Confidential

Methane sorption by activated carbons

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Contents

Appendices

Summary

In 2023 16% of the Dutch energy production has to come from renewable energy sources. This includes wind and sun energy, but also the production of energy out of biomass, e.g. biogas. This biogas is produced with a steady production rate while the demand fluctuates over time. In order to synchronize the steady production of biogas with the fluctuating demand, decentralized biogas storage is an interesting option.

Biogas mainly consists of methane and carbon dioxide. After separation the methane can be stored. One specific storage method is by using activated carbon, which can give higher storage ratio's compared to compressed methane storage. Two activated carbons were investigated "MaxSorb" and "BrightBlack". The research focussed mainly on the storage ratios. Experiments were carried out on a closed reactor filled with activated carbon and a methane inlet pressure of ~40 bara..

It is concluded that the MaxSorb adsorbent had the better gravimetrical[1] ratio while the BrightBlack adsorbent had a better volumetric ratio[2]. Notice that the latter one has a different bulk density which enhances its volumetric aspect. Side note for BrightBlack is that there was only one reference at room temperature, which makes the results not indisputable. Therefore it is recommended to do additional testing on the BrightBlack adsorbent.

Furthermore the effect of heat production during adsorption on the storage capacity showed to have a lesser effect on BrightBlack then it had on MaxSorb. Because only the temperature of the bed in its core was measured, an accurate temperature profile could not be constructed. Therefore additional research is recommended.

Also a phase change material (PCM) was added to the BrightBlack adsorbent in order to investigate the potency of PCM being implemented as a thermal management system. This implementation of PCM would absorb a lot of the heat, what is released during adsorption and would return that heat during desorption. This resulted in a higher gravimetrical storage ratio while the volumetric storage ratio decreased for as the PCM will not adsorb methane.

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[1] Gravimetric ratio calculations can be found in Appendix A.1.2 & A.1.3, while for the model the equation Eq. 1 of Van der Vaart et al. [**2**] was used.

[2] Volumetric ratio calculation can be found in Appendix A.1.1

Samenvatting

In 2023 moet 16 % van de energieproductie uit duurzame bronnen gewonnen worden. Dit kan zijn uit wind en zon, maar ook uit biomassa zoals biogas. De productie van biogas is stabiel terwijl de vraag naar gas ernstig fluctueert als functie van de tijd. Om deze constante productie af te stemmen met de fluctuerende vraag van gas, kan decentrale gasopslag een interessante optie zijn.

Biogas bestaat voornamelijk uit methaan en koolstofdioxide. Wanneer deze twee van elkaar gescheiden worden is het mogelijk om het methaan op te slaan in actieve kool door middel van adsorptie. Deze methode is veiliger doordat de opslag bij relatief lage druk mogelijk is, terwijl het dan ook een betere opslagcapaciteit heeft dan met behulp van compressie. Voor dit onderzoek zijn twee geactiveerde koolsoorten onderzocht genaamd: “MaxSorb” en ”BrightBlack”. Dit onderzoek heeft zich voornamelijk gericht op de maximale opslagcapaciteit van deze kolen. Wat gedaan werd door een specifieke hoeveelheid kool in een afgesloten reactor te stoppen en er vervolgens gas in te laten stromen tot een druk van ~40 bara.

Dit resulteerde in een betere gravimetrische opslagcapaciteit[3] voor MaxSorb en volumetrisch[4] was BrightBlack beter. Hierbij moet wel genoemd worden dat deze twee kolen verschillende stortdichtheden hebben. Verder moet ook vermeld worden dat er voor BrightBlack geen thermogravimetrische analyse beschikbaar was. Hiervoor was slechts èèn referentie beschikbaar bij kamertemperatuur. Op deze referentie is onder meer het model gebaseerd en dus zijn de resultaten van dit model niet onweerlegbaar voor andere temperaturen. Hierdoor is verder onderzoek voor BrightBlack nodig.

De degradatie van de opslagcapaciteit als functie van de temperatuur bleek minder effect op BrightBlack te hebben dan op MaxSorb. Hierbij moet wel vermeld worden dat de temperatuur slechts op een punt, in de kern van het bed wordt gemeten. Hierdoor is het niet mogelijk om een temperatuur profiel voor de gehele reactor op te stellen.
Ook is een thermal management oplossing toegepast in de form van een fase overgangs materiaal om de potentie van de toevoeging van zo’n materiaal te onderzoeken. Hieruit

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[3] De vergelijkingen voor de gravimetrische ratios zijn te vinden in Appendix A.1.2 en A.1.3, terwijl voor het model de vergelijking Eq. 1 welke te vinden is in het onderzoek van Van der Vaart e.a. [**2**].

[4] De vergelijkingen voor het berekenen van het volumetrische ratio zijn te vinden in Appendix A.1.1.

is gebleken dat het een duidelijk positief effect laat zien tijdens ad- en desorptie, maar ook wanneer gekeken wordt naar de gravimetrische opslagcapaciteit.

1

Introduction

The Dutch government has decided, according to the SER energy agreement, that in 2020 14% of the consumed energy will need to come from renewable energy sources and in 2023 16%, e.g. wind, solar or biomass. This investigation focusses on biomass and its production of biogas, because the production of wind and solar energy is fluctuant it cannot be produced at a constant rate while the production of biogas can.

When biogas is produced from biomass it has a relatively low pressure, almost ambient. Currently the natural gas that is used for the grid is extracted from the soil with pressures in the range of 100-200 bara, when getting closer to the end-user the pressure in the grid will drop, to just above ambient. The reason why decentralized gas storage could be interesting is because it can store the natural gas at a relatively low pressure. And furthermore because it can satisfy the fluctuating demand during day and night but also during summer/winter. This is very clearly shown in Figure 1: (a) shows the gas demand (dark blue) and biogas production (pink) while (b) shows the charge (red) and the discharge of the storage.

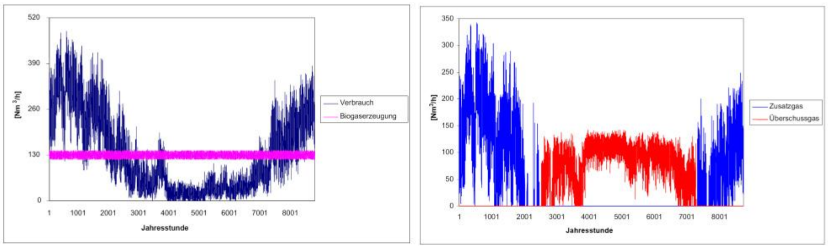


Abbildung 53: Jahreslastgang des Mikronetzes „Ländliches Ortsnetz" und Jahreserzeugungsprofil der Biogasanlage(n) bei mittlerem biogenem Deckungspotenzial

Abbildung 54: Jahresgang des Biogasüberschusses und des Zusatzgases des „Ländlichen Ortsnetzes" bei mittlerem biogenem Deckungspotenzial

Figure 1: Local residential biogas grid (a) Comparison gas consumption and gas production (b) the storage charge- and discharge rate [1] (Bärnthaler et al., 2009 [23])

There are several ways to store gasses, for instance by liquefying or by compressing it at high pressures, i.e. 200-300 [bar]. These ways work quite well but they consume a lot of energy. An alternative technology is Adsorbed Natural Gas (ANG) storage by adsorption of methane in activated carbon. This technology also requires compression but at lower pressures ~35 bara.

This research primarily focusses on gathering data of how much gas (methane, CH_4) can be adsorbed by a specific amount of activated carbon at different pressures, flows and temperatures of the gas but also the density of the packed adsorbent bed. A side effect of gas storage in carbon is the production of heat and what effect this heat has on the storage capacity which still isn't fully understood.

This research will focus on:

1. Experimentally determine the gas storage capacities of selected adsorbents.
2. Experimentally determine heat effects during adsorption and desorption.
3. Determine concepts for thermal management of ANG storage systems. And determine which concepts are most effective for each application through model calculations.

This will be done by letting gas in a closed reactor filled with activated carbon and monitor the amount of gas that goes in and out but also the temperature of the carbon. This will be further explained in chapter 4.1.

Structure:

In chapter 2 there is some general information about ECN. Chapter 3 will tell some general things about gas storage and explain the basics of gas adsorption. Chapter 4 describes the experimental procedure while chapter 5 includes the results and the discussion. Chapter 6 will tell some things about thermal management. Chapter 7 contains the conclusions of this investigation.

2

About ECN

ECN is the largest energy research institute of the Netherlands. With around 500 employees they are active in joint ventures with the industry, governments and other research institutes.

2.1 History

1955

ECN started in 1955 under the name Reactor centrum Nederland (RCN). That time they focussed on the development of nuclear energy. That time energy was expensive, filthy and dangerous, mainly because it was produced out of coal. Nuclear energy promises to be a cheap and clean energy that will empower the needs of generations to come.

Back in 1955 the Dutch government wanted to safeguard the energy supply. So they decided to build their own experimental reactor. This High Flux Reactor (HFR) was built in Petten away from the population and in the vicinity of coolant.

1975

Then in 1975 energy is in the centre of discussion in the politics. When the Arabs closed the oil supply to the Netherlands in 1973, the vulnerability of the energy supply became noticeable for everyone. Furthermore there was another problem called “nuclear waste” which caused a lot of commotion. Because of this a lot of people were against the construction of new nuclear power plant.

It was clear that the energy supply of the future could not only consist of nuclear energy. The demand for alternative energy research, like solar and wind energy, tidal energy and biomass but also energy efficiency came into existence. RCN was appointed as the leading institute to investigate the matter.

1979
After the second oil crisis in 1979, coal turns out to be the fuel of the future again but a lot cleaner than in the past. In a short period of time a big national research programme was developed for coal. A part of this programme was assigned to ECN. When this research turns out to be not viable, ECN aims their focus on the gasification of coal. Which is the foundation of the biomass gasification research today.

In the years to come ECN puts a lot of effort in the development of fuel cells. In other countries the development seems to go in rapid succession. With this research there was also the hope for the Netherlands that they could construct their own energy industry whit ECN in the core of this research. But unfortunately due to market perspectives their ambitions had to be altered. Nevertheless nowadays ECN is developed as a leading authority regarding fuel cell technology.

1989
In 1989 “Harry van den Kroonenberg” stepped up as CEO. Under his guidance the business units were introduced. The main focus of these units is to approach research in a more business-like approach. They are accounted for the financial result and therefore they need to take the wishes of the client in account but also keep an eye on the costs and the gain.

Late 90’s the business unit structure seemed to have some detrimental effects for the coherence and effectiveness of the research. Because of this the work of ECN was more associated with the government policies. Furthermore ECN should interpret the transition to a sustainable energy supply and play a role in the knowledge economy.

1999
At a large evaluation of research/technology institutes the government emphasizes again, that “ECN should not become a market organization”. Its work must be in correlation with the policy of the government. Nevertheless these decisions will not be rolled back, ECN needs to keep an eye on the market and develop products that contribute to the Dutch economy.

From 1999 and on
The climate problem became a recognized long term issue. The hole in the ozon layer is mainly made by greenhouse gasses like carbon dioxide. Which come “free” through energy consumption, e.g. gasoline. Therefore it is important to drastically reduce the CO_2 emission.

From this moment on the ECN research programme was determined by the “trias energetica”, which states:

1. Reduce energy consumption
2. Use renewable energy sources were possible
3. When using fossil fuels, do it as clean and efficient as possible

2.2 What does ECN provide?

ECN is a research institute that develops high-grade knowledge mainly concerning sustainable energy systems. But they also give advice to companies on what systems they need to install. So one could say “ECN does almost everything if it concerns energy”.

2.3 Organization

The organisation of ECN consists of multiple structures. These are the hierarchy, staff and a functional structure. A graphical representation of this organisation can be seen in Figure 2.

