Surface excess adsorbed amount in coal

Introduction

The ever increasing world-wide demand for fossil fuels has led to renewed interest in alternative energy sources. An alternative source for methane is the production of gas from underground coal, referred to as coal-bed methane (CBM). The production of CBM is already occurring commercially in the United States, and many other possible commercial reservoirs exist all over the world.

At first the production of CBM is usually done by directly pumping of all fluids from the reservoir. When primary production of CBM is no longer or not commercially interesting, the enhancement of production by simultaneous gas injection is an option to increase production. This procedure is referred to as enhanced coal-bed methane (ECBM) production.

Burlington Resources (REFERENCE)demonstrated ina field experiment that ECBM can increase methane production. The decision to use ECBM at a certain stage of production, or even the decision to exploit a CBM reservoir is based on a break even analysis. Also the decision of what kind of gas is to be injected is based on such an analysis. Analysis is held back by the lack of accurate predictive models for coal-bed methane reservoirs in general, and the influence of gas injection in particular.

The limiting factor in the development of accurate models is that the behavior of gas and mixtures of gases in coal-beds is still poorly understood, despite some groundbreaking work by ***. An improvement in the understanding of the gas-water-coal system as found in underground coal is limited by a lack of experimental data, especially under in-situ conditions.

The difficulties in obtaining experimental data is due to:
* heterogeneous nature and complex structure of solid and ground coal,
* the technical difficulties associated with experiments under simulated reservoir conditions.
* Time needed for processes.

The reservoir conditions involve pressures from 80 to 150 bar and temperatures from 35 to 50 °C. Additional experimental difficulties occur when using a gas mixture. Therefore, the focus of this part of the program is to measure the behavior of pure and mixed gases in coal.

The behavior of gases in coal is investigated with a volumetric sorption apparatus is based on Clarkson (19…) and Krooss (19….). The excess sorption is calculated from mass balance combined with the real gas law. Excess sorption is defined as the difference between the amount of gas added and the amount observed. No volume corrections for coal swelling/shrinking or change in free volume caused by the formation of a sorbed phase are used. Quantitative corrections as mentioned above, are suggested by *** and ***. They have a large influence on sorption results but have not yet been experimentally confirmed.

The behavior of two coal types have to be investigated at reservoir conditions (~ 48.9°C, between ~20 and ~ 150 bar). The gases of interest are H_2, CH_4, CO_2, N_2 and mixtures.

The following experiments have been performes:

- Two duplicate carbon dioxide experiments,
- two duplicate mixture (~80% hydrogen with ~20 % carbon dioxide) experiments,
- two repeat hydrogen experiments followed by two repeat methane experiments. A duplicate experiment is defined as a similar but independent experiment. A repeat experiment is defined as the same experiment performed on the same coal directly after the first experiment.

No experiment agrees with another or with common curvatures for sorption behaviour. The lack of repeatability in the repeat experiments for hydrogen and methane indicates that the coal sample does not remain inert during the experiments, one of the main assumptions necessary for data interpretation. This is also evident from the change in pre- and post experimental weights and volumes of the sample. The lack of repeatability of the duplicate carbon dioxide experiments is caused by the existence of systematic errors in the used temperature measurements.

The peculiar behavior of the methane and hydrogen and mixture experiments is caused by the use of the incorrect ideal gas equation of state. The strange behavior of the carbon dioxide component in the mixture experiments is due to insufficient mixing of the two gases. The assumption of constant composition throughout the setup is not valid, and renders these calculations useless.

The usefulness of the obtained experimental data is hampered by the paucity in the repeatability and the invalidity of the required assumptions of inert adsorbent and constant composition. This has severe ramifications for the feasibility of the aim of the study to measure the behavior of gases in coal. The appropriateness of the current experimental approach must be reexamined, or the focus of the study must be redefined.

Materials and Methods

Experimental accuracy

   The setup (Figure 1) is based on the experimental setups of Clarkson (…)and Krooss (…), which in turn modified after the setup as described by Mavor (..). The set-up consists of IN 3 ZINNEN UITLEGGEN wat er werkt. The main improvements of this new setup are the inclusion of inline sample valves and a larger sample cell. The larger samples reduce heterogeneity of the coal. The inline sample valves minimizes system disturbance when taking of gas samples (~0.1 µL).

The setup is designed to perform duplicate experiments. The experiments are duplicates to increase reliability and to save time. Throughout the experiment, pressure and temperature are recorded every ten seconds.. The pressures and temperatures at equilibrium are the parameters of interest. The pressure and temperature equilibrium in an empty cell is reached in several minutes. When filling or emptying an empty cell with gas, at least 10 minutes are used. The pressure and temperature in a cell with a coal sample is at equilibrium when the pressure decreases with less than 0.2 bar/hr. To reduce the random uncertainty in the measurements, 50 consecutive measurements at equilibrium are averaged. The estimated random uncertainty of the measured volumes and excess sorbed amounts are calculated from the standard deviation of mean in pressure and temperature. The influence in the dead volumes of the valves is considered negligible.

   The temperatures are measured with type K*** thermocouples, with a digital step size varying from0.002 and 0.003 °C. For the thermocouples in the reference cells, the random uncertainty in temperature measurements was about 0.06 °C. The standard deviation of mean of the temperature measurements is 0.02 °C. The temperature in the reference cells varied due to the day-night cycle in a wavelike pattern with an amplitude of 0.05 °C. The temperature measurements usually have a systematic uncertainty of 0.2°C or less.

   The pressures are measured with a Drück^{TM} PTX 611 pressure transducers, having a digital step size vary from 0.007 to 0.008 bar. The random uncertainty of the pressure transducers was 0.01 bar. The standard deviation of mean of the pressure measurements was also 0.01 bar. The pressure measurements have an estimated systematic uncertainty of 0.5 % or less. The pressure transducers measure the pressures relative to the air pressure. These measurements are converted to absolute pressures by adding 1 bar. Variations in air pressure are negligibel. The pressure transducers are not suited for pressure measurements below atmospheric. After evacuation the pressure is estimated to be 0.001 bar with an uncertainty of 0.001.

Sample preparation

: A high rank (Semi Anthracite, R_{max} 2.41%) from Selar, South Wales Coalfield, and a low rank (Sub-bituminous B/ High volatile Bituminous A, R_{max} 0.53 %) coal sample from the Nottinghamshire and North Derbyshire Coalfield are used in this study. The coal samples are stored as blocks (~200 dm^3) under room conditions for several years(10 and 20 °C). The coal was sealed in plastic foil to minimize water loss and oxidation. From both coal types batches of samples for experimentation were prepared.

Coal blocks were first broken to hand-size pieces, followed by crushing to three sieve fractions, by using a steel crushing jaw and a grinder:

- For the Nottinghamshire into a >2.0 mm fraction, a <1.5mm fraction and a fraction between 1.5 and 2.0 mm,
- For the Selar into a >2.0 mm fraction, a fraction between 1.4 and 2.0 mm. The sieving procedure was as brief as possible, to minimize fracturing of coal particles to dust.

