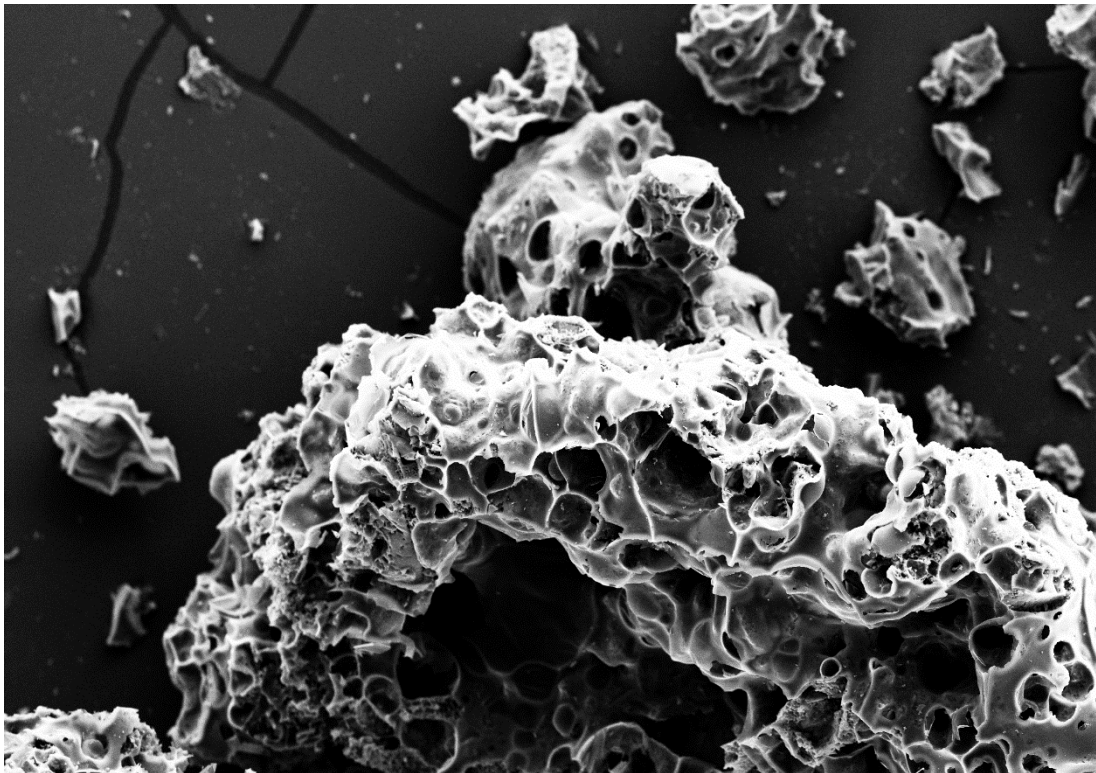


DEFINE OPTIMUM PROCESS CONDITIONS TO PRODUCE CO₂ ADSORBENTS FROM PUR MATERIALS

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Abstract

The Carbon Capture and Storage method has been acknowledged for the capabilities of reducing up to 20% CO₂ emissions. Development of porous carbon materials prepared from polyurethane foam adsorbent were investigated for capture of CO₂. In this thesis work, the carbon material was chemically activated through the direct and indirect methods. Pre-carbonization, mass ratio KOH/char, activation temperature, and activation time, the effect of the preparation conditions on the porous adsorbent were evaluated for the purpose of managing pore sizes and developing high adsorption capacity of CO₂. During the direct method, polyurethane foam was directly treated with KOH before activation. Whereas during the indirect method, the foam was pre-carbonized to form char, which was treated instead. The indirectly and directly activated adsorbent prepared at optimum conditions show adsorption capacities of 152,10 and 151,29 mg/g at 1 atm and 25°C respectively. The produced adsorbents were evaluated for their CO₂ separation performance with a thermogravimetric analyser with 100% CO₂. The CO₂ uptake and pore sizes were directly affected by the different parameters. A moderate activation time and temperature presented a higher adsorption capacity, where it decreased after reaching a higher time and temperature. A higher KOH/char mass ratio leads to a higher CO₂ uptake, where it steadily increases from the lowest mass ratio.

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1 INTRO

1.1 Background

1.11 Intro CO₂

The abundance of anthropogenic emissions, where CO₂ is the most prominent, in the atmosphere and is growing at an alarming rate. According to Nasa, an estimated amount of CO₂ of 417ppm has been measured, pushing us closer to a critical level of CO₂. A median level of CO₂ during the evolution of the humankind that was constant up to the 1950's was around 280-300 ppm CO₂, these are the estimated optimum levels of CO₂ that we should try to achieve (Moseman, 2021). Even if the global CO₂ emissions would stop today, the current CO₂ levels would persist for about 1000 years (Holmes, Lively and Realf, 2021). Therefore, it is crucial that negative CO₂ emission technologies gets further research.

A solution for this is developing sustainable sorbents to both lower the emission from industrial factories and adsorption facilities to pull CO₂ directly from the air. This is called carbon capture storage or CCS. This implies that flue gases generated from combustion of fossil fuel are to be captured and stored. The captured CO₂ can then be stored in for example emptied gas fields at bedrock level where the CO₂ is under such pressure that it's turned to liquid.

1.12 Post combustion

The process in focus is post-combustion capture which implies that CO₂ needs to be separated from mostly N₂ but also other miscellaneous gases like SO₂, and NO₂ after burning of fossil fuel before capture can happen. This technique can be utilized for several different materials and method for separation and capture of CO₂ from the flue gas. Post-combustion capture is therefore, among a few others, one of the most used methods at industrial scale (Ahmed et al., 2020).

1.13 CCS intro

This method has been acknowledged for the capabilities of reducing up to 20% CO₂ emissions. This procedure entails the direct removal of CO₂ from the source, e.g., post-combustion processes. The amount of CO₂ produced from the different types of sources, such as from power plants, are crucial in the selection of an appropriate technique. Even though CCS is an effective carbon capture method some other aspects need to be considered such as the economic factors. Whereas the cost should be minimum for the entire process, there should be minimal environmental impact, and it should be sustainable for the future. (Ahmed et al., 2020).

1.14 Adsorption methods

There is a need to develop an economical, efficient, environmentally sustainable, and easy to use CO₂ capture method. There are different ways to capture carbon, two of the most used and well-known methods are absorption and adsorption. According to research, adsorption is the most promising technique when it comes to capturing and separating CO₂ from other gasses. For chemical absorption, amine-based absorbents are the most efficient, around 98%, and are widely used in industries. However, when plenty of the amine-based absorbents are used, the usage leads to equipment corrosion. Special materials are required for the equipment to withstand the corrosion. Solid adsorbents in this case, are easier to handle due to the corrosion and formation of chemically unstable compounds during the heating process of absorbents. Furthermore, the strong chemical interaction between CO₂ and amine solvents encompasses a higher total energy consumption for solvent regeneration. A separate alternative for CCS could be the solid adsorbents (Rashidi and Yusup, 2016).