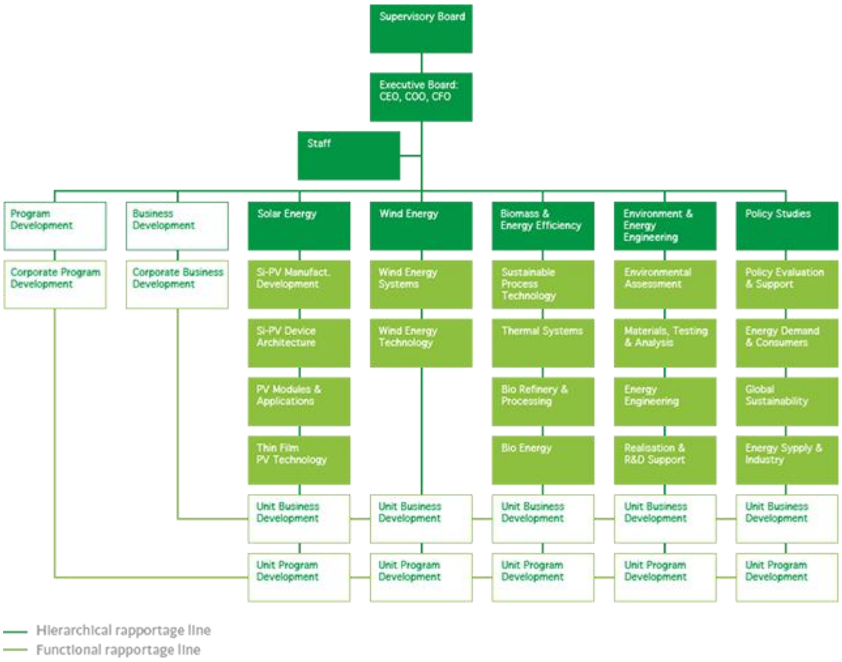


Figure 2: Graphical representation of ECN's organisation structure; (https://www.ecn.nl/nl/over-ecn/structuur)

2.4 Education

Estimated 300 to 500 people work at ECN, mainly researchers with an education varying from a bachelor’s degree to university professors.

2.5 Culture and atmosphere

At ECN there is a relaxed and informal atmosphere and culture. Off course there is a hierarchy and such, but the interaction between boss and subordinate is more like the interaction between colleagues. Furthermore it is a research facility with a lot of experimental work, resulting in a difference in work pressure compared to production facilities where you have multiple deadlines.

2.6 Rules and laws

There are several rules and laws active inside the research facility of ECN. The most important ones are the ones that have aspects relating to safety and environmental issues. This results in courses for new employee’s regarding “hazardous substances”, “gas cylinders” and such.

3

Gas storage

In today's society it is almost impossible to imagine a world without the consumption of natural gas, in particular the use of methane (CH_4). Nowadays it is used for heating our houses, for cooking and even for driving. A side effect of the methane now used is that it isn't coming from a renewable source. Together with the large consumption it will become a problem in the near future. For the fact that in 2020, 14% of all energy consumed in the Netherlands has to be sustainable. This is a reason why biogas, which is produced from biomass, is an alternative worth investigating. One disadvantage is that biogas is produced at a continuous rate and at a low pressure. This rate cannot cope with the fluctuating demand, hence making it interesting to store the surplus and using it when the demand cannot be met.

3.1 What is Natural Gas

Natural gas is a fossil fuel formed by layers of buried plants and animals (fossils) that are exposed to intense heat and pressure for a prolonged period of time, e.g. thousands of years. This gas is a non-renewable source of energy (Figure 3) because it takes such a long time to replenish. Hence a renewable equivalent of this gas, such as biogas, could be a very interesting alternative since fossil fuels are not everlasting.

3.2 Ways to store Natural Gas

There are several ways to store gas, the most common ones are:

1. Compressed natural gas (CNG).
2. Liquefied natural gas (LNG).
3. Adsorbed natural gas (ANG).

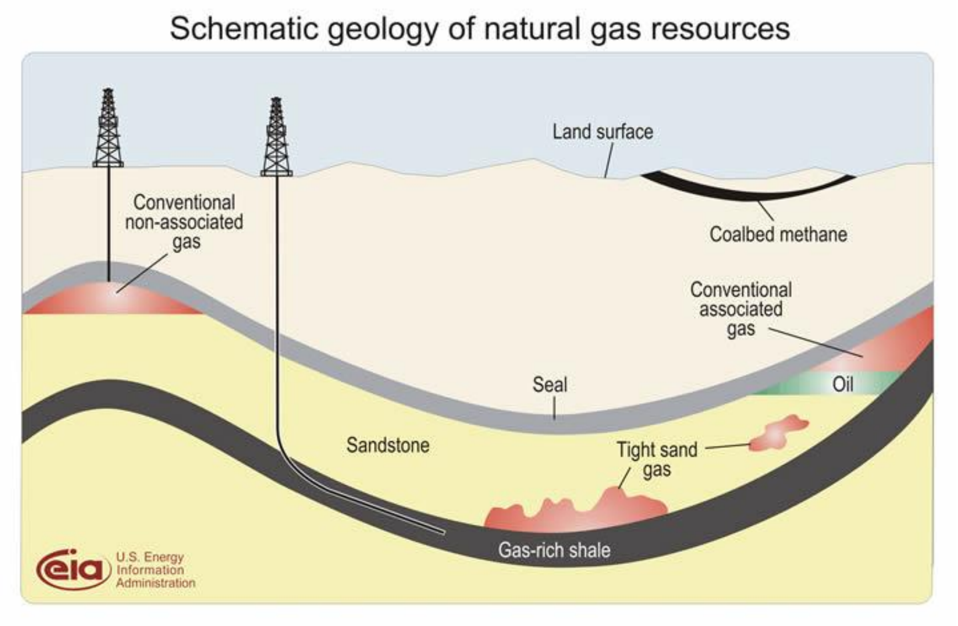


Figure 3: Schematic geology of natural gas resources (http://en.wikipedia.org/wiki/Natural_gas)

3.2.1 Compressed Natural Gas

Compressed Natural Gas is made by compressing natural gas to high pressures, so that it’s volume is a fraction of what is was before compression. The compressing pressure of 200-300 Bara requires a multiple stage compressor and the storage and shipping of CNG requires heavy and sturdy containers. This is mainly done in giant industrial facilities (see Figure 4).

Figure 4: The McMahon natural gas processing plant in Taylor, British Columbia, Canada (http://en.wikipedia.org/wiki/Natural_gas)

3.2.2 Liquefied Natural Gas

On the other hand there is liquefaction, here the gas needs to be treated to remove impurifications like dust, acid gasses, water and heavy hydrocarbons. After that it needs to be cooled to -162 ^{o}C. This all takes up a lot of energy, however on a volumetric basis it takes around $\frac{1}{600}$ of the space (see Figure 5) the gas would take at a gaseous state, which is quite good. While in its liquid form it is inflammable, it first has to vaporize to burn. In case of a leakage, the LNG will vaporize rapidly and mix with oxygen in the air. Creating a hazardous situation.

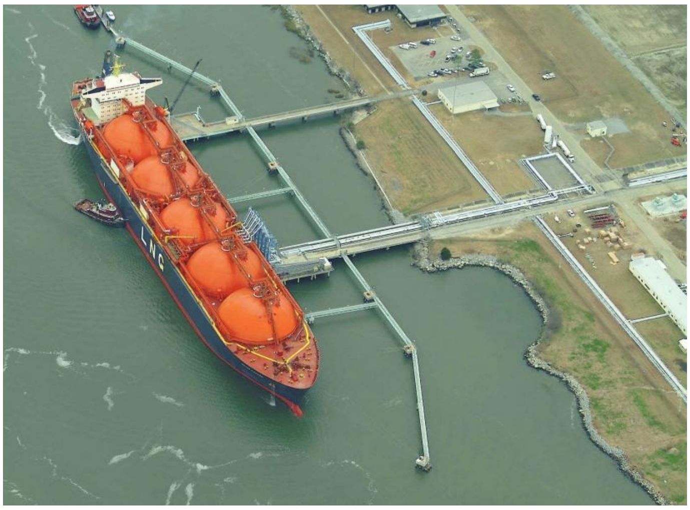


Figure 5: A giant LNG transportation ship (http://www.bbkinternational.com/blog/lng-blog)

3.2.3 Adsorbed Natural Gas

The other possible storage solution on which this research focuses is, the storage of gas in activated carbon by adsorption (Figure 6). This solution is primarily interesting because it works on a relatively low pressure while biogas also is produced at a low pressure but more importantly it makes it much safer, i.e. the lower the pressure the lower the risks. Therefore the compression can be done with a two-stage compressor, making it more economical then compressing the gas to higher pressures. The storage capacities of ANG on a volumetric basis are, at lower pressures (like 40 bara), better than CNG storage. When compared to LNG this capacity is worse but so is the energy consumption in the process to gain LNG.

Figure 6: ANG (a) diurnal storage, (b) for vehicular application (GL industrial services)

3.3 Theory of adsorption

When the molecules (in this case molecules of methane) are in a gaseous state the molecules are relatively far away from each other and they bounce from one side to another. Therefore this gaseous state takes up a lot of space, which is not preferred when storing. If the gas is adsorbed by the activated carbon, all of the molecules are nicely sorted on the inner and outer surface area of the carbon as can be seen in Figure 7, making the volumetric space that the gas occupies a lot smaller. Do note that the pores of the carbon are also counted as surface, giving highly porous carbon a very large surface to adsorb. This can add up for some activated carbons to 3000 m^2*g^{-1} and for metal organic frameworks this can add up to 11000 m^2*g^{-1}.

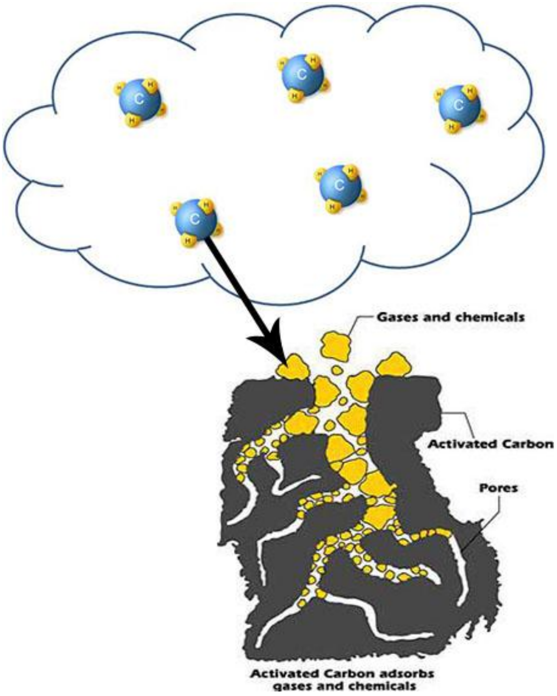


Figure 7: Adsorption of methane (gaseous form) in activated carbon

While the latter of the two is a synthesized material, it has the largest surface area and potentially the biggest storage capacity. It is also the most expensive thus making it a non-ideal material for commercial use. Therefore this report focusses on activated carbons.

Adsorption characterization:
An adsorption isotherm is determined by doing a custom thermo gravimetric analysis (TGA) experiment conducted with a TGA apparatus (Figure 8) In this experiment a little bit of activated carbon is put on a scale of inert material and placed inside a room in the apparatus which will be filled with methane. The weight of the activated carbon is monitored very closely while the pressure is steadily increased with small steps and the temperature is kept at a constant level. By doing this experiment a very accurate adsorption isotherm will be obtained.