After sieving, the fractions were split into batches of ~70 cm^3. The batches were stored in glass jars of 100 cm^3 filled with argon at an n overpressure of 2.0 mbar. The samples were stored in a refrigerator at 3°C to 6°C, until selected for experimentation.

Sample preparation for an experiment

The sample is equilibrated with moisture at 96 to 97 % relative humidity at 30 °C to approachin-situ conditions. The procedure is patterned on the ASTM standard for equilibrium moisture determination (D 1412), modified to handle a larger sample. Place the sample batch (30 to 40 g) into a 500 ml glass bottle and add a surplus of double distilled water. Shake the bottle mechanically for 30 to 60 min, and then place it in a constant temperature oven for at least 3 hours. At the end of the wetting procedure, remove the excess water by filtering on a Büchner-type funnel, using suction supplied by a water filter pump. Two different funnel sizes and a range of different filter types were used. The purpose of the filtering is to remove the excess water; it is thought that the difference in funnel size and filter types had no influence on the end result of the equilibration process. Use a minimum amount of water to transfer the coal to the filter. After transfer of the coal, close the funnel with a rubber stopper fitted with a glass tube through which air saturated with water vapor is passed to prevent drying of the coal. The air is saturated with water vapor by passing it bubbling it through a glass bottle filled with double distilled water. Distribute the samples in evenly distributed layers over four sample dish. Place the uncovered sample dishes in a small vacuum-type desiccator containing a saturated solution of K_2SO_4 in the bottom for maintaining the relative humidity of 96 to 97 %. An excess of crystalline K_2SO_4 shall extend above the solution level. Evacuate the desiccator with a rotating pump for 15 to 60 min, and then place it in an insulated air cabinet, maintained at 30 ± 0.2 °C for at least 48 hour. The samples in our experiment were usually equilibrated for at least a couple of weeks. The pressure is restored by slowly admitting dry air for a period of ~ 5 min. The air is dried by passing it through a glass bottle filled with silica grains. Open the desiccator, weigh the sample dishes and place the sample inside the sample cell. Close the sample cell and connect it to the experimental setup. These last steps should occur as fast as possible, to minimize loss

of water due to evaporation. It was observed that the coal rapidly lost weight due to water evaporation.

The Selar coal was treated ~6 months after the Nottinghamshire one.

Experimental procedure

The experimental setup with the built-in coal samples is tested for leaks. The setup is tested for leaks by filling the entire setup with incrementally higher pressures of helium up to the maximum pressure of the experiment (here ~200 bar). When pressure shows no discernible pressure drop over a period of 24 to 48 h, the setup is considered leak tight. This corresponds to a leak of 4e-5 bar K^{-1} h^{-1} or less. The effect of varying temperature in the lab needs to be accounted in the assessment of the pressure variation. Once leak tight, the setup is heated to the temperature of interest (48.9°C). The thermostatic bath is filled with tap water and heated. Some of the helium pressure in the setup is bled off to make sure that the pressure in the setup does not exceed the maximum pressure of the setup (206 bar). A second 24 to 48 h leak test with helium at ~200 bar is performed afterwards. The helium pressure is bled off to atmospheric and sometimes vacuumed with a rotating pump for anywhere between 10 min and several hours.

The free volume (: the volume accessible to gas) in the sample cell is measured using the principle of helium expansion. The reference cell is filled with a helium pressure while the sample cell if filled with a known helium pressure from a previous measurement. Then the pressure is equilibrated over both the reference cell and the sample cell. The pressure and temperature is always allowed an equilibration time of at least 10 min. The recorded pressure and temperature of the reference cell is used in the calculation; the pressure and temperature of the sample cell is assumed to be equal to the pressure and temperature in the reference cell at the time of the previous step. Equation 1 is solved for the free volume (V_1). Equation 1 is based on the balance of mass combined with the real gas law. For helium, the compressibility (Z) is calculated using the McCarthy equation of state. After the volume determination the setup is vacuumed with a rotating pump for 1 to 24 hours.

The first part of the experiment is the measurement of the excess sorbed amount at increasing equilibrium pressures. The reference cell is filled with the gas of interest (e.g. CO_2, CH_4, H_2 or a mixture thereof) while the sample cell contains a known amount of gas from a previous step. The gas is then equilibrated over the two cells until the pressure is constant. The pressure is considered constant when it changes less than 0.2 bar per 1 to 3 h.

The second part of the experiment is the measurement of the excess sorbed amount at decreasing equilibrium pressures. The reference cell is kept at vacuum by a rotating pump, while the sample cell contains a known amount of gas from the previous step. The gas in the sample cell is then equilibrated over the two cells until the pressure is constant.

The excess sorbed amount for the experiments with pure gas is calculated from equation 2. The pressure and temperature in the sample cell is assumed to be equal to the pressure and temperature of the reference cell at the appropriate equilibrium. The equation is derived from mass balance considerations combined with the real gas law. No separate term for gas dissolved in the aqueous phase has been introduced. The

compressibility (Z factor) is calculated from an equation of state: The reference equation of state by L. Sun (2005) was used for carbon dioxide; for the other gases (CH_4 and H_2) the ideal gas law is used. Note the difference between equation 2 and equation 3. There have been rumors that equation 3 is the prevalently used formula for excess sorbed amount calculation. Equation 2 is clearly superior to equation 3 in three respects: Equation 3 is more prone to influence by random and systematic errors in pressure and temperature and volume due to the inclusion of an additional summation term; Equation 3 relies more heavily on the assumption of constant temperature; Equation 3 cannot be adapted for use with mixtures.

The excess sorbed amount for the experiments with mixtures is calculated from equation 2 and 4. The total excess sorbed amount is calculated with equation 2, assuming the gas behaves as an ideal gas. The excess sorbed amount of the CO_2 component is calculated with equation 4. The excess sorbed amount of other components can also be calculated with equation 4, but the H_2 peak measurements were corrupted by coelution. Because the CO_2 are much larger than the H_2 peaks, the CO_2 peaks suffered less…. Equation 4 is a variation on equation 2: The amount of CO_2 present is calculated from the partial pressure of CO_2, measured by the gas chromatograph. The compressibilities in mixture experiments are always assumed to be 1.

Experiment 1 was performed in duplicate with a 80 -20 % H_2-CO_2 mixture. Experiment 2 was performed in duplicate with CO_2. Experiment 3 was performed with Ar twice, H_2 twice and CH_4 twice.

After the last equilibration step (at a pressure between 1 and 25 bar), the volume of the experiment is measured again using helium expansion. The setup is first vacuumed with a rotating pump for 1 to 24 h, and then the method as described above is repeated.

