$ (ml/s) is the feed rate in the adsorption step, $w_{CO_2,out}$ is the CO2 mole fraction of exit gas in the adsorption step, $V_{out,ads}$ (ml/s) is the flow rate of exiting gas in the adsorption step, and t_0 (s) is the adsorption time.

The following assumptions were made for modelling the equations in COMSOL5.0 for running the ESA process.

- The gas flow in each channel is at the same velocity
- The monolith wall is assumed to be homogenous, with uniform porosity and density
- Ideal gas behaviour is assumed
- The electric resistance in the monolith linearly decreases with.

5. Results - the ESA process using Brown Coal Monolith

The kinetic coefficient (k_{LDF}) for the linear driving force (LDF) model was obtained by matching breakthrough data to the simulation as shown in Figure 5. The simulation result with k_{LDF} = 0.2 was in a good agreement with experimental data, and this kinetic coefficient was further verified in the following desorption step.

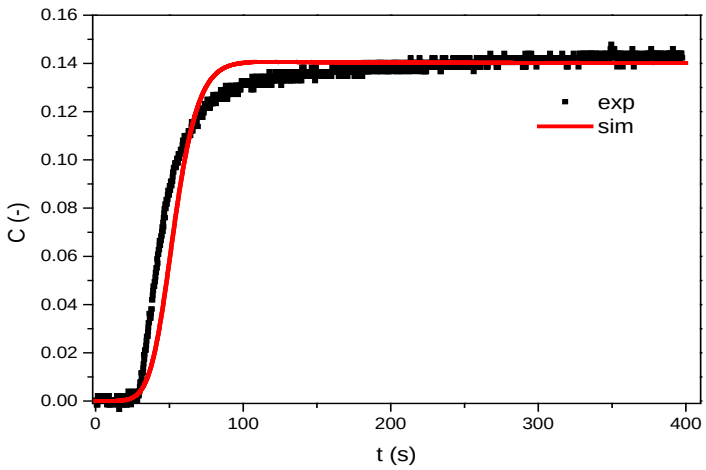


Fig. 5 Simulation of breakthrough at the flowrate of 300ml/min (K = 0.2 1/s)

In the electrification (desorption) step, an electric current of 12A and an electrification time of 60 s was applied. During this time, the electric energy consumed is 815 J. In the desorption step, N_2 was employed to purge CO_2 from the column. The N_2 purge rate was 300 ml/min (0.047 m/s), and the purge time was set to 100 s in the simulation. During this time period, the adsorbed CO_2 is completely desorbed and the monolith temperature reaches 84°C.

The regeneration curve is shown in Figure. 6. As with the MAST commercial carbon monolith, the CO_2 concentration rapidly increases upon electrification and then decreases as nitogen purge gas elutes from the column.

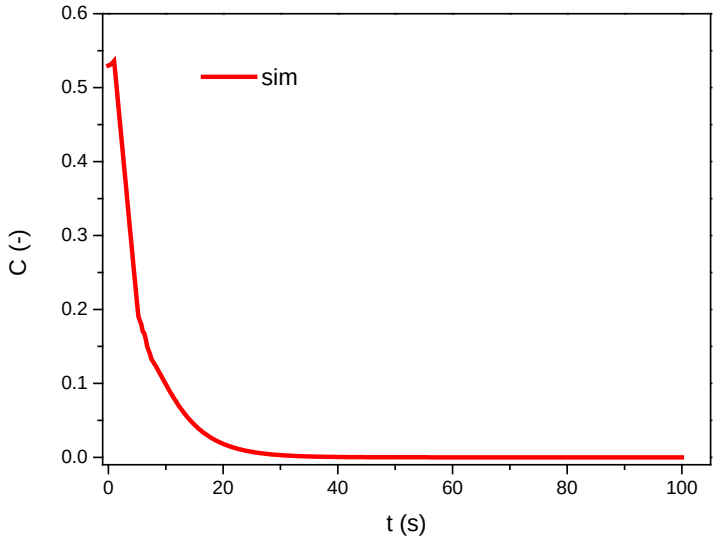
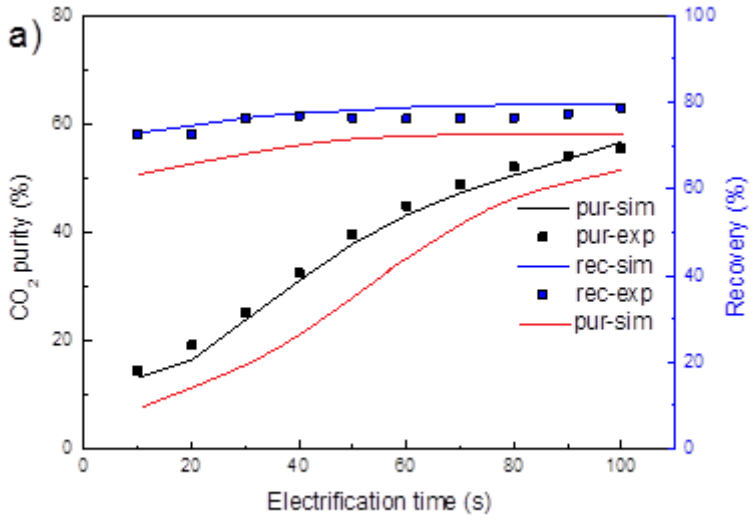


Fig. 6 CO2 concentration in exit gas from desorption of CO2 from the brown coal monolith as a function of time.