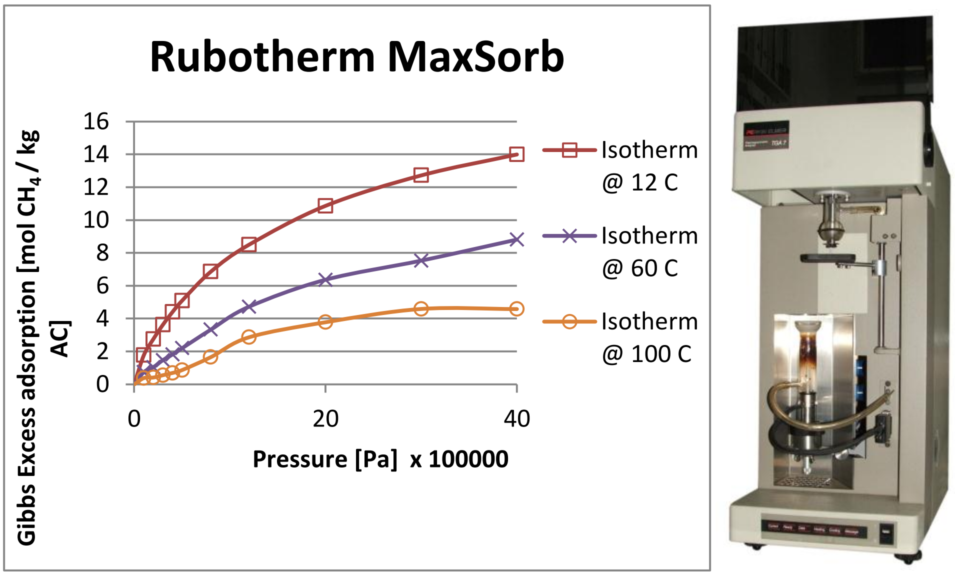


Figure 8: (a) Adsorption isotherm of MaxSorb 3000, made with a TGA. (b) A typical TGA system; (http://en.wikipedia.org/wiki/Thermogravimetric_analysis#Methods)

When the gas is adsorbed, the hydroxide (H) molecules of the gas make a covalent bond with the carbon (C) molecules of the activated carbon. This connection produces heat during adsorption and requires heat when the adsorbed gas molecules need to be released. This heat is called the heat of sorption and it is a very important aspect of adsorption. Because when the production of heat becomes higher, the carbon will warm up and adsorb less methane. However during desorption the opposite occurs. Meaning the colder the carbon gets the less gas can be subtracted from the carbon. These effects are quite substantial because they drastically affect the storage capacity. Hence it is a point of interest to fully understand the heat effects, so a system can be developed that negates/manages the occurring heat effects. Furthermore storage of gas in carbons is relatively cheap, while maintaining a high storage density. This gravimetric storage capacity can be derived with the use of Eq. 1 found in an investigation of Van der Vaart *et al.* **[2]**.

$$q_{eq} = \frac{q_m * b_0 * e^{\frac{-DH}{R*T}} * P_{vap}}{1 + b_0 * e^{\frac{-DH}{R*T}} * P_{vap}} \qquad \textbf{Eq. 1}$$

Where q_{eq} is the storage capacity ratio [mol CH_4*kg^{-1} of AC],q_m is the maximum capacity of the adsorbent [mol CH_4*kg^{-1} of AC] , b_0 is the adsorbate monolayer capacity [Pa^{-1}], DH is the activating energy of the AC [J*mol^{-1}], R is the gas constant which is 8,310 [J*mol^{-1}*K^{-1}], T is the temperature of the AC [K] and P_{vap} is the pressure of the gas [Pa]. Unfortunately not all variables (q_m, b_0 and DH) where known, so they needed to be found. This was done by filling in values for those variables and compare the adsorption isotherm to an accurate measurement, the so-called TGA measurement (see Figure 9). In this graph the red lines are formed by the TGA measurements at different temperatures. As can be seen in the graph these lines become unstable at higher temperatures. Therefore, the fitting of the curves focused mainly on the curve of 12 °C, which is the top line.

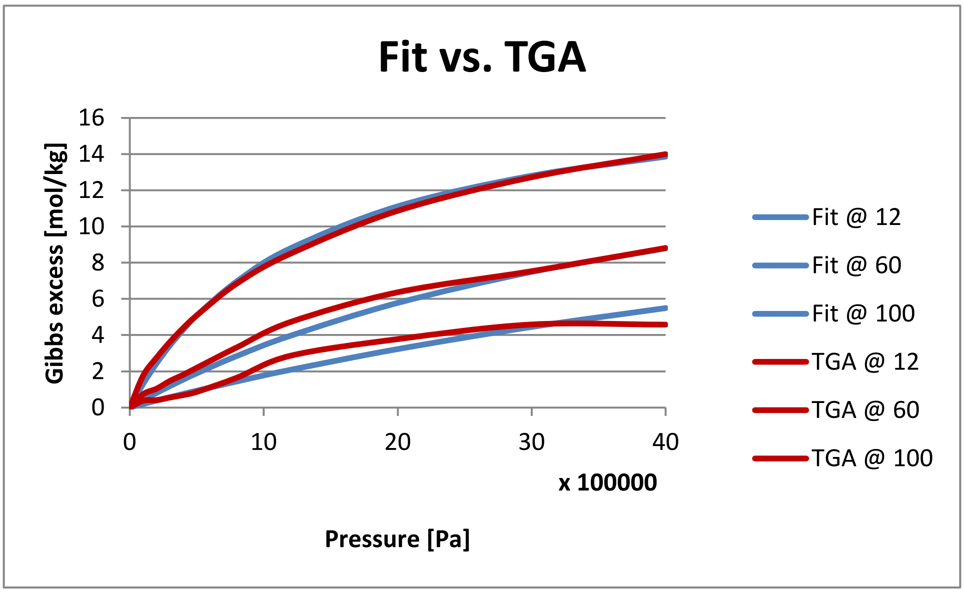


Figure 9: Comparison of the model fit vs. the TGA measurements. The lines describe the Gibbs excess adsorption isotherm of methane on MaxSorb AC at 12 °C (upper), 60 °C (middle) and 100 °C (bottom).

The values found for q_m, b_0 and DH are respectively 18,5 mol CH_4*kg^{-1} of AC, 1,85E-10 Pa^{-1} and -19800 $J*mol^{-1}$. With these variables a temperature and pressure dependant graph was constructed as can be seen in **Figure 10**. The amount of CH4 per kilogram of activated carbon for the model is calculated with temperature and pressure at point '*i*' of the experiment see Eq. 2. In this table, point '*i*' is the last data point in the set of data.

$$q_{eq_i} = \frac{q_m * b_0 * e^{\frac{-DH}{R*T_i}} * P_{vap_i}}{1 + b_0 * e^{\frac{-DH}{R*T_i}} * P_{vap_i}} \qquad \textbf{Eq. 2}$$

Thanks to this equation it is possible to produce 3D graphs with MATLAB that are both pressure and temperature dependent. Figure 10 shows such a graph within the experimental boundaries, which makes it quite accurate. Furthermore the graph shows that lower temperatures have a bigger influence on the storage capacity than an increase in pressure would do.

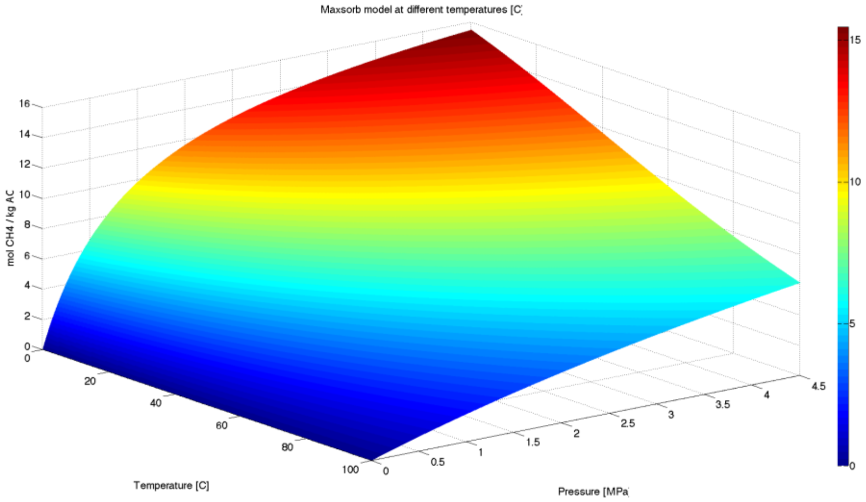


Figure 10: Model for MaxSorb capacity; temperature and pressure dependent; ranges concur with experimental conditions

This effect can also been seen when comparing the model to the research of Loh *et al.* **[3]**, as shown in the graph in Figure 11. When the experimental data is compared to the Loh data at 5 ⁰C, the model matches quite well till around 1,5 MPa. After that point the model's gradient becomes less steep and shows data under the Loh data. At higher temperatures this effect occurs at lower pressures. This difference can be explained by comparing the TGA data with the Loh data as can be seen in Figure 12. Here the adsorption capacity curves are quite even until they reach 1 MPa and then the TGA data becomes lower than the Loh data. This could be an indication that the experiments of Loh *et al.* were conducted under different conditions then the TGA. Also when the plots of the TGA at 60 and 100 ⁰C are taken in consideration, inaccurate or faulty data can't be ruled out unfortunately.

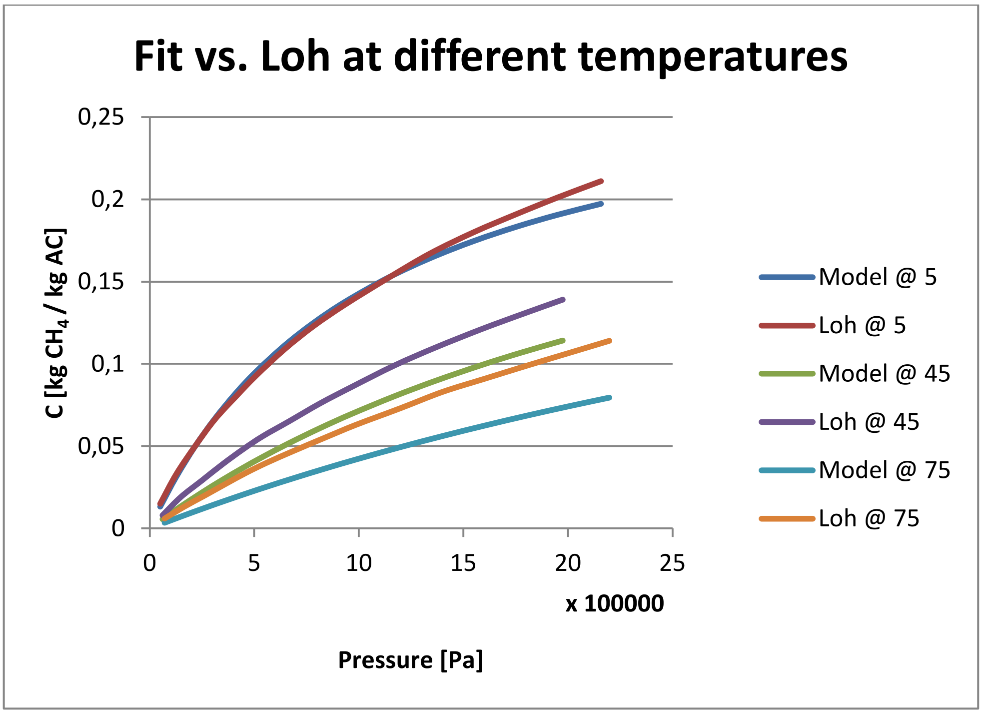


Figure 11: Model vs. Loh at different temperatures; 5, 45 and 75 [°C]

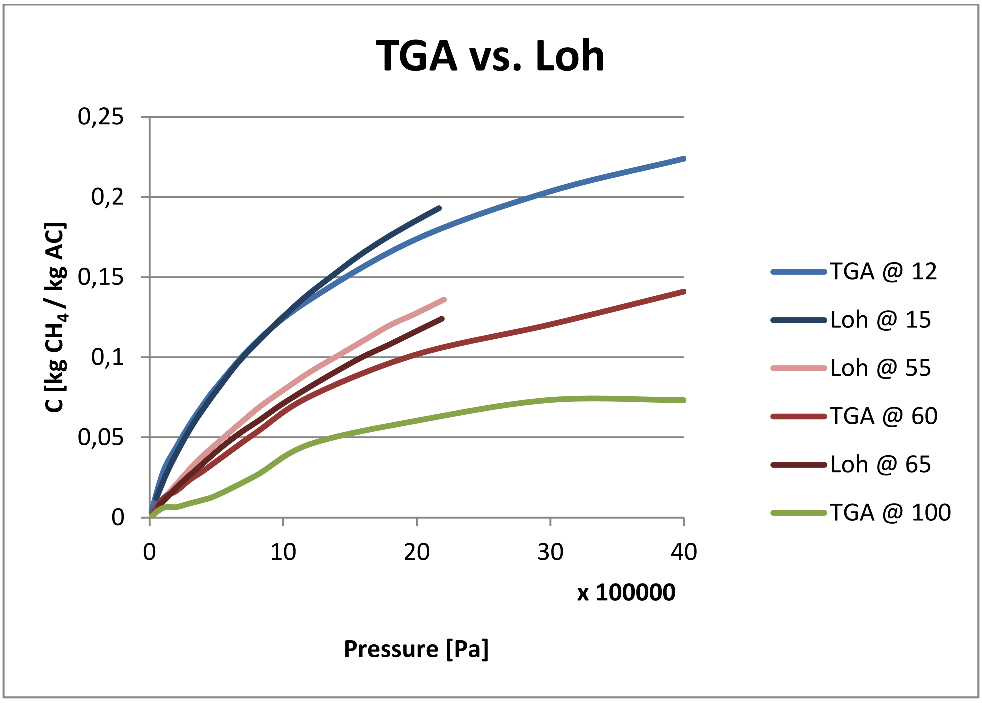


Figure 12: TGA measurements vs. Loh data

4

Experimental

This chapter describes the experimental apparatus (Hystore), what data is collected and what can be done with the data. But also describes the actions taken during a particular experiment.