The helium is bled off to atmospheric and the setup cooled to room temperature. The thermostatic bath is emptied and the sample cells removed and cleaned in an ultrasonic bath.

Results & Discussion

Two questions influence the results in this section. First. the 3 to 4% volume inaccuracy of the reference cells introduces a systematic error of 3 to 4% in all measured volume and excess sorbed amounts. Secondly, the measured volumes and excess sorbed amounts with decreasing equilibrium pressure (second phase) are less accurate than the same measurements with increasing equilibrium pressure (first phase). The two causes for the second question are the inaccuracy of the pressure transducers at low pressures and the addition to the system of a small amount of gas from the dead volume of the valves. Because there is a large difference in the gas pressure in the dead volume (~150 bar) and the gas pressure in the reference cell (~ 0 bar), this addition of gas has the largest influence at the start of the second phase. The influence of dead volume of the valves was considered to be negligible throughout the entire experiment.

Table 1 shows the weights of the coal samples at different stages, and the measured free volumes. The varying precision in weight measurements is dependent on the used equipment, except for the measurements of the saturated and pre-experimental coal. The rapid decrease in weight caused by the evaporation of water severely limits the reproducibility and thus the precision of the measurement. The difference between the weight of the saturated coal and the coal at the beginning of the experiment in experiment 2 B is because not all of the coal fitted into the sample cell. The coal samples show a varying decrease in weight during storage. The coal samples show a varying decrease in weight during the equilibration procedure, associated with the loss of excess water.

The coal samples show a weight decrease during the experiment. A common hypothesis is the loss of water during the experiment, especially when evacuating the setup. The excess sorbed amount per gram coal is calculated using the average of the pre and post experimental weight. The actual calculation (equation 2) of excess sorbed amount is independent of the amount of gram.

The free volume in the setup is not constant during the experiments. Thus the volume of the coal sample changes during the experiment. Common hypotheses are the loss and addition of water during the experiment or coal shrinkage and swelling. It is interesting to note that the weight and volume change of the sample do not agree, rendering the loss or addition of water hypothesis less likely. The free volumes of experiment 2 and 3B were not measured due to the existence of large leaks in the setup. The excess sorbed amounts were calculated using the average of the pre and post experimental free volumes. The actual calculations (equation 2) of the excess sorbed amount are very sensitive to changes in the free volume. A change of 1 % in the used free volume can change the calculated excess sorbed amount by 10%.

Table 1: Measured coal weights and free volumes for the three experiments.

Experiment		Coal	fraction (mm)	storage (g)		saturation (g)		experiment (g)		Free volume (ml)	
				start	finish	start	Finish	start	finish	start	finish
1	A	Tupton	1.5<>2.0	40.51	38.36	43.74	38.9	38.9	37.7871	45.75	45.90
	B	Tupton	1.5<>2.0	39.48	39.28	44.95	41.0	41.0	40.0938	42.9	42.89
2	A	Tupton	>2.0	40.96	39.97	-	40.79	40.79	38.87	44.45	
	B	Tupton	>2.0	44.46	44.00	-	44.46	42.51	41.84	41.14	
3	A	Tupton	>2.0	32.18	31.77	34.65	32.19	32.19	30.289	51.64	52.60
	B	Tupton	>2.0	37.50	36.60	40.5	37.50	37.50	37.049		

The changes in the weights and volumes during the experiment demonstrate that the coal sample does not remain inert. The cause of these changes is not known, but the most common hypothesis is a change in the amount of water in the sample cell. If correct, the experimental procedure should be modified in such a way that the change in the amount of water is negligible. A possible approach is the use of dry coal and more pure gases. This is essential, because changes in free volume have a very pronounced effect on the calculated sorption isotherms.

Figure 2 and 3 show the two duplicate CO_2 sorption isotherms. These duplicate experiments vary significantly. The primary cause is a systematic error of ~1°C in the temperature measurements of the second experiment. Other additional causes are systematic errors in the pressure measurements, errors in the used reference cell volumes or changes in the free volume and properties of the coal. The ~1 °C deviation in the temperature measurement was affirmed during the independent regauging of the thermocouples. (The measurements at increasing equilibrium pressures start at approximately 25 bar.)

The excess sorbed amount with decreasing equilibrium pressure (second phase) corresponds fairly well to the excess sorbed amounts with increasing equilibrium pressure (first phase) for the first experiment and acceptable for the second experiment, with the exception of measurements at equilibrium pressures between 90 and 110 bar. The large systematic error in temperature of the second experiment causes the larger deviation between the two phases in the second experiment.

The measurements performed at equilibrium pressure below ~90 bar show the expected smooth increasing behavior with increasing equilibrium pressure, as reported by e.g. Siemons. The measurements above 90 bar suffer from a large uncertainty, non-smooth behavior and do not exhibit increasing behavior.

The strange behavior above 90 bar are caused by the existence of systematic errors in the pressure and temperature measurements. Their influence is magnified by the rapid change in density of CO_2 at pressures between 90 and 110 bar and temperatures at approximately 48.9°C. A possible additional problem was the creation of a leak in the second experiment, which was noticed during the post experimental volume measurements.

The argon volume measurements of experiment 3A are of no real interest. They correspond to the helium volume measurements in order of magnitude, but the use of the

incorrect ideal gas law equation of state introduces a too large systematic deviation for a real comparison.

Figure 4 and 5 show the hydrogen and repeat hydrogen experiments. The repeat experiments vary significantly. The deviation is caused by a change in available free volume between the two experiments. An alternative suggestion is that the properties of the system have changed during the hydrogen experiments.

The excess sorbed amount with increasing and decreasing equilibrium pressure in both experiments shows no correspondence. This is caused by the use of the incorrect ideal gas law equation of state. The effect of the incorrect equation of state is more pronounced during the second phase of the experiment. This has two causes: During the second phase, the pressure difference between the sample cell and reference cell is larger, which means that the difference in compressibility is larger; The error increases with each equilibrium step and during with increasing equilibrium pressure the mistake is cloaked because the error in compressibility merely shifts the measured excess sorption.

The first phase of the hydrogen experiments shows smooth increasing behavior. This corresponds to the expected physical behavior.

Figure 6 and 7 show the methane and repeat methane experiment., performed right after the hydrogen experiment. No experiment with decreasing equilibrium pressure was performed due to an operational oversight. The two phases of the first methane experiment vary significantly. As with the hydrogen experiment this is caused by use of the incorrect ideal gas equation of state for methane. The variation between the two first phases of the methane experiment is caused by a change in free volume of the coal sample.

The strange shape of the first phase methane measurements, which is similar in both experiments, is caused by the use of the incorrect ideal gas equation of state for methane.