1.15 Thermo swing process

Another aspect which makes adsorption a suitable choice for CCS is the fact that the regeneration process can lower the total energy consumption. Solid adsorbents will be regenerated using the thermal swing process (TSA). So that the adsorbents can be used for the next adsorption cycle, the CO₂ is released during this process. The sorbent is heated by percolating a hot gas. In which, the CO₂ desorbed from the adsorbent and can be used once more (Lei et al., 2013).

1.16 Activated carbon

The relatively low energy consumption, simple equipment and low corrosiveness are some of the aspects that makes adsorption a viable option for CO₂ capture. Activated carbon, bio-chars, zeolites, porous polymers, amines, and metal organic frame are some of the adsorbents that have been developed (Ochedi, Liu and Adewuyi, 2020). Activated carbon and zeolites are the most suitable adsorbents for post-combustion capture at low operating temperatures, mostly because of the inexpensiveness and low impact on the environment. The high CO₂ and N₂ selectivity, fast kinetics, and stability in multi-cycle adsorption are some of the aspects present in activated carbons (Rashidi and Yusup, 2016). The activated carbon is also a suitable adsorbent because it could adsorb larger capacities of CO₂ at higher pressures, is less sensitive to moisture, easily regenerates, and has potential to be low cost compared to other adsorbents.

Activated carbon can be derived from a plethora of raw materials through pyrolysis (Martín et al., 2010). However, these precursors must activate easily so that the physicochemical characteristics are preserved. For future commercialization, the selection of these adsorbents are fully dependent on the availability of the raw materials, the preparation of the sorbent, and the operating costs. Adsorbents such as amines are an effective CO₂ capture but are expensive (Ge et al., 2019).

1.17 PUR adsorbents

Polyurethane or PUR is a highly versatile polymer that can be altered to be rigid and dense or, as in our case, a foam. It's high heat resistance and high deformability as an expanded foam gives it several uses such as isolation in houses or for pipes and cushioning in furniture or mattresses etc. Due to PUR being a petrochemical-based polymer, it's highly important to recycle it whenever possible. Even though PUR tonne for tonne contains the same amount of energy as coal, it would work as an effective reagent for incineration, but it would also mean it emits a large amount of CO₂ in the process. Other means of recycling are therefore highly sought after.

The by-product of pyrolysis of polymer wastes, char, can be used in the advancement of adsorbents. The carbon could chemically be activated either indirectly or directly through the addition of Potassium hydroxide (KOH) and pyrolysis. The pores are formed through chemical activation and also encourage the formation of high textural carbons (Ochedi, Liu and Adewuyi, 2020). Polyurethane waste (PUR) is one of the interesting materials to be used for adsorbing purposes. The carbons contain a large volume, narrow micropores, high surface areas, and high concentration of nitrogen can increase the adsorption ability. The low cost of the material can be the aftermath of the operational costs, where the adsorbent needs minimum energy input to regenerate. For these reasons, polymer waste such as polyurethane foam (PUR) can be used as a means of production in an industrial setting (Ge et al., 2019). Enhanced morphology, pore size and distribution are attainable due to the ability of controlling the chemical compositions. The porous structure and surface area, with the help of electrostatic and Van der Waals forces, attracts the adsorbate onto the surface, in physical adsorption. The pore structure and the properties of the surface chemistry is a deciding factor in the effectiveness of the adsorbent (Martín et al., 2010).

1.18 Waste polymers

Waste polymers, such as PUR, are a great option for the production of adsorbents because the end of the product's life cycle, polymers cannot be used. The polymers that cannot be used are in part responsible for the huge amounts of wastes being generated. Reusing and regenerating used PUR can be high energy and time consuming, making it an unnecessarily expensive process. Instead of pursuing the possibility of regenerating the polymer, it is usually burned. Huge amounts of NO and CO₂ are emitted into the atmosphere leading to a negative impact on the environment (Ge et al., 2016).

1.19 Paper explanation

There are several different parameters and tangents to evaluate, but since this is a bachelor's thesis, a few limits had to be predetermined. For example, the temperature tested is scaled by intervals of 50°C. For more precise evaluation and optimization, smaller intervals should be examined, this applies to the time and KOH concentrations as well. Methods to increase the yield from the pre-carbonization are also a factor that are worth looking into. Studies show that adding Fe⁺³Cl generates more char after pyrolysis. The urethane linkage is more easily broken, leading to less fluid product yield and enhanced production of char and gases (Terakado, Yanase and Hirasawa, 2014).

1.2 OBJECTIVE

Testing of activated carbon obtained from direct and indirect chemical activation during different conditions modified by KOH impregnation, time, and temperature, with the goal to investigate CO₂ adsorption capacity from the different sorbents made.

- What are the differences in structure and CO₂ adsorption capacity between direct and indirect chemical activation?
- What parameters regarding time, temperature and KOH concentration yields the best CO₂ adsorption capacity?

2 THEORIES

2.1 Adsorption vs absorption

Due to the adsorption process being fully reversible to extract the adsorbed CO₂, adsorption is a favourable separation technique. The CO₂ is attached to the pores at the surface, of the sorbent which makes it easy to treat with heat for easy separation. The sorbent also regenerates makes it reusable. According to a study from (Terakado, Yanase and Hirasawa, 2014), the sorbent had a reusability retention of 90.8% after 20 adsorption/regeneration cycles. Furthermore, adsorption has a low cost to utilize and required simple equipment to operate.

2.2 Production of activated carbon

The most important step to produce the highly porous carbonaceous material, activated carbon, is activation. The process entails the conversion of the raw material into a pure carbon form that contains randomly dispersed pores. Some of the fundamental variables of activation that can alter the properties of the activated material are the temperature of activation, flow rate of inert gas, and the attributes and physical qualities of the raw materials and char. Activation time, temperature, and mass ratio Potassium hydroxide (KOH)/char will be evaluated (McDougall, 1991).

2.3 Activating carbon

The carbon can be activated using two methods, either physical activation or chemical activation. Both methods consist of two separate stages that are needed for activation, the pyrolysis and activation process. The initial stage, carbonization of the material under inert gas, is considered as a devolatilization process. Whereas during this method, the material degrades and components volatile, and form char. The 650 °C temperature is chosen for carbonization. The activation process of the char occurs under an inert gas at the temperatures of 550-650 °C (Rashidi and Yusup, 2016). However, before the chemical activation transpires, an activating agent is mixed with the char. The production of by-products, mostly tar and volatile compounds, can be prevented by the addition of an activating agent, such as KOH. Depending on the ratio of KOH/char, the activation temperature, heating rate and activation time the final product will affect the different pore sizes, specific surface areas and carbon yields. Washing the product from the impurities and residues only transpires during the chemical activation. The obtained activated carbon is washed with HCl solution and deionized water until the solution reaches pH 7 (Ahmed et al., 2020).