4.1 Hystore

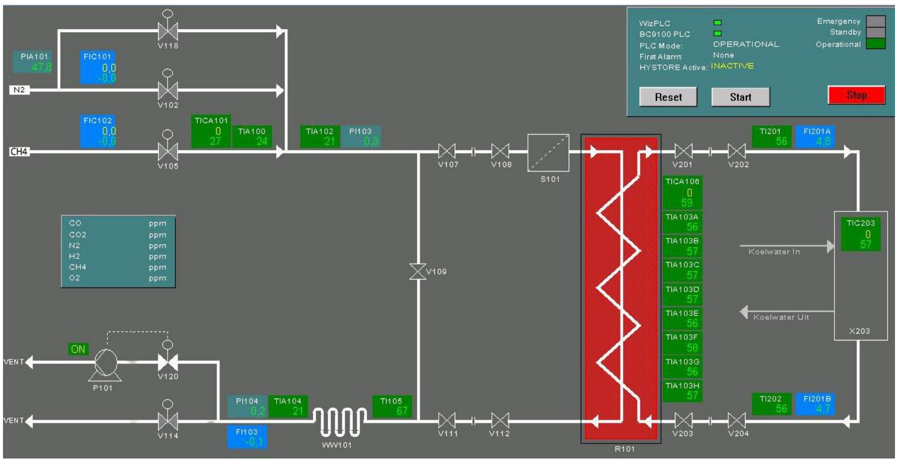
The Hystore apparatus (Figure 13) is capable of measuring the volumetric flow, the temperature and the pressure of the gas in both the inlet circuit as the outlet circuit. While the flow is measured in the inlet circuit it is also controlled. Furthermore it is capable of measuring the temperature of the activated carbon inside of the reactor. This is of great importance as it greatly influences the storage capacity.

Figure 13: Hystore apparatus

By capturing the measured data, it is possible to tell, with a degree of certainty, the amount of gas that is inside the reactor. So on, the volumetric and gravimetric storage capacity can be determined, assuming the two of the following three parameters are known:

1. Volume of the activated carbon.
2. Mass of the activated carbon.
3. Density of the activated carbon.

The Hystore apparatus was initially a device for the testing of sorption capacities with hydrogen as adsorbent. For the sake of this experiment it was slightly adapted for the use of methane. This means that the flow controller (FIC102) was reprogrammed, however it still needs a small adjustment in the form of polynomial function of the fourth order. The flow indicator (FIC103) needed a polynomial function of the sixth order. Both FIC102 and FI103 can be seen in Figure 14 and in Figure 15.



WizPLC
BC9100 PLC
PLC Mode: OPERATIONAL
First Alarm: None
HYSTORE Active: INACTIVE

Figure 14: Graphical representation of the HyStoRe apparatus

Figure 15: Photo of the controllerboard, the arrows mark the different flowmeters/controller and the direction of the flow

Also the temperature indicator, TI105 in Figure 14, is connected to a thermocouple that is placed inside the packed adsorbent bed. This is done because the other thermocouples (TIA103A – TIA103H see **Figure 16**) are mounted through the reactor wall into the packed bed and thus partly measuring the temperature of the reactor wall, as can be seen in Figure 16.

Figure 16: Photo of one side of the reactor, here 5 thermocouples can be seen which measurement is influenced by the temperature of the reactor wall. The other side is slightly mirrored, because there is a small deviation in the height of the thermocouples.

4.2 Procedure of the experiment

This paragraph will describe what actions will be taken during a specific cycle. One could say that the cycle is built out of three phenomena. And to simplify the explanation it is cut into these three parts:

1. Adsorption
2. Desorption
3. Regeneration

4.2.1 Adsorption

First thing that needs to be done is to start the preheating of the bed (if necessary) because this takes some time. When the bed is preheated the flow will be set in 'FIC102'. Then the main valve will be opened[5] and the gas starts to flow into the reactor (Figure 17). Currently the reactor cannot be filled automatically to a given pressure, because there is no pressure controller. Therefore this is done manually by keeping a close eye to the pressure indicator 'PI103' and manually closing the main inlet valve 'V105' to cut of the supply of methane.

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[5] Manual valves to the inlet of the reactor should be closed V107 & V108 plus the bypass and reactor outlet should be closed V109, V110 & V111

Figure 17: The reactor of the hystore apparatus

4.2.2 Desorption

The desorption process can be started right after the adsorption process has ended[6]. Before starting the desorption process the needle valve 'V121' needs to be in its almost closed position. Then valve 'V114' must be opened[7] and directly after it manual valve 'V110'. When the pressure indicator 'PI104' shows a pressure that is lower than 1.8 bara (for safety reasons) the vacuum pump can be started. Then valve 'V120' must be opened and 'V114' closed. After that flow indicator 'FI103' will not register a flow anymore and the experiment is finished.

4.2.3 Regeneration

Only thing that remains is the regeneration. This done under the exact same circumstances as desorption, the only thing that differs is that the carbon is heated to around 200-250 ^{0}C. This heat combined with the vacuum makes it possible to extract all of the remaining methane molecules from the activated carbon. However the regeneration is not mandatory, meaning it is possible to do 'n' amount of cycles before regeneration. Downside of this is that there will be less and less methane stored in the carbon during adsorption and there will also be a decline in retrieved methane from the activated carbon during desorption.

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[6] The adsorption will continue after the main valve 'V105' is closed, data shows that this loss is minimal and can therefore be discarded

[7] Manual valve 'V111' should be opened

4.2.4 Overview

When the experiment is done there is data available on adsorption and desorption. Unfortunately there is no data available concerning the flow rate during the regeneration process. This is because the flow is so low that it is out of the detection limit of the flow meter.

5

Results and discussion

This chapter describes the results of different measurements that were conducted on two different activated carbons, namely MaxSorb 3000 and BrightBlack, were the first one consists of powder and the latter one consists of pellets of approximately 200-300 microns. These experiments were done with a maximum pressure of 40 bara to maintain some consistency between the different experiments, while experimenting with the following parameters:

- Incoming gas flow.
- Bed temperature.
- Heating/cooling temperature.
- Different carbons.

5.1 MaxSorb 3000

The experimental parameters and the results are summarised in Table 1. In here the following details are shown per experiment. Furthermore it has a bulk density of 26 $g*cm^{-3}$.

Set parameters
The following parameters are set during the experiment:

- Flow: the rate at which the gas enters the reactor and is set at the start of the experiment.
- T_{Julabo}: the temperature of the oil inside the heat exchanger that surrounds the reactor, which is also set at the start.

Derived and calculated data

The following data is subtracted or is calculated:

- T_{bed_init}: the temperature of the activated carbon and is also measured at the start.
- V/V_0: the amount of gas (expressed in volume) that can be stored in a volume of activated carbon. This is derived by using the method in Appendix A.1.1.
- Experimental: describes the amount of actual adsorbed gas gravimetrically. This value is calculated with the help of the expressions stated in Appendix A.1.2 and A.1.3.
- Model: expresses the maximum amount of gas, in a mass-to-mass ratio, that theoretically can be adsorbed. This is done with Eq. 1 found in an investigation of Van der Vaart *et al.* **[2]**.
- % of Model: simply compares the experimental data with the data from the model and returns a percentage, see Eq. 3.

$$\% \; of \; Model = \frac{Experimental}{Model} \cdot 100 \qquad \textbf{Eq. 3}$$

Table 1: Experimental parameters for the MaxSorb 3000 adsorbent

Experiment	Flow [$dm^3 \cdot min^{-1}$]	T_{bed_init} [°C]	T_{bed_max} [°C]	T_{bed_end} [°C]	T_{julabo} [°C]	V/V_0 [dm^3 CH_4 * dm^{-3} AC]	Experimental [mg CH_4 * g^{-1} AC]	Model [mg CH_4 * g^{-1} AC]	% of Model
1	0,5	~20	29	25	Na	97	173	202	83%
2	2,0	~20	43	35	Na	96	181	186	86%
3	5,0	~20	70	65	Na	91	166	135	94%
4	5,0	~20	66	59	Na	93	175	143	96%
5	0,5	40	48	41	40	89	156	174	78%
6	2,0	40	60	50	40	89	189	159	83%
7	2,0	60	77	67	60	75	143	128	79%
8	2,0	100	113	108	100	66	116	80	58%

Experiment 3 and 4 look a lot alike, the only difference is that the regeneration process, during experiment 3, was done at a higher temperature for a longer time. This was done to check if the current procedure was sufficient, because the V/V_0 were not as expected. As can be seen the V/V_0 ratio differs slightly but so little that it is safe to say that the current method of regeneration is sufficient.

5.1.1 MaxSorb adsorption equilibrium

In table 1 the ratio's V/V_0 and experimental are calculated with the equations stated in appendix A.1. The model is based on equation Eq. 2, which was found in the literature of Van der Vaart *et al.* **[2]**. **Figure 18** and **Figure 19** show the different storage capacities of the adsorbent as function of temperature of the adsorbent right after the experiment. A trend line was added for a better graphical interpretation and with an R-squared value of 69 for m/m_0 and 76% for V/V_0 it is a good fit. From this interpretation it is clear that a rising bed temperature has a degrading effect on the storage capacity. This effect is stronger when the ratio is on a gravimetric basis, because only the adsorbed gas is taken into account while on a volumetric basis also the gas in the void is included. In other words: the gravimetrical view only shows the adsorbed gas.

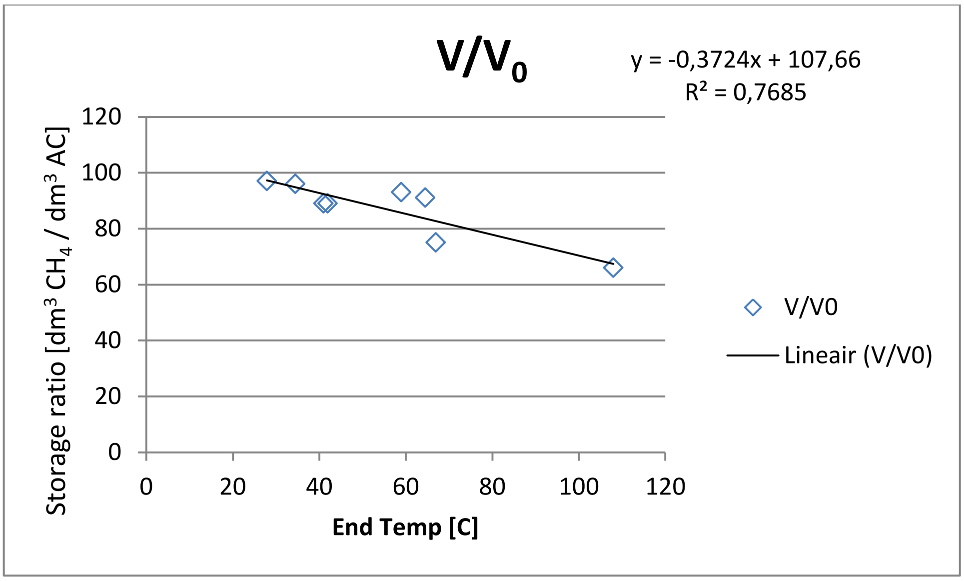

Figure 18: Set of V/V_0 data points as function of the temperature of the bed at the end of the experiment, for the MaxSorb 3000 adsorbent.

Another noticeable effect is a lower storage ratio when a higher flow is used, as can be seen in **Table 1**. This is caused by heat development, which comes with a faster increase in pressure. And thus heats the adsorbent bed and decreases the adsorption capacity, as can be seen in Figure 18 & Figure 19.