Figure 8 shows the excess sorbed amount of the total gas and CO_2 for the two duplicate mixture experiments. The excess sorbed amount of the total gas of the two duplicate experiments show similar behavior. The shift in data points is due to some systematic error. The excess sorbed amount of CO_2 corresponds only for the first few data points.

The second phase of the experiment shows an increase in sorption with decreasing pressure. This is caused by the incorrect ideal gas law as the equation of state, as explained in a previous paragraph.

Figure 9 shows the excess sorbed amount of CO_2 plotted vs. the CO_2 pressure as measured by the gas chromatograph. Except for the first few data points the two duplicate experiments show slightly similar behavior. The measured behavior is very peculiar. The cause of this peculiar behavior is that the necessary assumption of constant composition at pressure equilibrium throughout the sample and reference cell is not valid, rendering the calculation obsolete. Some additional observations that the assumption is not valid have been made throughout the experiment: It was noticed that the partial pressure of CO_2 in the reference cell filled with the mixture was not 40 bar (20 % of 200 bar), but ~10 bar; It was noticed throughout the experiment that the measured CO_2 partial pressure in the reference cell and sample cell varied considerably; It was noticed that the partial pressure of CO_2 varied with time in the sample cell. These observations and the peculiar

behavior of the measured excess sorbed CO_2 indicate that the constant composition assumption is not valid.

Conclusion

The aim of the study is to measure the behavior of different gases in coal. The excess sorption of hydrogen, methane, carbon dioxide and a 20-80% mixture of hydrogen-carbon dioxide on water equilibrated coals from Nottinghamshire was measured with the volumetric sorption technique. The experiments were not duplicable and showed some peculiar behavior. There are four different causes for these difficulties: Systematic errors in the used pressure, temperature and volumetric data; Use of incorrect equations of state; The properties of the coal sample change during the experiment; The composition of a mixture is not constant throughout the cell. These difficulties need to be solved if the aim of the study remains unchanged.

Short summary of current known problems and best solutions:

1. The 4% inaccuracy in the used reference volume, causing a possible 4 % shift in the measured isotherms. Measure the reference volumes more precisely.
2. The use of incorrect equations of state for pure gases. Use reference equations of state.
3. The use of incorrect equations of state for mixtures. Experimental study on the compressibility behavior of the mixtures of interest.
4. The changes in the properties of coal sample resulting in a shift for repeat experiments. Confirm the loss of water hypothesis, and then change the experimental procedure to prevent this effect.
5. Validity of the CO_2 calibration. Check calibration.
6. Systematic errors have a very large influence in the pure CO_2 experiments. Obtain more precise equipment.
7. Imprecise measurement of low pressures. Obtain additional pressure transducers for the low pressure range.
8. The constant composition assumption is not valid. Induce mixing by installing a pump.
9. Determination of the type of processes occurring in the coal. Experimental study.

Nomenclature

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N	number of different containers used for the volume determination	(-)
M	step of interest in the sorption measurements	(-)
P	pressure	(bar)
T	temperature	(K)
Z	compressibility	(-)
V	volume	(cm^3)
R	universal gas constant	$(mole \cdot K \cdot bar^{-1} \cdot cm^{-3})$
n	amount of gas	(mole)
c	partial pressure of the gas divided by the compressibility	(bar)

Subscripts
ads	adsorbed.
cell	sample cell.
ref	reference cell
s	start of sorption measurements
M	step of interest in the sorption measurements

Superscripts
s	start of volume determination
c	complete at end of volume determination
start	start of sorption experiment
b	beginning
eq	equilibrium
x	component
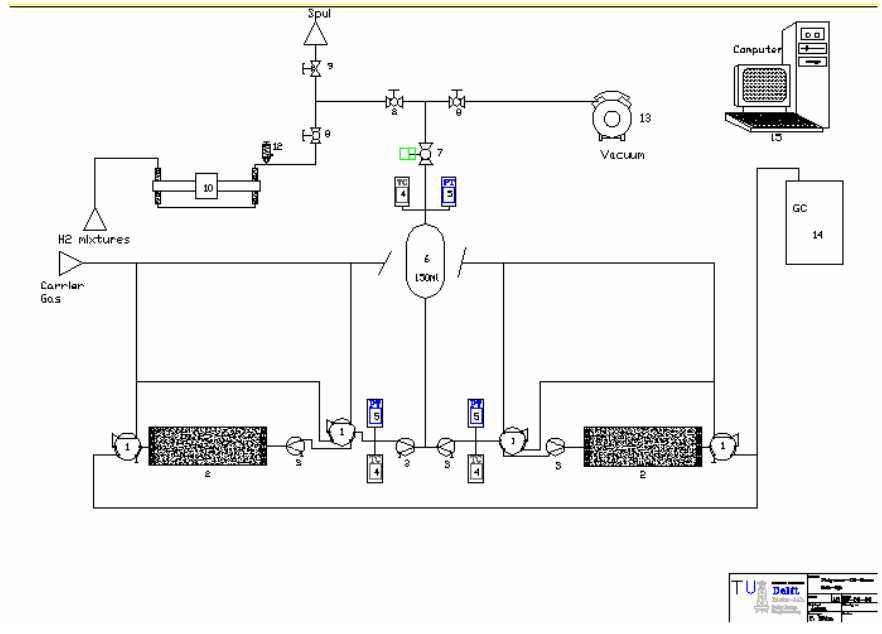
Figure 1: Schematic drawing of the experimental setup.
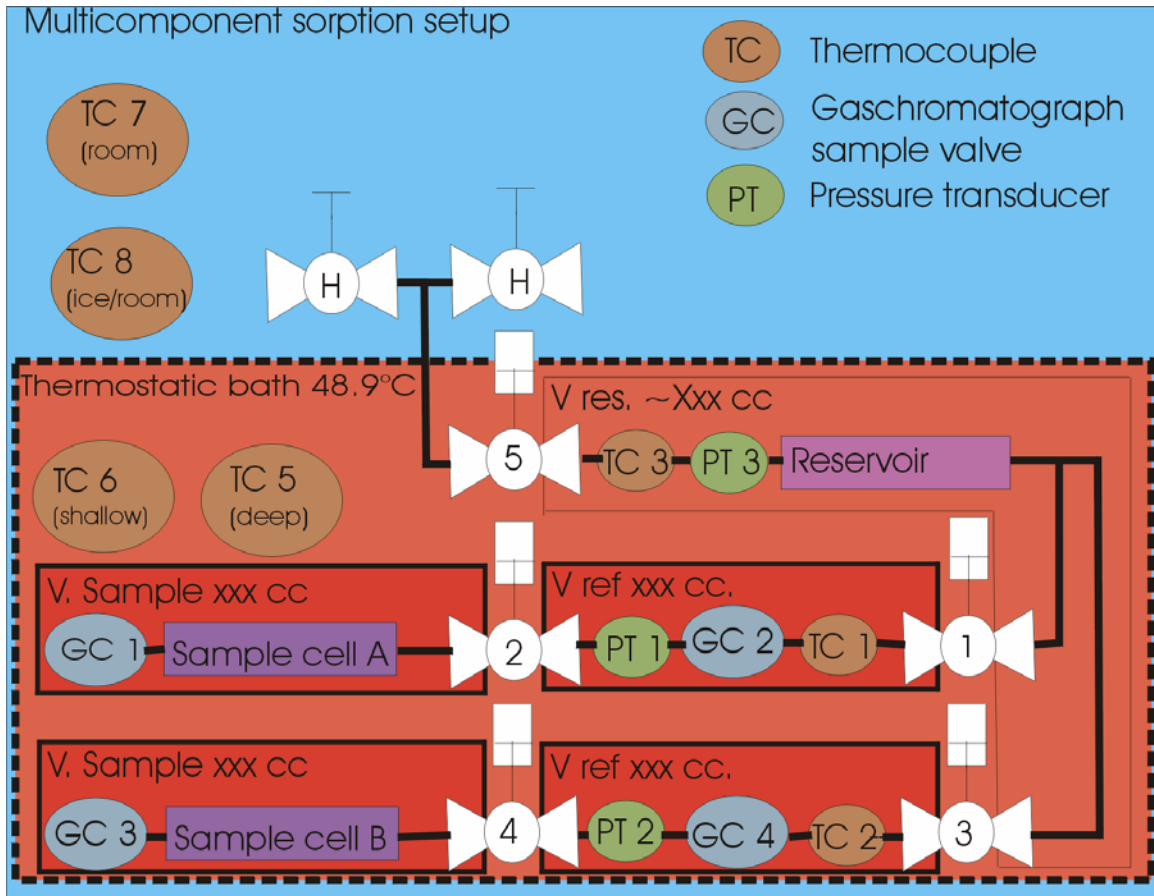
Figureb 1: Other option for schematic drawing of the experimental setup.