2.4 Indirect vs Direct

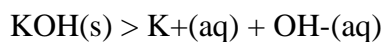
There are two different ways to attain an activated carbon through chemical activation, indirect and direct. The previously mentioned chemical activation is known as the indirect method. The pyrolysis and chemical activation process occurs simultaneously in the direct method. During pyrolysis of PUR, only a certain percentage developed into activated carbon or char, the rest converted into tar and other volatile compounds. This phenomenon is important to note, especially in the direct method. In this method, PUR is directly mixed with the activating agent, KOH, before pyrolysis. The ratio can be described as KOH/expected char. The expected char was determined through a simulated pyrolysis in the TGA. The activating step is the same, nonetheless (Ahmed et al., 2020).

2.5 Optimization

The production of adsorbents can be aimless without setting distinct parameters which can be controlled. Optimisation can entail a higher efficiency and a more economical way of production. The adsorbed amount of CO₂ on the activated carbons are affected by activation time, activation temperature and ratio KOH/char. These parameters are what affects the adsorption effectiveness, the sorbents porosity. To increase the adsorbent's efficiency, these parameters can be optimized. Experiments on these values were conducted (Ahmed et al., 2020).

2.6 KOH treatment

Pores can form in the presence of KOH during chemical activation. Potassium and other alkali metals have the attribute of infusing into different materials, which could be the basis for pore formation. The first step in the process of pore formation is dissociation of KOH in water.



Potassium ions in aqueous solutions spread and surround the material. The ions start embedding into the carbon materials when they are heated and become energised during chemical activation, which forms pores. The carbon material is washed with HCl to neutralise and remove the potassium ions. KCl is a salt which is formed from the reaction between HCl and K⁺, that needs to be washed away with water, as seen in figure 1. (Memahami et al., 2015).

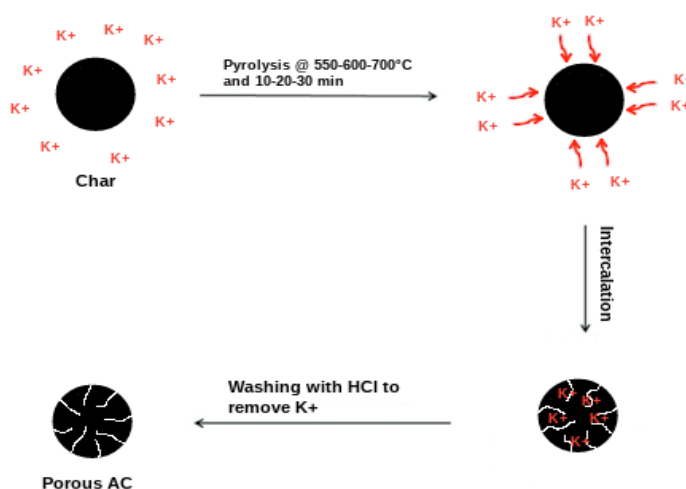


Figure 1 Schematic of KOH impact on char during pyrolysis and washing with HCl

2.7 Comparisons to other work

According to (Ochedi, Liu and Adewuyi, 2020), chemical activating agents such as KOH enhance the formation of better pores. Activated carbons treated with KOH showed different adsorption capacities depending on the activation parameters. The capacities first increased then decreased with increasing temperature and time. The surface area and micropore volume increased 3-fold when activated with KOH in comparison to non-activated samples. The authors mentioned that the textural properties of the sorbent depended on the concentration KOH, although the CO₂ capacity depended on the volume of the formed micropores.

To verify how the parameters affected the CO₂ efficiency, the activated carbons were prepared at different preparation parameters; KOH/char mass ratio and activation temperatures. The biggest impact on the possible adsorbed amount of CO₂ is the mass ratio KOH/char according to (Deng et al., 2014) while activation time exhibits a lower impact. However, it was also shown that a higher and lower mass ratio are not better for the adsorption capacity, the moderate ratio was more appropriate. Likewise, the moderate temperature was adapted because a higher and lower temperature displayed less suitable results. It is therefore shown that both activation temperature and mass ratio KOH/char have significant effect on the micropore volume and distribution.

According to (A. R. Hemmati, A. Ghaemi., 2020), the activated carbon adsorbent modified with KOH solutions were performed to optimize the adsorption capacity. Different mass ratios KOH/char were evaluated to demonstrate the effect of KOH on the adsorption efficiency. It was shown that with a moderate mass ratio, a higher capacity was displayed. However, the optimal mass ratio KOH/char should be noted because an increased concentration of KOH molecules can fill up pores in the activated carbon. A reaction between the activated carbon and KOH can produce the salt KCl which, consequently, can decrease the adsorption capacity and the recovery capacity. Activated carbon modified with 30 weight percent of KOH solution demonstrated the highest CO₂ adsorption capacity.

2.8 TGA

To check the adsorption capacity, the thermogravimetric analysis (TGA) was used. The adsorption and desorption of CO₂ has been investigated as a cycle by purging the CO₂ gas for adsorption and heating up for desorption. The sample is first heated up to 200°C to relieve the sorbent of its preadsorbed gases. The condition for this process is constant at 100% CO₂ at 150 ml/min. After the sorbent has reached 200°C the temperature is lowered to 25°C and it can effectively adsorb the CO₂.

3 METHODS

3.10 Experimental work

To validate and investigate the influence of the parameters, the activated carbons were prepared and activated at different times, temperatures, and mass ratio. One of the parameters was alternated one at a time, while the others stayed the same. The CO₂ capacity could vary depending on the differences within a parameter, where the best capacity of a parameter was chosen. Another parameter was changed but the previous parameter which showed a higher capacity was chosen.

Direct activation:

The PUR sample from a commercial product was crashed to fine powder. 7,5 g of this PUR sample was measured into a beaker, mixing with 3,2, 6,4- or 9,6-ml 4M Potassium hydroxide (KOH) and deionized water until a slurry was formed. After 60 minutes of mixing, it was dried in an oven at 105°C overnight. When dried, the sample was put into a glass rod with a plug of mineral wool sealing one end. The other end was plugged with an inlet of nitrogen gas with a gas flow of 200ml/min for 30 minutes. When 30 minutes had past, the area of the tube that contained the PUR was placed into the oven to be pyrolyzed at altering times and temperatures for different samples. The char was then cooled down, milled, and mixed with 1M HCL and then washed with deionized water. The char was then dried at 105°C, milled and then stored for future analysis such as TGA.