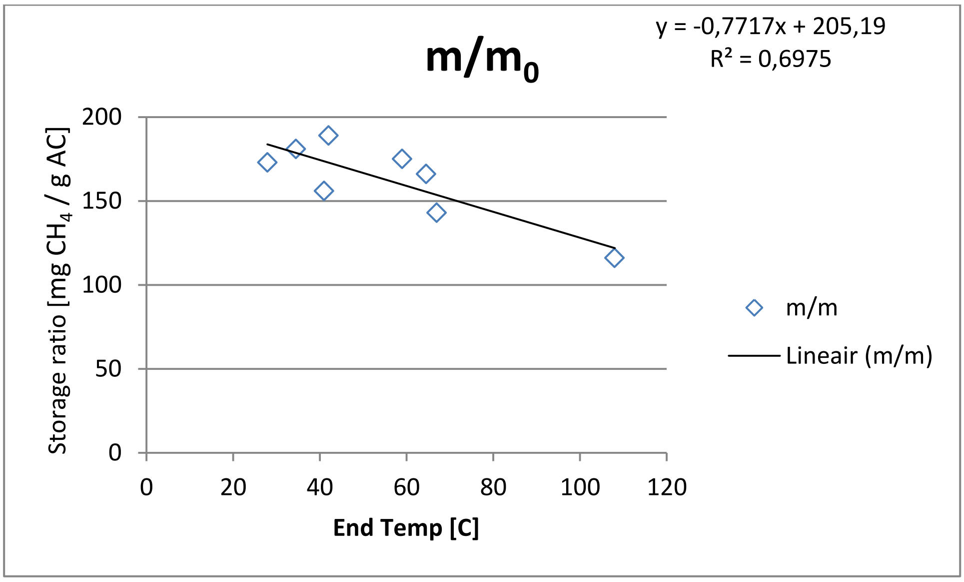

Figure 19: Set of m/m$_0$ data points as function of the temperature of the bed at the end of the experiment, for the MaxSorb 3000 adsorbent.

5.2 BrightBlack

The experiments with the BrightBlack adsorbent (see **Figure 20**) are conducted with the same parameters as where used with the MaxSorb 3000 adsorbent, while BrightBlack has a bulk density of 62 g*cm^{-3}. This is done for the sake of simplicity when comparing one to another, as can be seen in **Table 2**. However due to some unexpected results experiments, increase in storage capacity with an increase in flow rate, 9 & 10 where added. Furthermore experiments 3 & 4 are also different compared to the MaxSorb experiments; in this case the latter one is conducted without the preliminary regeneration. An important side-note for the model is that it is not very accurate yet. This is due to the lack of a TGA measurement, therefore the model was based on an investigation of Solano et al. [12]. Unfortunately this research contained only data for room temperature.

Figure 20: BrightBlack adsorbent, photo was made with a microscope with 2.5 times magnification; squares have a size of 1x1 mm

Table 2: Experimental parameters for the BrightBlack adsorbent

Experiment	Flow [l·min^{-1}]	T_{bed_init} [ºC]	T_{bed_max} [ºC]	T_{bed_end} [ºC]	T_{julabo} [ºC]	V/V_0	Experimental [mg CH_4 * g^{-1} AC]	Model [mg CH_4 * g^{-1} AC]	% of Model
1	0,5	~20	35	29	Na	97	89	91	97.8
2	2,0	~20	54	39	Na	92	85	88	96.6
3	5,0	~20	74	60	Na	119	118	82	143.9
4	5,0	~20	70	57	Na	112	112	83	134.9
5	0,5	40	50	41	40	112	107	88	121.6
6	2,0	40	68	49	40	112	108	86	125.6
7	2,0	60	85	68	60	104	101	80	126.3
8	2,0	100	119	108	100	93	91	67	135.8
9	5,0	40	87	67	40	109	106	78	135.9
10	10	~20	90	68	Na	114	118	74	159.5

Figure 21 & Figure 22 are made with the use of Table 2 In this set of data a trend line is also added. There it has an R-squared value of 1% for V/V_0 and 0,6% for m/m_0; it is nothing more than a visual aid in interpreting the data. Also in this data set it can clearly be seen that while increasing the final bed temperature the storage capacity will decrease, as was expected.

5.2.1 BrightBlack adsorption equilibrium

When taking a closer look at experiments 3 & 4, it can be seen that not regenerating the adsorbent will result in a lower storage ratio. Confirming the fact that not all gas molecules are retrieved from the adsorbent by only using a vacuum to retrieve the gas. However this effect seems reasonable small, giving the idea that after a couple more cycles the ratio will decrease less and eventually stabilize, see paragraph 6.1.

Another remarkable thing is a higher storage ratio with higher flows, which can be concluded from Table 2 This was not expected, the expectation was a linear negative trend.

Figure 21 shows the volumetric ratios as function of the end temperature. The trend line doesn’t have a good fit, however it shows a line with a negative gradient what was expected. Furthermore the data points tend to show a parabolic connection between one another. This needs further research because a linear trend was expected.

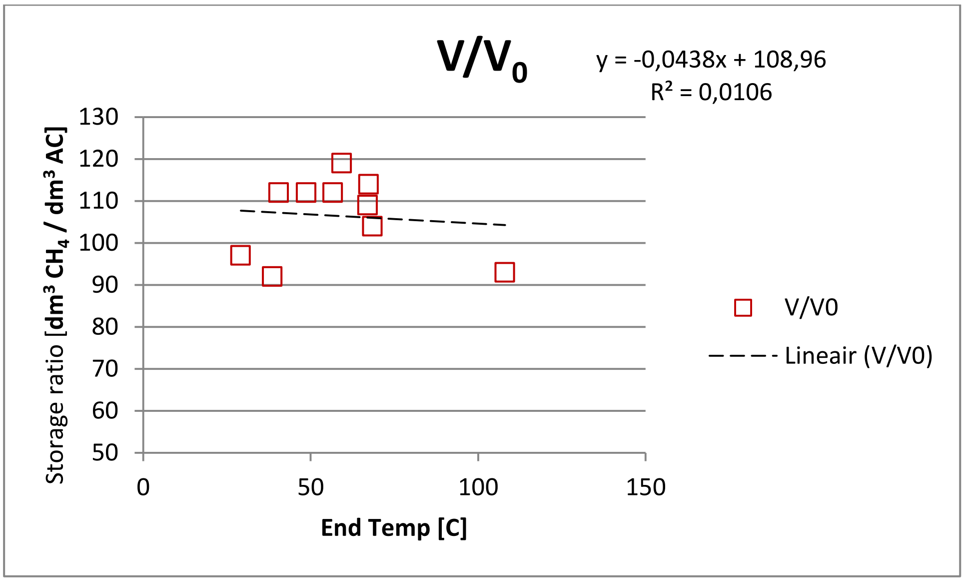

Figure 21: Set of V/V_0 data points as function of the temperature of the bed at the end of the experiment, for the BrightBlack adsorbent.

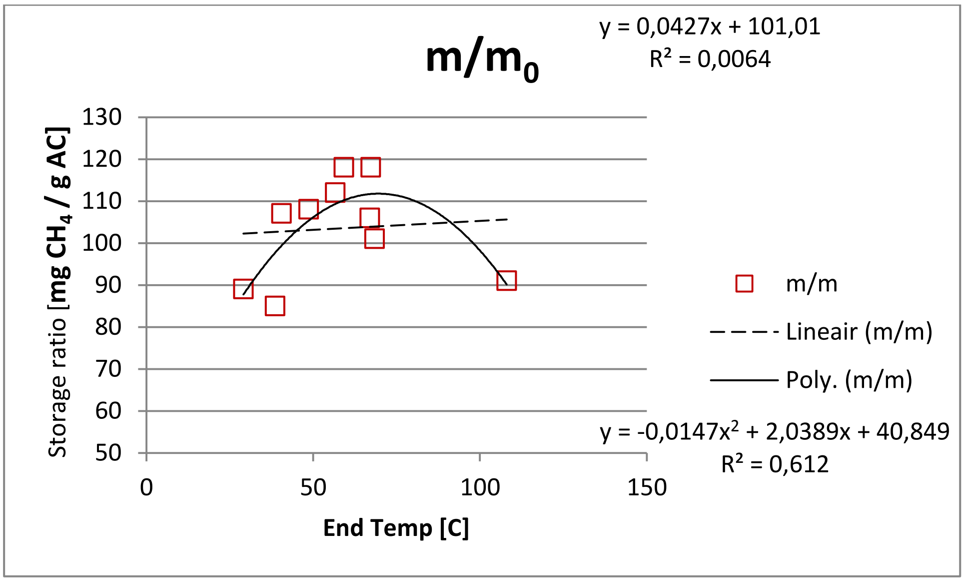

Figure 22: Set of m/m_0 data points as function of the temperature of the bed at the end of the experiment, for the BrightBlack adsorbent.

Figure 22 shows the gravimetric ratios, where the linear trend line has a fit of 0.6% and a positive gradient and polynomial trend line with a fit of 61%. Therefore it seems that the BrightBlack adsorbent does not have linear dependency with the bed temperature but a polynomial one. However to confirm this presumption further research is needed

5.3 MaxSorb 3000 vs. BrightBlack

So which adsorbent is the best? Unfortunately there is no “best” adsorbent, it all depends on the application for which the adsorbent will be used. As can be seen in **Figure 23** the BrightBlack adsorbent has the better V/V_0 values even at high flow rates, while the “MaxSorb” adsorbent has better m/m_0 ratios (**Figure 24**). Keeping this in mind a simple table of the most prominent pros and cons can be constructed as can be seen in **Table 3**. Furthermore a list of the three most important specifications can be made.

- Sorption capacity
- Bulk density
- Heat of sorption

Table 3: Pros and cons of MaxSorb 3000 and BrightBlack

	MaxSorb 3000	BrightBlack
V/V_0	Con	Pro
m/m_0	Pro	Con
Temperature dependency	Con	Pro

Another important noticeable phenomenon is a stronger temperature dependency of the MaxSorb adsorbent. This is not as strong noticeable when comparing volumetric ratios (see Figure 23) where the gradient of the trend lines is a lot alike. It is however when looked at it with a gravimetric point of view Figure 24 where the gradient of the lines differs a lot.

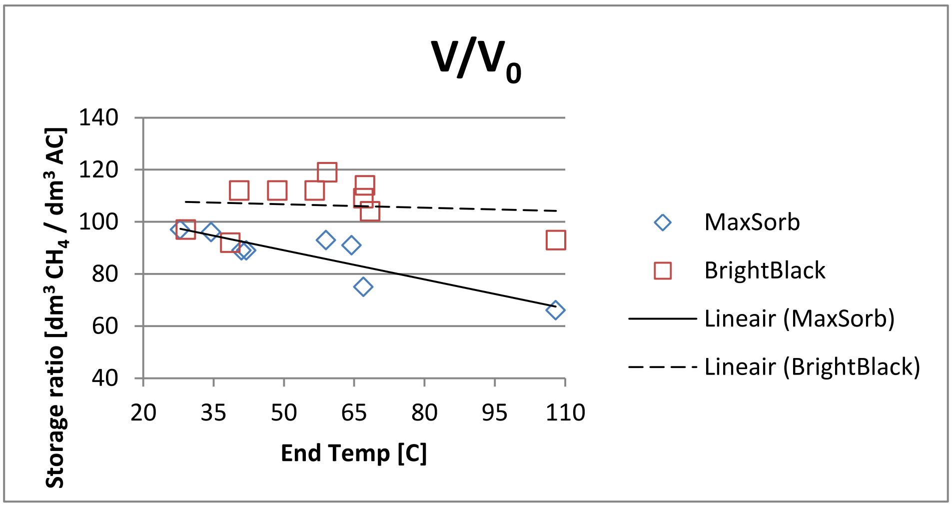

Figure 23: V/V_0 comparison between MaxSorb 3000 and BrightBlack

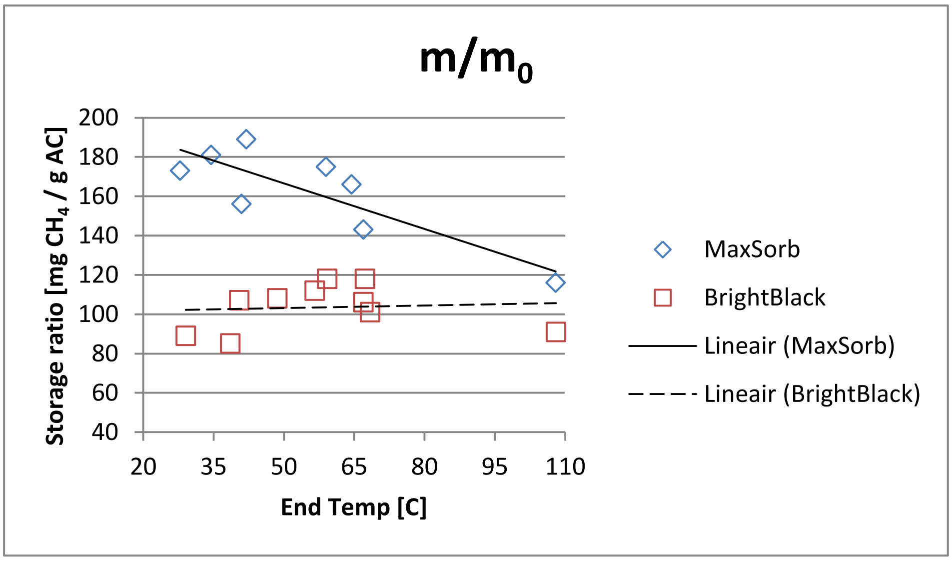

Figure 24: m/m_0 comparison between MaxSorb 3000 and BrightBlack

5.4 Measurement accuracy

It is known that indicators and controllers have a slight deviation. Because the storage ratios in this report are solely based on the measured data from the flow indicator FIC102. It is important to know what error margins these ratios have.