Equation 1

$$\sum_{i=1}^{N} \frac{P_i^s V_i}{T_i^s Z(P_i^s, T_i^s)} = \sum_{i=1}^{N} \frac{P^c V_i}{T^c Z(P^c, T^c)}$$

Equation 2

$$n_{excess} = \frac{P_s V_{cell}}{Z(P_s, T_s) R T_s} + \sum_{i=1}^{M} \frac{P_i V_{ref}}{Z(P_i, T_i) R T_i} - \sum_{j=1}^{M} \frac{P_j V_{ref}}{Z(P_j, T_j) R T_j} - \frac{P_M V_{cell}}{Z(P_M, T_M) R T_M}$$

Equation 3

$$n_{excess} = n_{ads}^{start} + \sum_{i=1}^{M} \frac{P_i^b V_{cell}}{R Z(P_i^b, T_i^b) T_i^b} - \sum_{i=1}^{M} \frac{P_i^{eq} V_{ref}}{R Z(P_i^{eq}, T_i^{eq}) T_i^{eq}} - \sum_{i=1}^{M} \frac{P_i^{eq} V_{cell}}{R Z(P_i^{eq}, T_i^{eq}) T_i^{eq}}$$

Equation 4

$$n_{excess}^x = \frac{c_s V_{cell}}{R T_s} + \sum_{i=1}^{M} \frac{c_i