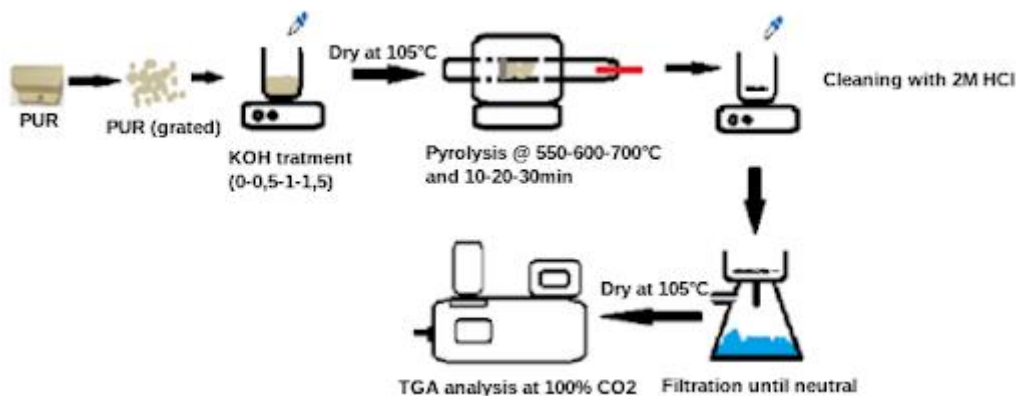


Figure 2 Schematic of methodology for direct chemical activated carbon.

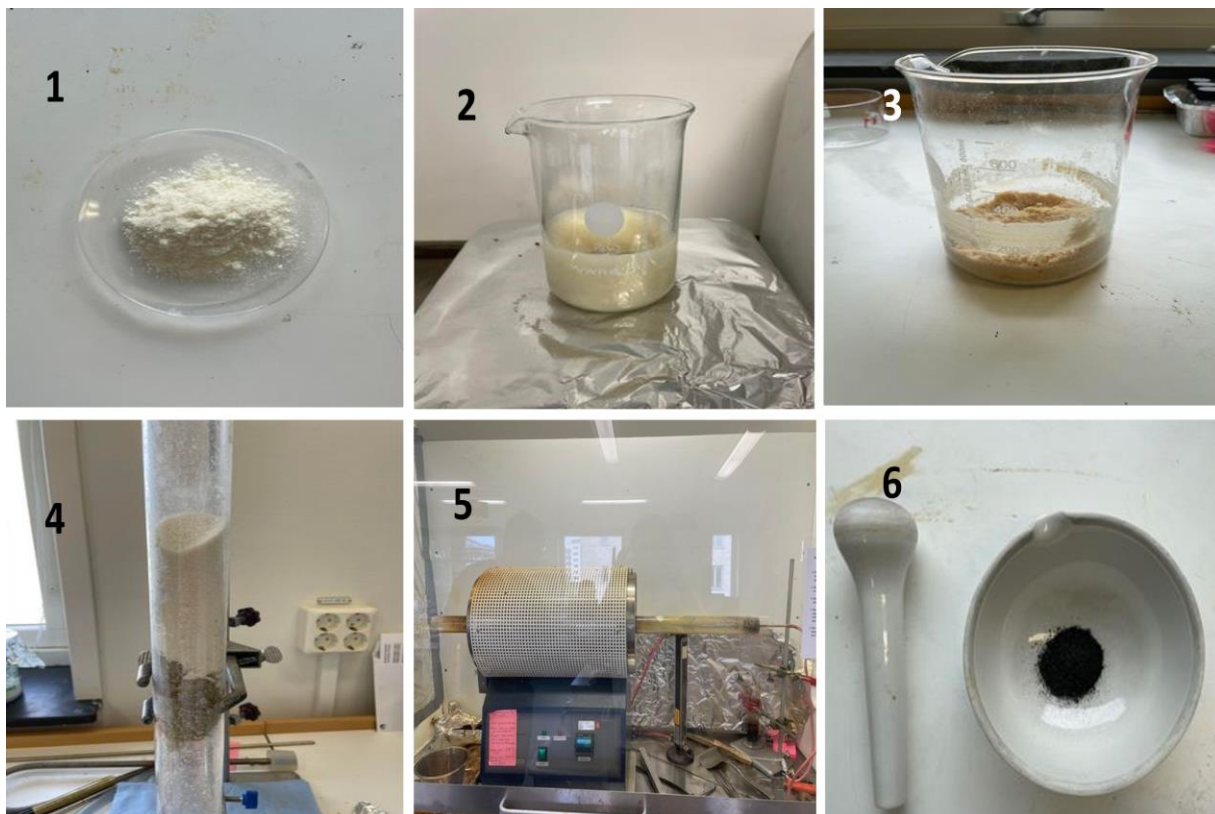


Figure 3 1) Raw PUR. 2) PUR mix with 4M KOH 3) PUR and KOH mix dried. 4) PUR in glasrod with steelwool plug. 5) Pyrolysis of PUR. 6) Milling of carbonized PUR.