The FIC102 is produced by Bronkhorst and the model name is F-232M. This controller has an error of 0.1% of its maximum flow plus 0.5% of its read-out. Eq. 4 & Eq. 5 show the formulas to calculate the error margin at a given point "i" during the experiment. While Eq. 6 will calculate the error in percentage, which Is graphically represented in Figure 25.

$$\dot{V}_{i,error} = 0.001 * \dot{V}_{max} + 0.005 * \dot{V}_i \qquad \textbf{Eq. 4}$$

$$\dot{V}_{i,range} = \dot{V}_i \pm \dot{V}_{i,error} \qquad \textbf{Eq. 5}$$

$$error_{i,\%} = \frac{\dot{V}_{i,error}}{\dot{V}_i} * 100 \qquad \textbf{Eq. 6}$$

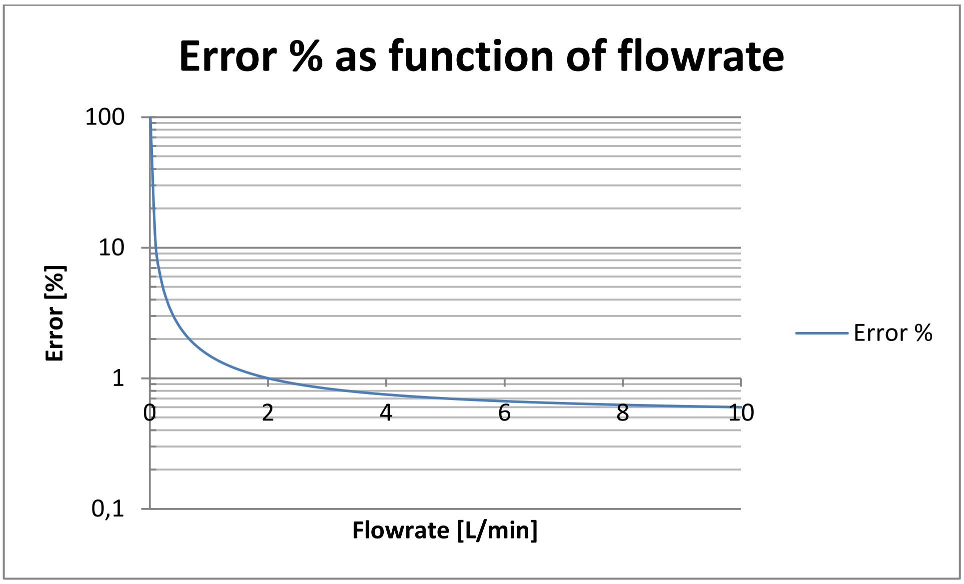

Figure 25: Deviation per flow rate on logarithmic scale

Figure 26 shows the difference in the V/V_0 when the error margin of the flow controller is taken into account. Notice that the range at 0,5 $L*min^{-1}$ is a lot bigger then when using a flow rate of 10 $L*min^{-1}$. This occurs mainly by the larger error on lower flow rates but is also enhanced by the time. Which is approximately 20 times bigger when using a flow rate of 0,5 $L*min^{-1}$ instead of 10 $L*min^{-1}$. This can clearly be seen in Table 4.

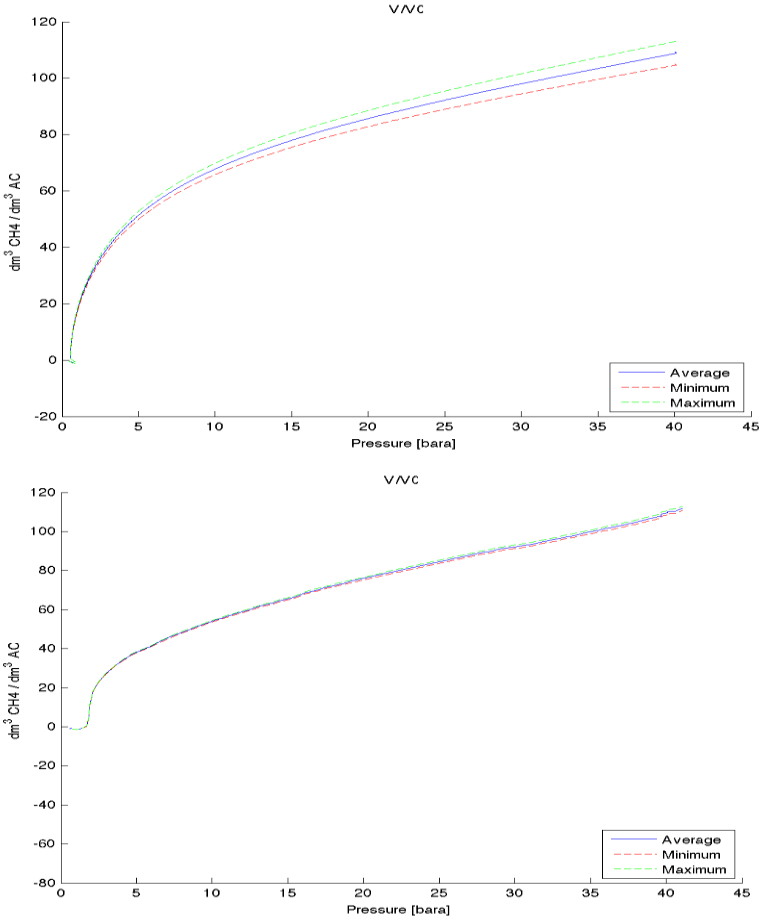

Figure 26: (a) Shows the range in V/V_0 @ 0,5 L*min^{-1}; (b) Shows the range in V/V_0 @ 10,0 L*min^{-1}

Table 4: Error percentage at a given flow rate and how this error effects the volumetric storage capacity

Flowrate [l/min]	0.5	2.0	5.0	10.0
Error margin for flowrate	± 2.50 %	± 1.00%	± 0.70%	± 0.6%
Error margin for V/V_0	± 4.45 %	± 1.79 %	± 1.13 %	± 0.96 %

6

Thermal management

The bed temperature of the adsorbent is an important factor of the storage capacity. This influence can also be seen in Eq. 1. Therefore during adsorption it would be desirable to keep the bed at the most ideal (lowest) temperature possible. This can be done with a phase changing material, because during the phase change it will absorb heat, as can be seen in Figure 27 while its temperature will not increase and so the bed temperature will also not increase. During desorption this process will be reversed. But of course there are different possibilities for thermal management, such as a heat exchanger built in the reactor, investigated by Rahman et al. [15]. Such a reactor with an heat exchanger has a much better thermal management when compared to one where PCM is implemented. However due to budget and the relatively easiness to implement PCM in the existing reactor only the use of PCM will be discussed in this chapter.

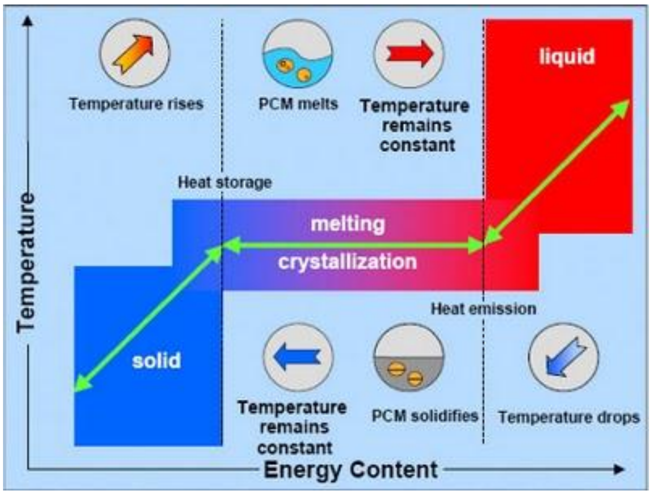

Figure 27: F Phase Change cycle; (https://tekes.dicole.net) [4]

Appendix 0 shows the calculation of the amount of PCM needed, expressed in volume percentage. It is desired to keep the volume of PCM as low as possible to maximize the storage of gas. In Appendix 0 Eq. 22 to Eq. 25shows how to calculate the needed amount of PCM expressed in volume, here can be seen that it is desired to have the latent heat and the density of the PCM as high as possible, while maintaining a similar particle size as the carbon in order to achieve a homogeneous mixture.

There are also experiments done with PCM added to the adsorbent which will be discussed in the next paragraph 6.2. For these experiments a PCM is used from the company of BASF, Micronal® DS 5038 X (see Figure 28 & Figure 29). This PCM satisfied the needs as far as possible with a latent heat of ~100 kJ*kg^{-1} and a density in the range of 300-400 kg*m^{-3} and almost the same particle size.

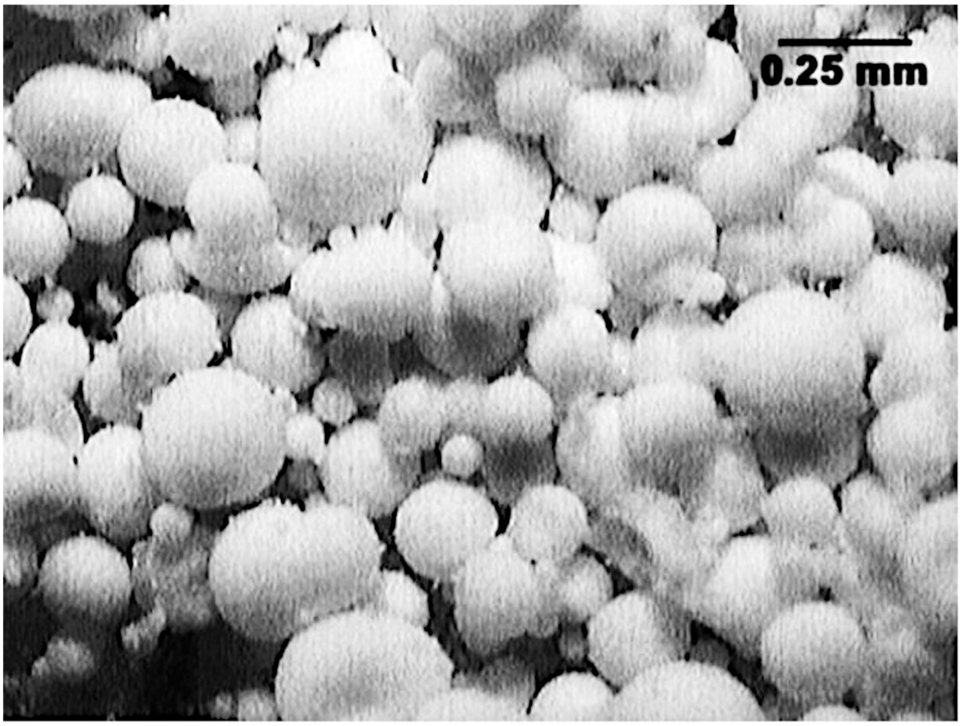

Figure 28: Picture of Micronal DS 5038 X grains made with a microscope, 2.5 times magnification.