Unfortunately, the Victorian brown coal monolith sample provided was not sufficiently large for use in our experimental cyclic ESA apparatus and therefore we were confined to the use of our validated mathematical model to assess the performance of the monolith. Future work should focus on securing larger samples to ensure experimental validation of our predictions.

The four steps included in our simulated ESA cycle include: adsorption, electrification, N_2 purge and cool down. In our previous report, we discussed ESA cycle results using the MAST commercial carbon sample. In that study, we collected CO_2 during the N_2 purge step but not for the entire purge time because the CO_2 product becomes increasingly diluted with nitrogen as the desorption proceeds. The period of time for which CO_2 is collected is called the harvest time – we control this so that we always collect the same average amount of CO2 (80% by mass). Hence CO_2 harvest time is a proxy for productivity. Figure 7 shows the comparison of the CO2 productivity and purity obtained from a simulation of the ESA process using the brown coal monolith compared to the MAST carbon sample. The Victorian brown coal sample provides lower purity and recovery than the MAST carbon sample. However, the harvest time for the same electrification time is shorter, indicating that the brown coal sample is "faster", which is supported by the higher linear driving force rate constant (0.2 vs 0.1 s^{-1}).
The lower purity and recovery of the Victorian brown coal sample are a consequence of the lower cell density (200 cpsi) and therefore higher voidage compared to the MAST carbon sample (400 cpsi).



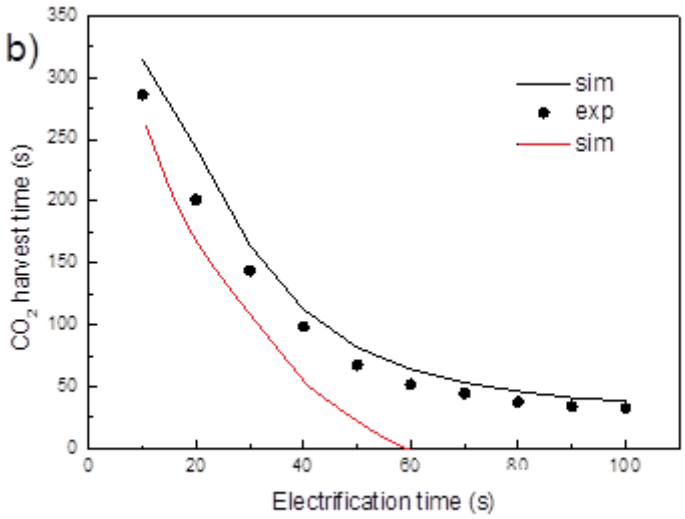


Fig. 7 CO2 purity and productivity comparison for ESA process (blue and black curves MAST carbon sample, red curves are Victorian Brown Coal samples)

Energy consumption in the ESA process occurs during the CO2 desorption process. An extension of electrification time and increase in electric current provides higher CO2 product purity and recovery, but requires more electric power. In our experiments, a specific energy requirement of 5.6 MJ/kg CO_2 was required when the electrification time was 80 s and an electric current of 12 A was employed for the MAST commercial carbon sample. In contrast, the energy consumption for the brown coal monolith sample was calculated to be 10.2 MJ/kg CO_2, which is considerably higher than the MAST commercial sample. Some of this difference can be attributed to the higher resistance of the brown coal sample (0.6 Ω/20 cm at 423.15 K compared to 0.2 for the MAST carbon sample). In addition, the adsorption capacity of the brown coal sample was somewhat lower than the MAST carbon sample, providing lower productivity and therefore higher energy per unit of CO_2 produced.

6. Conclusions

This study has investigated the potential for Victorian brown coal to be used in an electrical swing adsorption process. The work was undertaken at both Monash University (materials development) and The University of Melbourne (process development). In our process development work, we developed an experimental ESA system to evaluate the performance of conducting carbon samples. We also developed a mathematical model to allow us to understand the data obtained and predict performance. The system and model were validated using a commercial activated carbon monolith provided by MAST carbon and then applied to the Victorian Brown Coal monolith. We were not able to obtain experimental data on the Victorian Brown Coal monolith due to insufficiency of sample but we were able to obtain adsorption data and physical properties which, together with our validate model, allowed us to predict the performance of the brown coal monolith. Our initial data showed that the MAST carbon performance was superior to the Victoria brown coal performance (recovery and purity) but this may be attributed to the physical geometric parameters of the sample rather than any intrinsic deficiency of the brown coal itself. In addition, there is considerable scope to improve

the synthesis and application of the brown coal samples, especially given the very low base cost of the material and the relatively low synthesis cost.