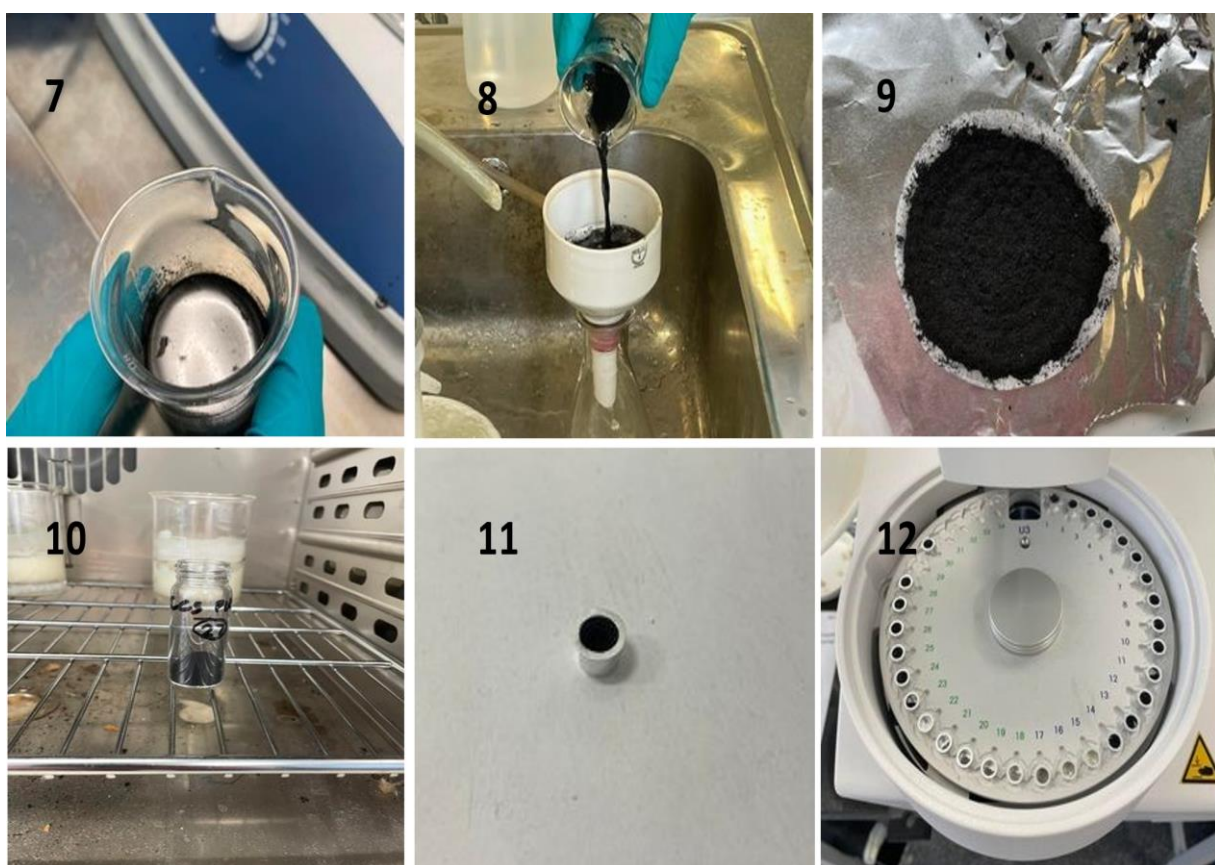


Figure 4 7) Cleaning char with 2M HCL 8) Filtration with deionized water 9) Char after filtration 10) Drying char at 105°C 11) Measuring char in TGA-cups 12) Analyzing in TGA

Indirect activation

The PUR sample from a commercial product was crashed to fine powder. 15 g PUR was measured into a glass tube with a plug of mineral wool sealing one end. The other end was plugged with an inlet of nitrogen gas with a gas flow of 200ml/min for 30 minutes. Meanwhile, the tube-oven was getting preheated to 650 °C. When 30 minutes had past, the area of the tube that contained the PUR was placed into the oven to be pyrolyzed for 60 minutes or until completely charred. The char was removed from the tube-oven and was set to cool while still connected to the nitrogen. When completely cool, the char was measured and milled. The now milled char was then mixed with KOH and deionized water during constant stirring for 30 minutes until a slurry is formed and then dried in an oven at 105°C overnight. After the char has dried, it was milled and 1g char was measured into a beaker with a magnet stirrer. Then 3,2, 6,4- or 9,6-ml 4M KOH was added into the beaker, and it was mixed for 60 minutes. The char was then dried in an oven at 105°C overnight and milled after completely dry. It was then placed in a ceramic dish which was put into a glass tube and was washed with nitrogen gas again for 30 minutes. Then the char was pyrolyzed at altering times and temperature for different samples. The char was then cooled down, milled, and mixed with 1M HCL and then washed with deionized water. The char was then dried at 105°C, milled and then stored for future analysing.

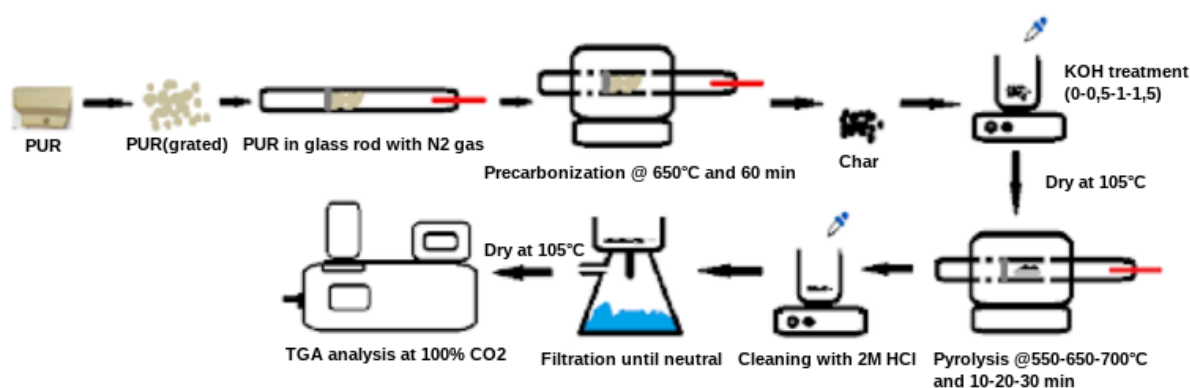


Figure 5 Schematic of methodology for indirect chemical activated carbon.