V_{ref}}{R T_i} - \sum_{j=1}^{M} \frac{c_j V_{ref}}{R T_j} - \frac{c_M V_{cell}}{R T_M}$$
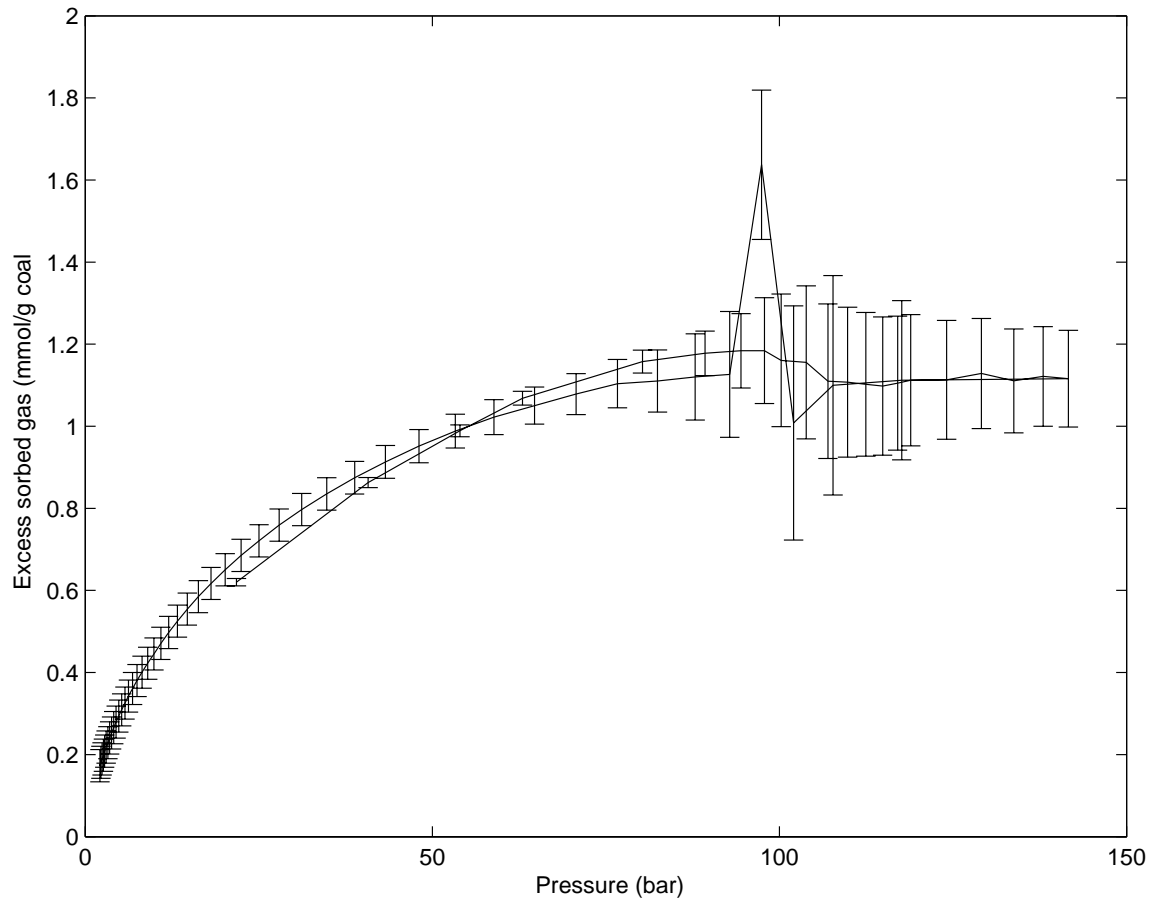
Figure 2: Sorption isotherm CO2 1
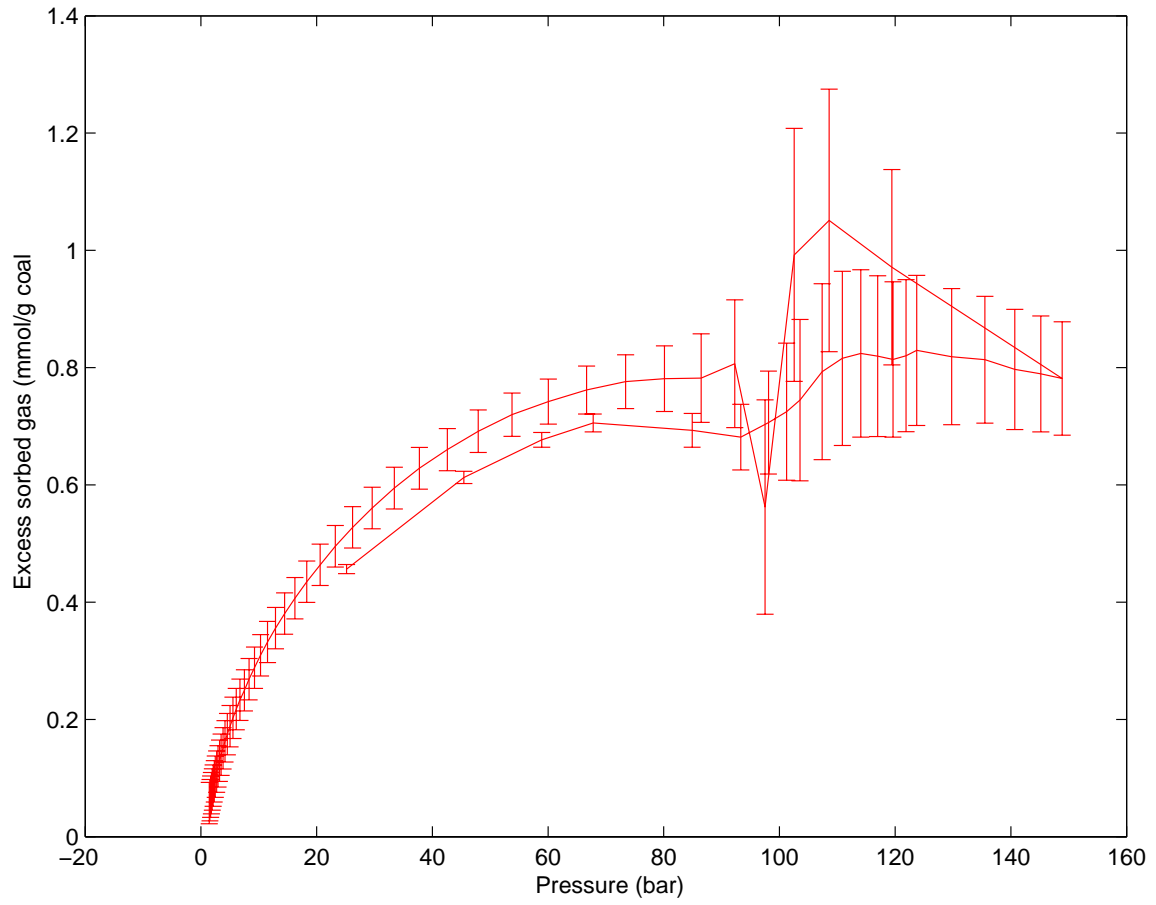
Figure 3: CO2 sorption duplicate 2
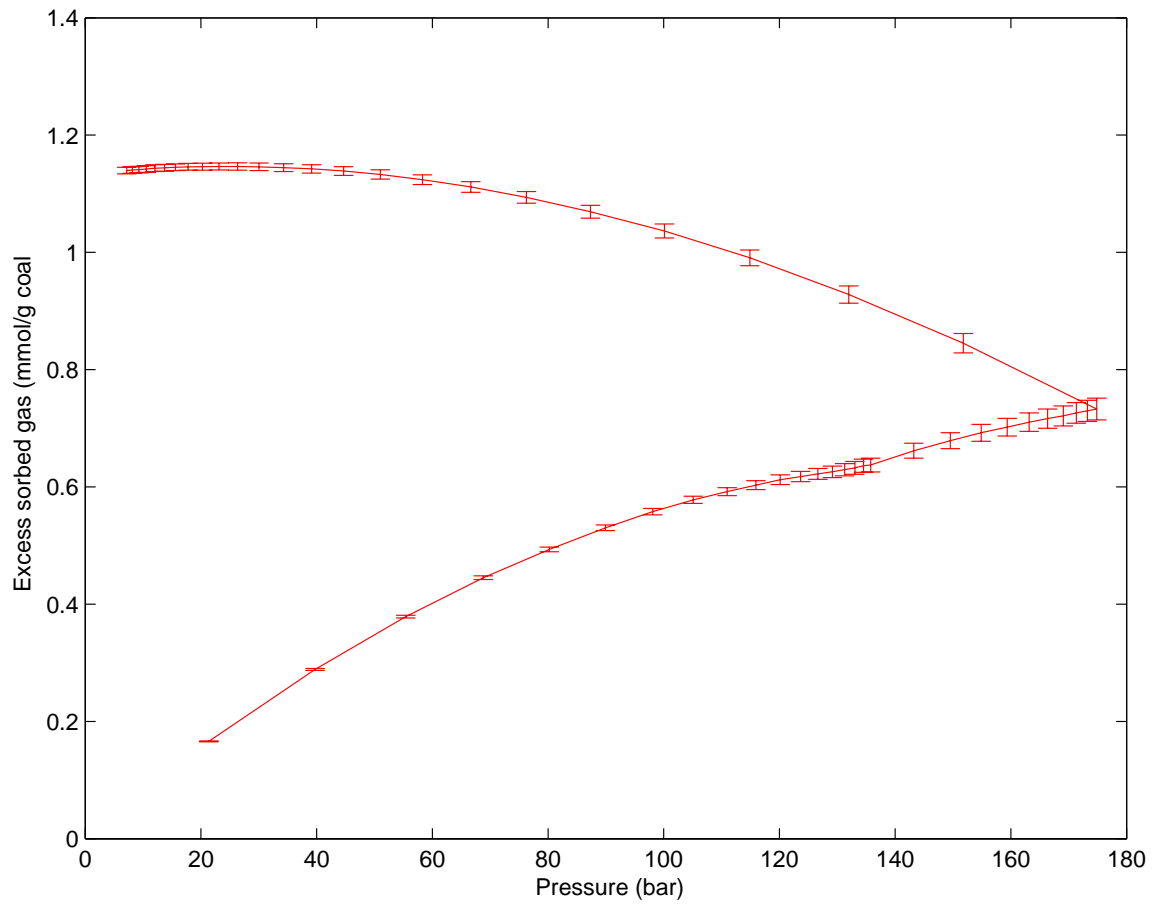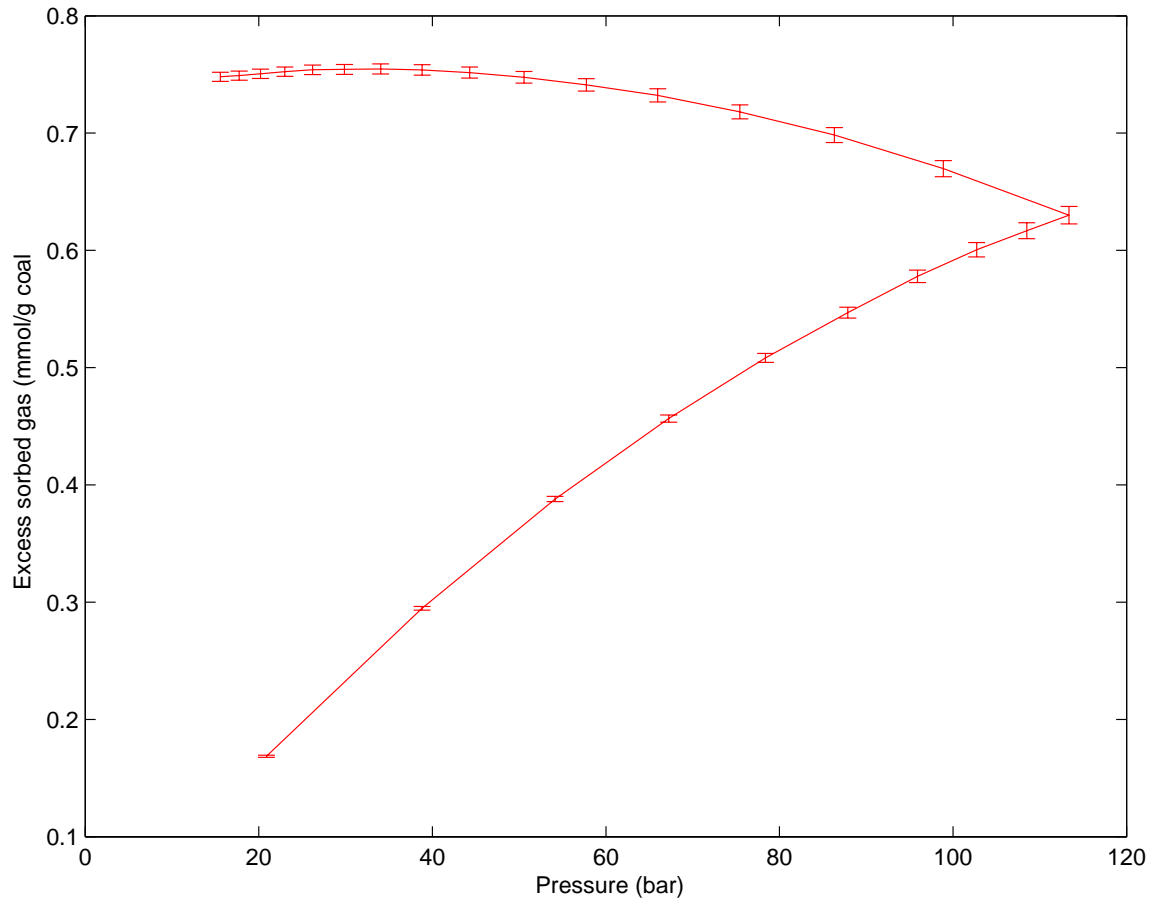