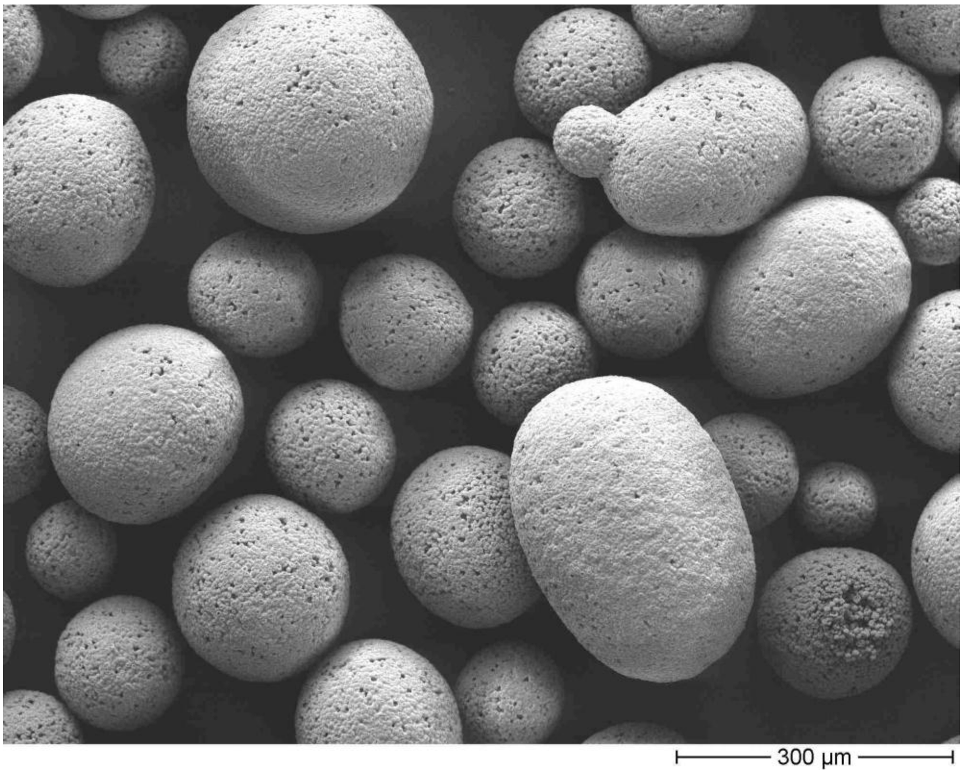

Figure 29: Picture of Micronal 5038 X, made with a Scanning Electron Microscope. Source: e-mailing from BASF

Figure 30 shows how much $V_{\%,PCM}$ should be added in order to absorb an amount of heat. The star marks the point where all heat is absorbed and the carbon should not heat up. This point is called the ideal point and is based upon a Gibbs excess adsorption of 85 mg of CH_4 / g of AC. Varying this ratio will shift the ideal amount of PCM over the blue curve, where a lower Gibbs excess results in shifting the ideal point to the left. However this curve can also be used to determine the added PCM while not absorbing all of the heat, thus reducing the amount of PCM in the reactor bed while maintaining a higher concentration of activated carbon. In this case it gives a rough estimation of what to expect in terms of how much the carbon will warm up.

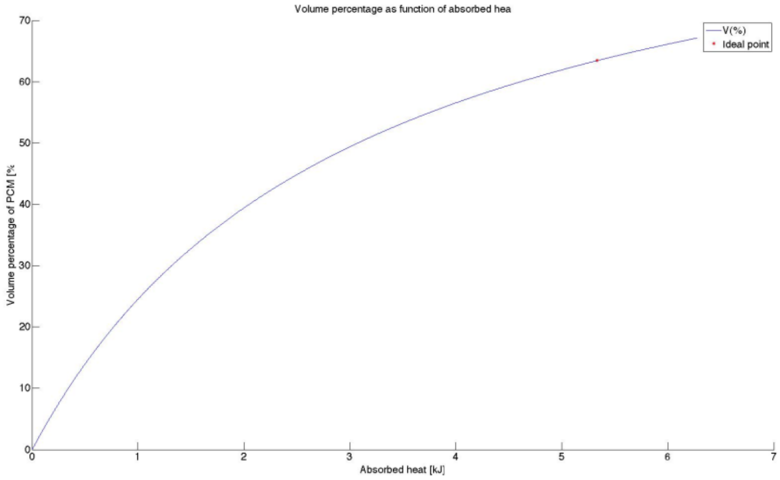

Figure 30: $V_{\%,PCM}$ as function of the adsorbed heat while the red star marks the spot where all heat is absorbed using a Gibbs excess adsorption of 85 mg of CH_4 / g of AC. The graph is based on BrightBlack and the volume of AC in the reactor bed.

6.1 Cyclic stability

As a practical part of the study the cyclic stability is also investigated. It basically comes down to: "How many cycles can be done without regeneration until the storage degradation is stabilized." Eq. 7 shows the mathematical representation, where "c" is the storage ratio and "n" the number of cycles until stabilisation.

$$c_1 \neq c_2 \neq .. c_{n-1} = c_n \qquad \textbf{Eq. 7}$$

To find "n", consecutively experiments are carried out where the adsorption is done with a flow of 5 $l*min^{-1}$ and the desorption is done to ambient pressure. This should represent a practical use of the system. Table 5 shows the degradation during 11 cycles, where the first cycle was done beginning with a vacuum and after cycle 10 the carbon was regenerated and put under vacuum so that cycle 11 had the same conditions as the first. This latest cycle was done to compare the results with the first cycle in order to see if there is also degradation after 11 cycles. Figure 31 shows the graphical interpretation during these cycles.

Table 5: Degradation of the storage capacity during 5 cycles

Cycle	1	2	3	4	5	6	7	8	9	10	11
V/V_0	85	66	65	65	66	65	65	65	64	64	85
m/m_0	78	53	52	52	53	51	52	58	50	52	76
T_{end}	57	43	41	39	39	37	37	37	36	36	51

From these graphs it is made clear that the carbon keeps its storage capacity throughout the cycles. Furthermore during these tests cycle 1 and 11 have been conducted with regeneration and vacuum, in order to examine the stability after 9 cycles which remained quite the same.

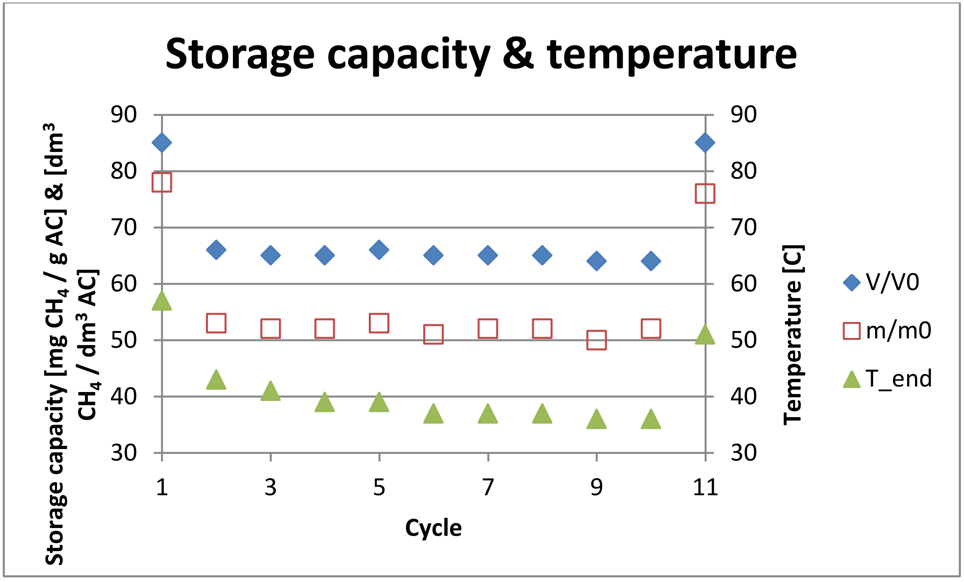

Figure 31: Effect on the storage capacity and end temperature over 11 cycles without regeneration except the first and the last.

6.2 BrightBlack plus PCM

As part of investigating thermal management a PCM was added to the BrightBlack adsorbent. However due to a relatively low density and latent heat of the PCM it was necessary to add ~65 $V_{\%}$ of PCM in order to absorb all of the sorption heat. Due to the fact that the Hystore apparatus has a relatively high thermal mass the decision was made to add 45 $V_{\%,PCM}$ (see Table 6) instead of the previous mentioned 65 $V_{\%}$. This results in 50 $m_{\%}$ of PCM as shown in Table 7.

Table 6: The amount of heat absorbed at 45 and 65 $V_{\%}$ and the excess which is not absorbed @ 45 $V_{\%}$

	45 $V_{\%}$	Excess @ 45 $V_{\%}$	65 $V_{\%}$
Heat [kJ]	2.51	2.82	5.33

Table 7: The amount of AC and PCM of the new bed.

	BrightBlack	PCM	Total
Weight [g]	38	19	57

When experiments are conducted the effect of the PCM can clearly be seen in the temperature gradient (Figure 32).

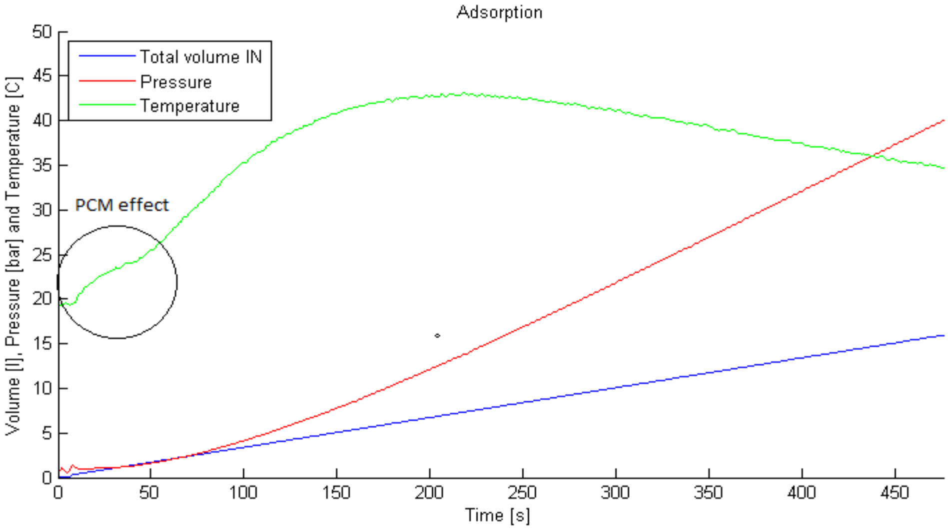

Figure 32: Effect of PCM while adsorbing

The results of the experiments with PCM can be found in Table 8 and Figure 33. When these results are compared to the experiments without PCM, there is a small increase in the gravimetrical storage ratio while the volumetric storage ratio decreases. Because there is a slight positive gradient it is recommended to do experiments in the future which contain enough PCM to absorb all of the sorption heat. The expectation is a degrading volumetric capacity while the gravimetric capacity will increase.