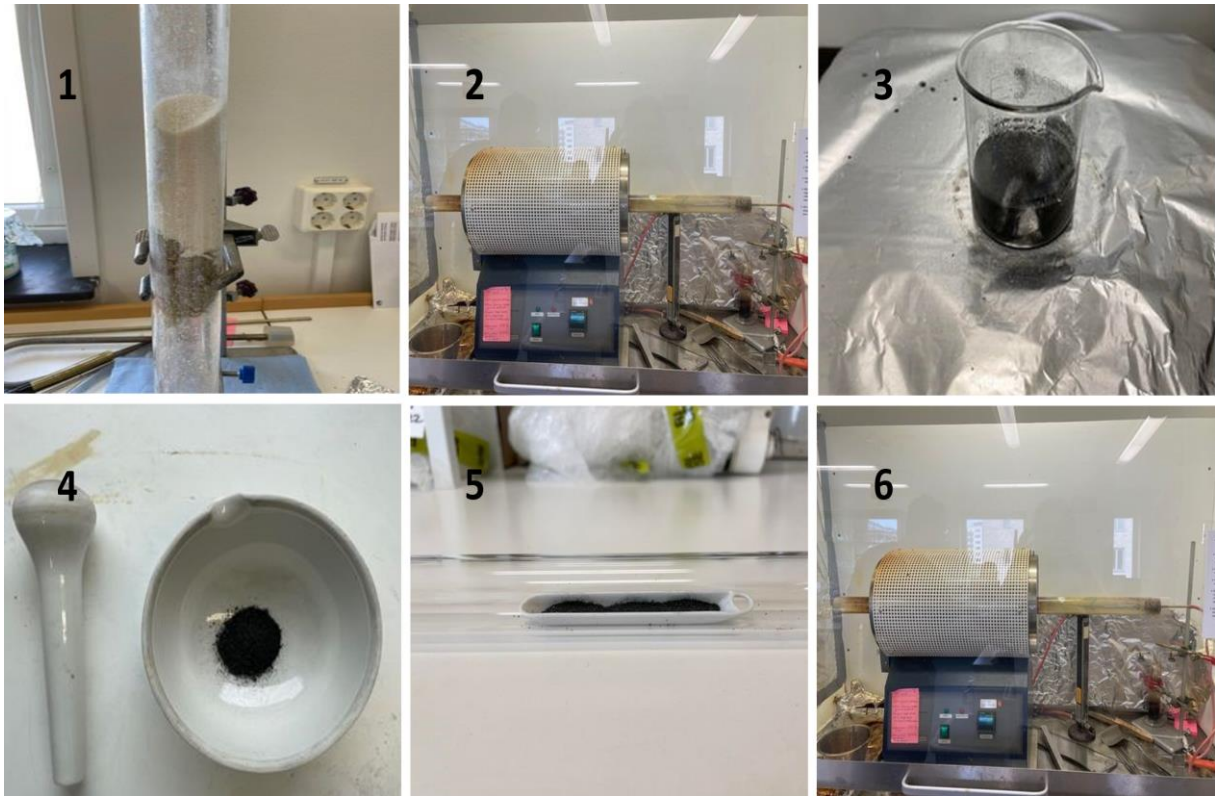


Figure 6 1) 7,5g PUR in glasrod with steelwool. 2) Precarbonization of PUR 3) Char mixed with 4M KOH 4) Milling of dried PUR 5) Char in ceramic boat in glasrodd 6) Activatoin of char

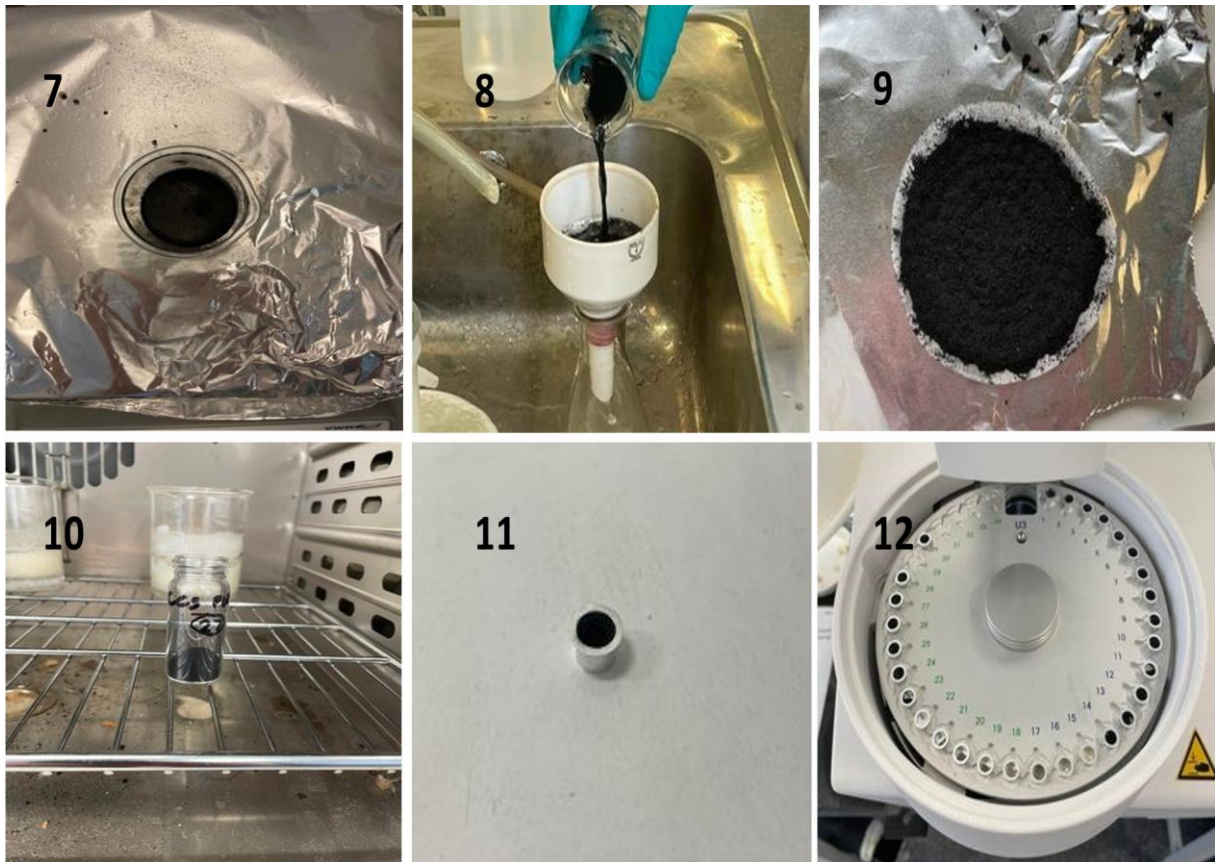


Figure 7 7) Cleaning char with 2M HCL 8) Filtration with deionized water 9) Char after filtration 10) Drying char at 105°C 11) Measuring char in TGA-cups 12) Analysing in TGA.

3.2 Evaluation methods

The adsorption and desorption capacity of the produced adsorbents by direct and indirect activation method were evaluated and determined using TGA.

TGA

To check the adsorption capacity the following method was used by TGA: the sample is first heated up to 200 °C when the purging gas was N₂, 150 ml/min, to relieve the sorbent of its preadsorbed gas. Then the temperature reduced to 25 °C when the purging gas is still N₂ with 150 ml/min. When the temperature is reached and stabled at 25 °C, the 100% CO₂ gas was purged, 150 ml/min for at least 50 minutes. After that the cycle was repeated when the temperature increased to 200 °C with N₂ as purged gas. The amount CO₂ adsorbed is determined by the difference in weight at the different temperatures.

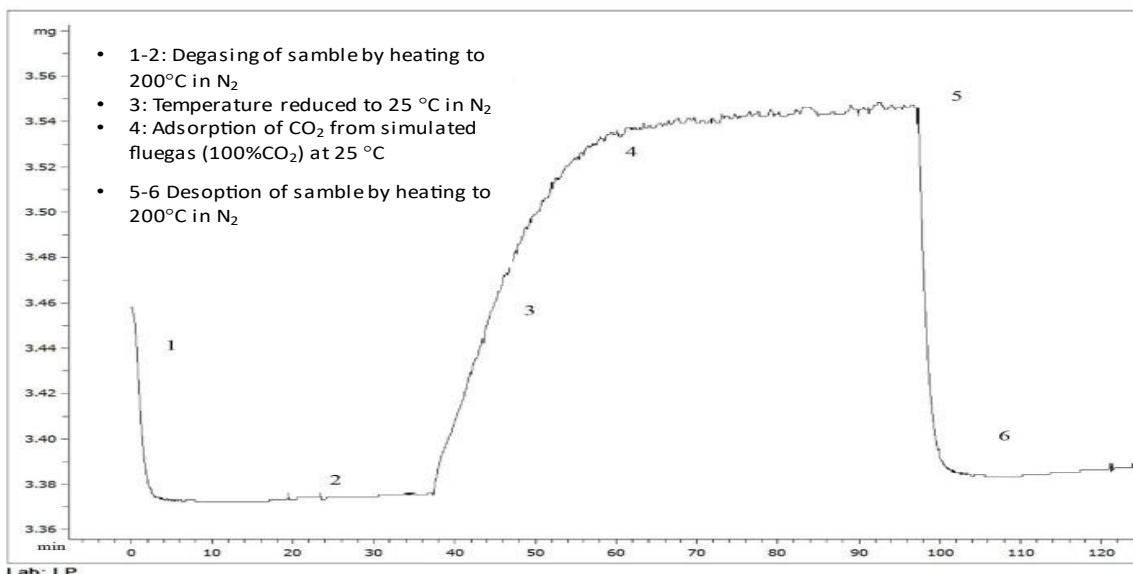


Figure 8 Graph showing the steps in how TGA measures CO₂ capacity regarding time and temperature.