Figure 4: H2 measurement 1
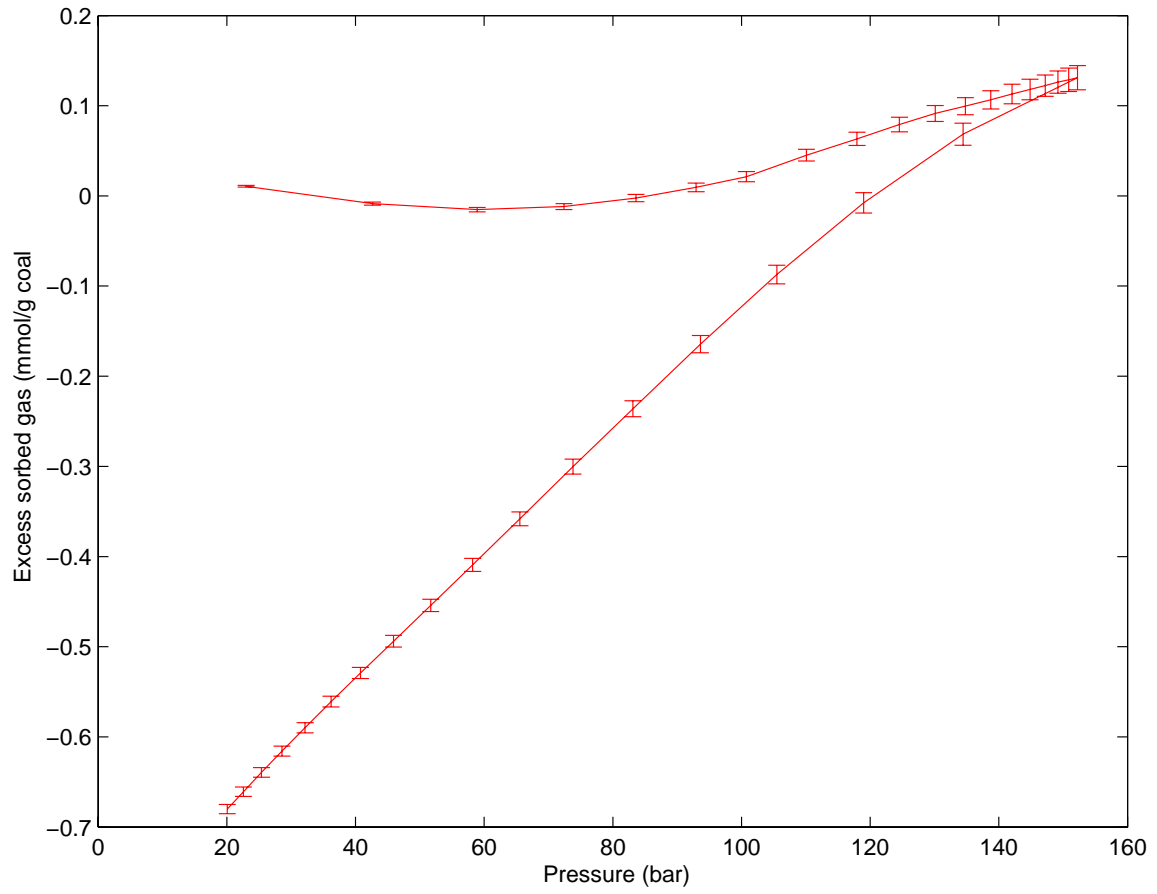
Figure 5: Hydrogen repeat 2
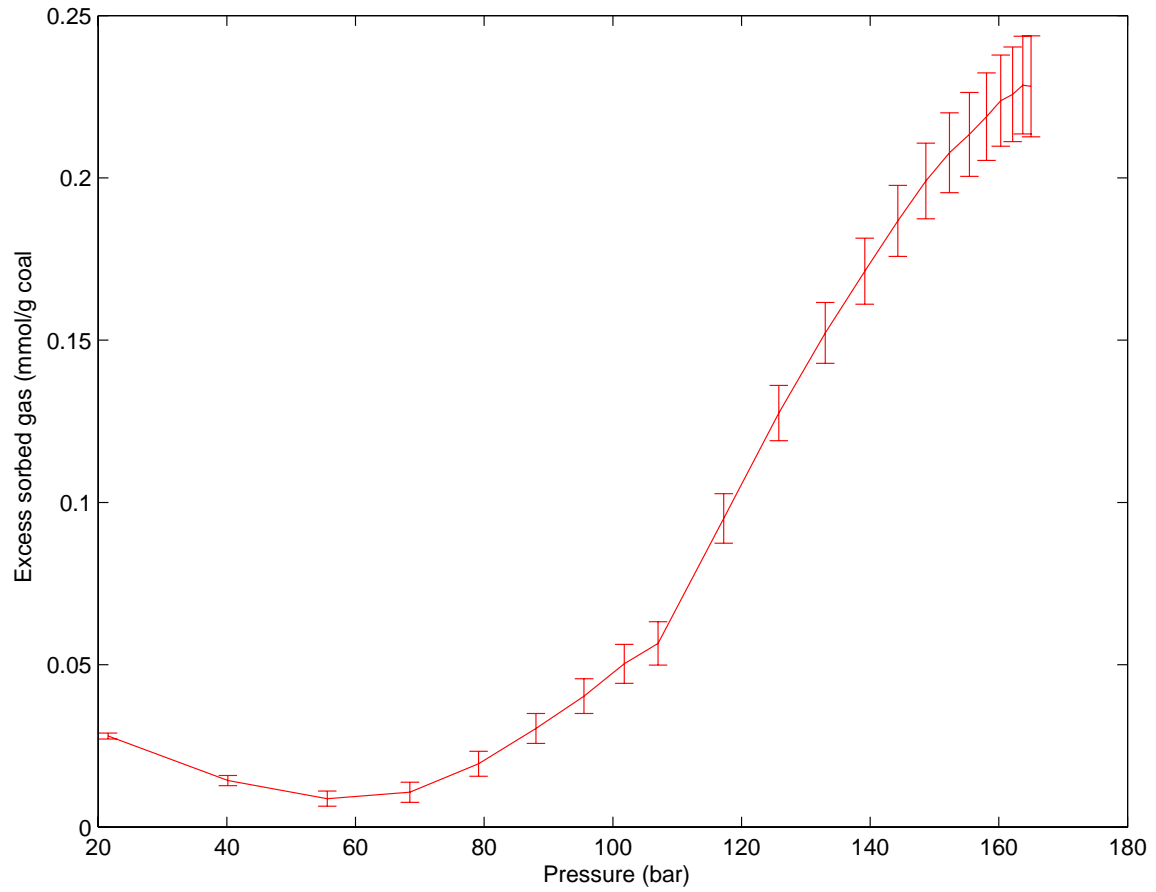
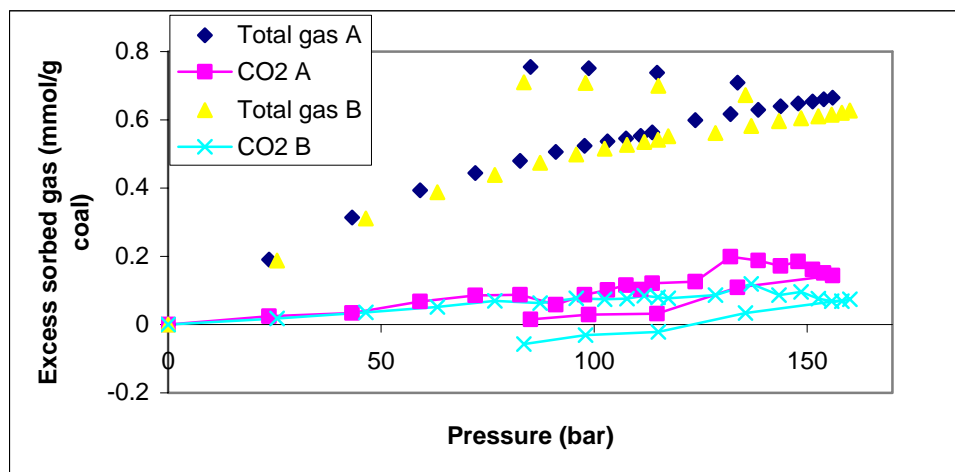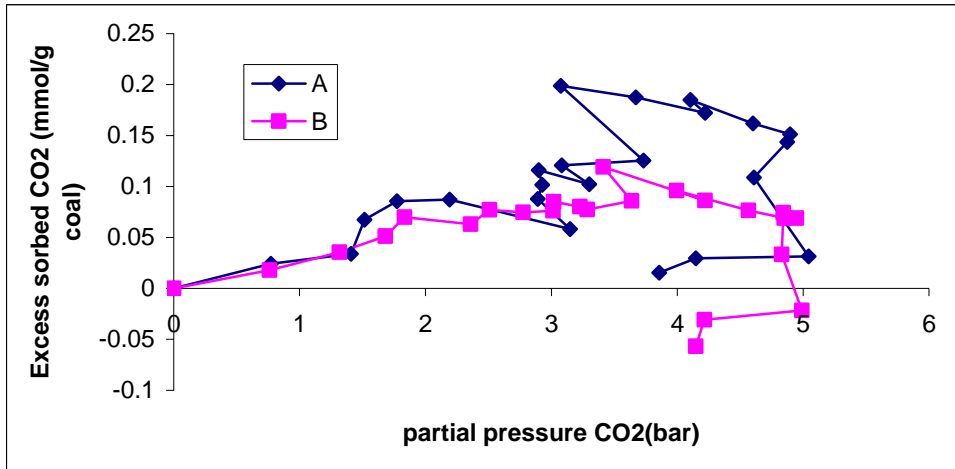**Figure 6: Methane sorption 1**

Figure 7: Methane repeat 2

Figure 8: Sorption mixture experiment

Figure 9: mixture CO2 sorption