Table 8: Experimental results of BrightBlack + PCM

Flow [l/min]	V/V_0 [dm^3 CH_4 / dm^3 AC]	m/m_0 [mg CH_4 / g AC]	T_{end} [C]
0.5	75	95	25
2.0	76	96	35
5.0	78	101	57

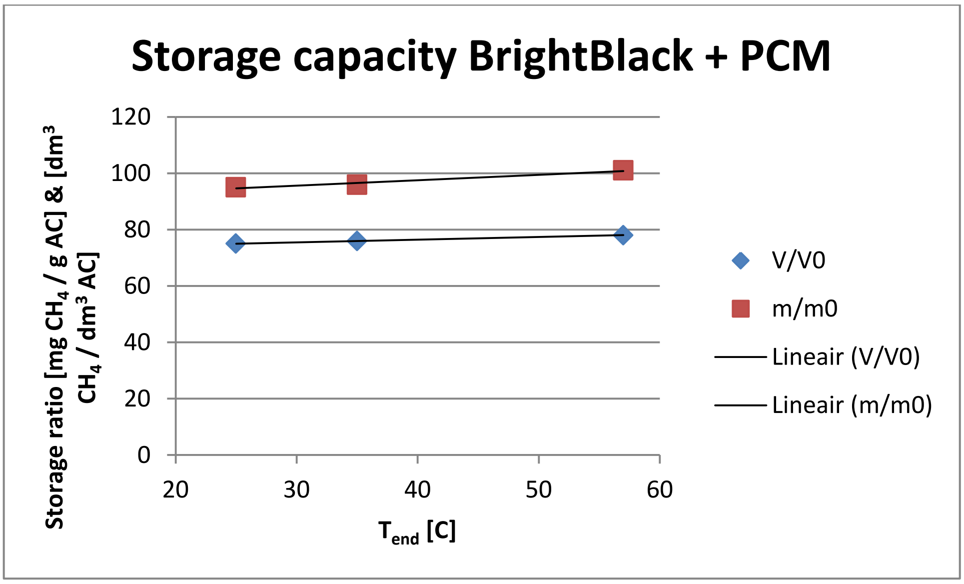

Figure 33: Storage capacity of BrightBlack + PCM as function of its ending temperature.

7

Conclusion

Storage of methane in activated carbons can be a good alternative for CNG or LNG, for it does not require high pressures (CNG) nor does it need cryogenic temperatures (LNG), thus making it a safer and a less energy consuming storage. It has reasonable storage capacities gravimetrically as well as volumetrically. In this investigation two different types of activated carbon were tested to examine the storage capacities, the heat effects that come with it. Also thermal management is studied by the use of PCM.

Storage capacity

The storage capacities of activated carbons differ per brand and per type. It can be concluded that the MaxSorb adsorbent (powder form) had an high gravimetrical storage ratio while the volumetric ratio was worse than that of BrightBlack. On the other hand there was the BrightBlack adsorbent (pressed pellets) with a higher density than the MaxSorb. It can be concluded that the gravimetrical storage was not as good as that of MaxSorb while its volumetrically storage ratio was a lot better.

Heat effects

During the binding and unbinding of the gas molecules to the carbon, heat will be produced or needed. This heat is called the heat of sorption and it negatively affects the storage ratio, gravimetrically as well as volumetrically hence it is important to take it into account when designing such a system. These effects occur primarily during adsorption and they degrade the storage ratio. While these effects also occur during desorption they are less important. The negative affect here is that the gas will released somewhat slower by the carbon.

Thermal management

This part of the investigation focussed on the possibility of mixing the carbon bed with a phase change material in order to have the PCM absorb some or all of the sorption heat. While it is not as effective as adding a heat exchanger it is much easier and budget friendly to implement it into an existing system. It was concluded that the amount of PCM needed to absorb all of the adsorption heat was of such a magnitude that a degrading effect on the volumetric storage capacity was noticed while still having a positive effect on the gravimetrical storage capacity.

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Appendix A. Adsorption calculation

A.1. Gas adsorption calculation, Methane on Activated Carbons

This document will describe how to calculate the Gibbs excess adsorption when adsorbing a gas in active carbon. Definition http://old.iupac.org/reports/2001/colloid_2001/manual_of_s_and_t/node21.html

This calculation will to make a comparison of analytical measurements of gas adsorption using the Rubotherm equipment and the practical adsorption levels obtained in a storage vessel filled with activated carbon.

Starting off the following definitions and standard values should be known.

- The density of the given gas at standard pressure and temperature ρ_{CH4} = ~0.68kg/m^3
- The skeletal density of the carbon ρ_{carbon} = ~2.25 g/cm^3]
- The weight of the carbon bed m_{bed} [g]
- The volume of the carbon bed as it is in the reactor V_{bed} [cm^3]
- The amount of gas that can be put in the filled reactor at a given pressure V_{CH4_ad} [dm^3]
- The amount of gas that can be put in the empty reactor at a given pressure V_{CH4_bl} [dm^3]
- The difference between the amounts of gas that can go in the reactor with and without activated carbon $\Delta V_{CH4}=V_{CH4\_ad}-V_{CH4\_bl}$ [dm^3]

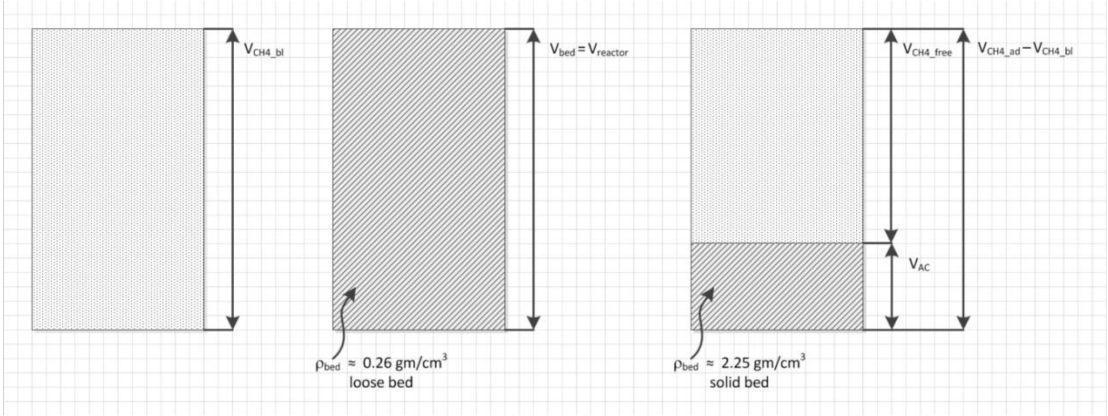

Figure 34: Schematically representation of the reactor

A.1.1 V/V₀

For practical means, a calculation of V/V_0 is normally used to indicate the gain in gas storage capacity between compressed gas storage and adsorbed gas storage. This calculation is simply performed as:

First the amount of gas needs to be calculated that fits the space of the bed.

$$V_{CH4\_in\_sorbent} = \frac{V_{bed} * P_{max}}{1000} = dm^3_{CH4} \qquad \textbf{Eq. 8}$$

When filling the reactor the carbon heats up and so does the gas that resides in the carbon. So to have an accurate difference on how much gas that goes extra in a reactor with activated carbon, a temperature correction has to be made.

$$V_{bl,i} = \frac{p_i}{p_{bl}} \frac{T_{bl} + 273.15}{T_i + 273.15} * v_{bl} = dm^3_{CH4} \qquad \textbf{Eq. 9}$$

The total amount of gas that fits the carbon can be derived as follows

$$\frac{V}{V_{0_{ad}}} = \frac{V_{CH_4 in} - V_{bl,i}}{V_{bed}} * 1000 = \frac{dm^3_{CH4}}{dm^3_{AC}} \qquad \textbf{Eq. 10}$$

Also the free space in the bed needs to be calculated in order to derive the amount of gas in that space. When there is no PCM in the bed, the last term with PCM can be left out.

$$V_{bed\_free} = v_{bed} - (m_{bed} * \rho_{AC}) - (m_{PCM} * \rho_{PCM}) = dm^3_{CH4} \qquad \textbf{Eq. 11}$$

The total amount of gas that fits the space where there is no carbon can be derived as follows

$$\frac{V}{V_{0_{free}}} = \frac{\frac{p_i}{p_{stp}} * \frac{T_{stp}}{T_i} * V_{bed\_free}}{V_{bed}} = \frac{dm^3_{CH4}}{dm^3_{AC}} \qquad \textbf{Eq. 12}$$

The V/V_0 ratio can easily be calculated by taking the extra-added amount of gas and dividing it by the volume of the bed.

$$\frac{V}{V_0} = \frac{V}{V_{0_{ad}}} + \frac{V}{V_{0_{free}}} = \frac{dm^3_{CH4}}{dm^3_{AC}} \qquad \textbf{Eq. 13}$$

To derive the amount of gas adsorbed on the surface of the carbon further calculations are required.

First off there is the easy calculating. This calculation is rather easy because the correction for the volume of the bed isn’t applied.

A.1.2 m/m₀

Start by calculating the mass of the adsorbed gas by multiplying the density of the gas with the difference of gas that can go into the reactor.

$$m_{CH4} = \Delta V_{CH4} * \rho_{CH4} = g_{AC} \qquad \textbf{Eq. 14}$$

Then to calculate the amount of Gibbs excess adsorption.

$$\frac{m}{m_0} = \frac{m_{CH4}}{m_{bed}} * 1000 = \frac{mg_{CH4}}{g_{AC}} \qquad \textbf{Eq. 15}$$

A.1.3 m/m₀ with skeletal density correction

Now there is a nice indication of the adsorption capacity of the carbon, but it should be calculated more exact by taking in consideration that the carbon itself has a volume and therefore this volume should be subtracted from the open volume of the reactor.

First the volume of the bed needs to be calculated as if it would be a nonporous bed

$$V_{AC} = \frac{m_{bed}}{\rho_{AC}} = dm^3 \qquad \textbf{Eq. 16}$$

Subtracting the volume of the nonporous bed from the volume of the bed as it is in the reactor. The free volume can be calculated (while assuming that the complete reactor is filled with sorbent so $V_{reactor}$=V_{bed})

$$V_{free} = V_{bed} - V_{AC} \qquad \textbf{Eq. 17}$$

Now the amount of gas needs to be calculated which would otherwise fill the porous cavities of the carbon

$$V_{CH4\_free\_volume} = \frac{V_{free} * P_{max}}{1000} = dm^3 \qquad \textbf{Eq. 18}$$

The total amount of excess adsorbed methane on the AC is

$$V_{CH4\_in\_AC} = V_{CH4\_ad} - V_{CH4\_free\_volume} = dm^3 \qquad \textbf{Eq. 19}$$

The amount of gas can now be converted from volumetric to gravimetric by multiplying it with its density

$$m_{ads} = \rho_{CH4} * V_{CH4\_in\_AC} = g \qquad \textbf{Eq. 20}$$

And finally the Gibbs excess can be calculated by dividing the weight of the gas over the bed of carbon

$$\frac{m}{m_0} = \frac{m_{ads}}{m_{bed}} * 1000 = \frac{mg_{CH4}}{g_{AC}} \qquad \textbf{Eq. 21}$$

Appendix B. V$_{\%}$ PCM calculation

B.1. PCM volume percentage calculation

This document will describe how to calculate the volume percentage when adding phase change material (PCM) to the activated carbon.

Defining the constants

dH = The heat of adsorption [kJ*mol^{-1}]

M_{CH4} = Molecular mass of methane [kg*mol^{-1}]

m_{CH4} = The mass of the actual adsorbed methane [kg]

m_{bed} = The mass of the activated carbon inside the reactor [kg]

G = The Gibbs excess ratio [kg of CH4/(kg of AC)$^{-1}$]

V_{bed} = The volume of the activated carbon inside the reactor [m^3]

ρ_{PCM} = The density of the phase change material [kg*m^{-3}]

L_{PCM} = The latent heat of the phase change material [kJ*kg^{-1}]

α_{PCM} = The expansion coefficient when phase change occurs [%]

h_{bed} = The height of the packed bed [m]

Formulas

First off the total amount of added gas needs to be calculated in kilograms

Eq. 22

$$m_{CH4} = G * m_{bed} \qquad kg_{CH4} = \frac{kg_{CH4}}{kg_{AC}} * kg_{AC}$$

After that the excess amount of heat needs to be calculated

Eq. 23

$$Q_{adsorption} = \frac{dH}{M_{CH4}} * m_{CH4} \qquad kJ = \frac{\frac{kJ}{mol}}{\frac{kg}{mol}} * kg$$

Than the volume of the phase change material will be calculated

Eq. 24

$$V_{PCM} = \frac{Q_{adsorption}}{\rho_{PCM} * L_{PCM}} \qquad m^3 = \frac{kJ}{\frac{kg}{m^3} * \frac{kJ}{kg}}$$

And finally the volume percentage can be derived

Eq. 25

$$V_{\%} = \frac{V_{PCM}}{V_{bed} + V_{PCM}} * 100 \qquad \frac{\%}{100} = \frac{m^3}{m^3 + m^3}$$

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