SEM

The morphology of the samples was examined by scanning electron microscope (SEM) at an acceleration voltage (ETH) of 10 kV and a working distance (WD) of around 10mm. The samples were coated in a gold palladium alloy before they were inserted in the SEM.

EDS

To confirm that the flakes shown in future SEM images consisted of potassium, an Energy Dispersive X-ray Spectroscopy (EDS) connected to the SEM was used. An elemental analysis where then performed for characterization of elemental composition of char.

4 RESULTAT

4.1 Expected char and amount of KOH

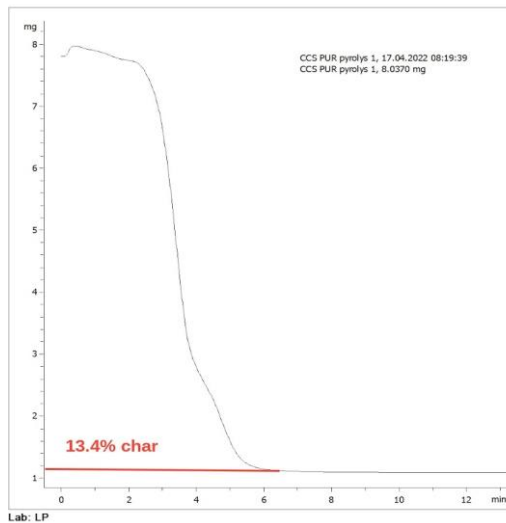


Figure 9 Graph showing optimum yield char during pyrolysis in TGA.

A certain percentage of pyrolyzed PUR developed into activated carbon or char. While the rest of the material degrades during pyrolysis reaction in an inert atmosphere. Figure 9 demonstrated a simulated pyrolysis of PUR to demonstrate the yield char that is needed for further calculations. The PUR breaks down completely at around 5 minutes at 650°C. 13.4% is the expected char yield. For the direct chemical activation method, KOH is mixed directly with PUR before pyrolysis, and for the indirect activation method, KOH is mixed with the char formed after pyrolysis. To calculate the volume KOH added to the carbon materials, to achieve the mass ratio, these formulas were used. See table 1 for values.

$$\begin{aligned}
 \text{mass expected char } (m_{char}) &= m_{PUR} * \frac{13.4}{100} \\
 \text{mass K } (m_K) &= m_{char} * \text{mass ratio} \\
 \text{mol K } (n_K) &= \frac{m_K}{M_K} \\
 \text{Vol of KOH } (V_{KOH}) &= \left(\frac{n_K}{C_{KOH}} \right) * 1000
 \end{aligned}$$

m_{char} is the mass of char, m_K is the mass of potassium, M_K is the molar mass of potassium, n_K is the moles of potassium, V_{KOH} is the volume of potassium hydroxide, and C_{KOH} is the concentration of potassium hydroxide.

Table 1 Showing the amount KOH needed per gram char.

	mass, sample, g	expected char mass, g	mass K ÷ mass Sample	mass K, g	mol K	Vol of KOH required, ml
						if KOH conc. 4 mol/l is used
13.40%	7.5	1,005	0.5	0,5025	0,0128522	3,213055299
	7.5	1,005	1	1,005	0,0257044	6,426110598
	7.5	1,005	1.5	1,5075	0,0385567	9,639165897
mwt KOH		56,1056 g/mol				
mwt K		39,0983 g/mol				

4.2 Results and tables

The results of CO₂ capture capacity at 25 °C are presented in table 2 and table 3 and following figures for some samples. The samples have produced by different chemical activation method, indirect and direct. The material for all samples was PUR but the concentration of potassium, heating and time for activation were varied.

Table 2 Results from TGA showing CO₂ adsorption for indirect chemical activation

Run #	Sample	Activation method	K (m)÷ Sample m)	Temperature, °C	time, min	N2 flow, ml/min	CO2 adsorption temp. °C	Sample 1 (mg/g)	Sample 2 (mg/g)	Average
0	PUR	Indirect	0	650	20	200	25	51,17	51,24	51,2
1	PUR	Indirect	0,5	650	10	200	25	81,44	68,33	74,89
2	PUR	Indirect	0,5	650	20	200	25	66,55	77,46	72,01
3	PUR	Indirect	0,5	650	30	200	25	112,83	107,54	110,19
4	PUR	Indirect	0,5	650	40	200	25	49,42	68,2	58,81
5	PUR	Indirect	0,5	650	60	200	25	44,64	86,31	65,48
6	PUR	Indirect	0,5	550	30	200	25	38,09	31,55	34,82
7	PUR	Indirect	0,5	600	30	200	25	20,69		
8	PUR	Indirect	0,5	700	30	200	25	71,23	50,62	60,93
9	PUR	Indirect	1	650	30	200	25	73,02	95,52	84,27
10	PUR	Indirect	1,5	650	30	200	25	152,10	131,42	141,76

Table 3 Results from TGA showing CO₂ adsorption for direct chemical activation. (Due to TGA malfunctioning, run 18 and onward was unable to be analysed a second time)

Run #	Sample	Activation method	K (m)÷ Sample m)	Temperature, °C	time, min	N2 flow, ml/min	CO2 adsorption temp. °C	Sample 1 (mg/g)	Sample 2 (mg/g)	Average
15	PUR	Direct	0,5	650	10	200	25			
16	PUR	Direct	0,5	650	20	200	25	93,86	92,42	93,14
17	PUR	Direct	0,5	650	30	200	25	95,06	100,36	97,71
18	PUR	Direct	0,5	650	40	200	25	115,48		115,48
19	PUR	Direct	0,5	650	50	200	25	53,32		53,32
20	PUR	Direct	0,5	650	60	200	25	90,36		
21	PUR	Direct	0,5	650	90	200	25	90,49		90,49
22	PUR	Direct	0,5	550	40	200	25	22,17		22,17
23	PUR	Direct	0,5	600	40	200	25	53,59		53,59
24	PUR	Direct	0,5	700	40	200	25	116,35		116,35
25	PUR	Direct	1	650	40	200	25	124,28		124,28
26	PUR	Direct	1,5	650	40	200	25	145,48		145,48
27	PUR	Direct	1,5	650	40	200	25	151,29		151,29

4.3 Curve comparisons

CO₂ capture by adsorbent over time are shown in following figures for various chemical activation method, indirect and direct for some samples from table 2 and 3.

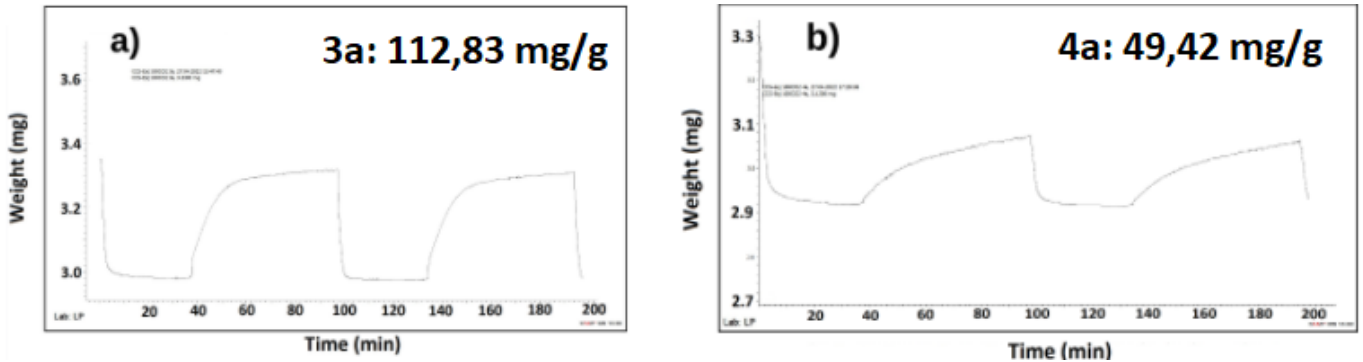


Figure 10 is showing the CO₂ capture by indirect activated adsorbent over time according to parameters used for producing where a) is sample 3 and b) is sample 4

CO₂ capture by adsorbent over time in figure 10 for sample 3 a) and sample 4 b). Comparison of the adsorption of CO₂ between a) and b) at 25 °C with various activation times with the same mass ratio of 0.5 and activation temperature of 650°C. The indirect chemically activated method has been used.

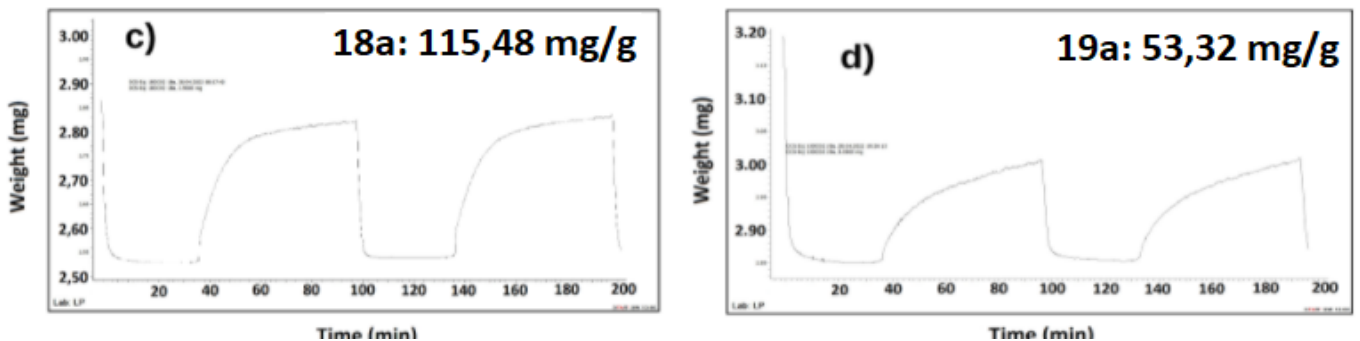


Figure 11 is showing the CO₂ capture by direct activated adsorbent over time according to parameters used for producing where c) is sample 18 and d) is sample 19

CO₂ capture by adsorbent over time in figure 11 for sample 18 c) and sample 19 d). Comparison of the adsorption of CO₂ between c) and d) at 25 °C with various activation times with the same mass ratio 0.5 and activation temperature 650°C. The direct chemically activated method has been used.

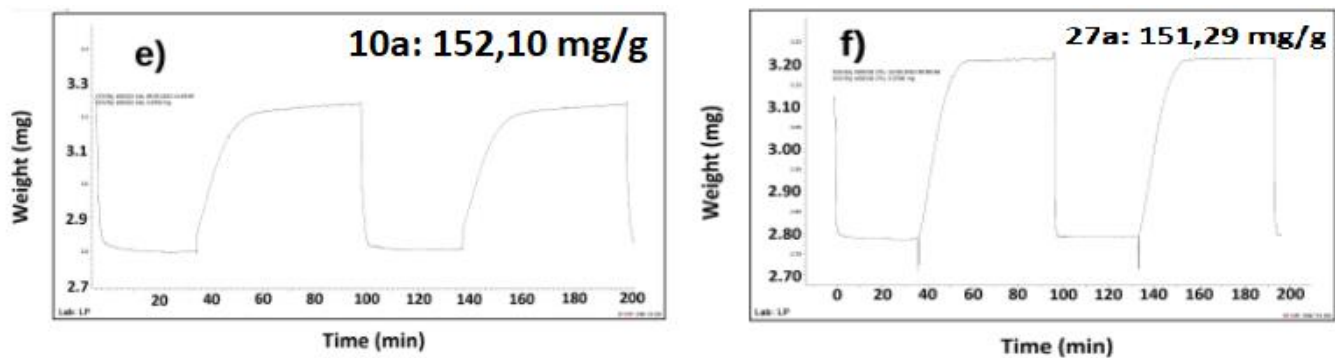


Figure 12 is showing the CO₂ capture by the most effective adsorbent over time according to parameters used for producing where e) is sample 10 and f) is sample 27

CO₂ capture by adsorbent over time in figure 12 for sample 10 e) and sample 27 f). Comparison of the adsorption of CO₂ between e) and f) at 25 °C with their respective optimal parameters. For e): activation time 30 min, mass ratio 1.5, and activation temperature 650°C. For f): activation time 40 min, mass ratio 1.5, and activation temperature 650°C

4.4 Analytics

SEM

SEM images of adsorbents at different time and mass ratios at indirect and direct chemically activated carbons. See table 2 and 3 for reference. Morphology and general surface inspection where the goal with these images since major structural and adsorbing differences were observed.

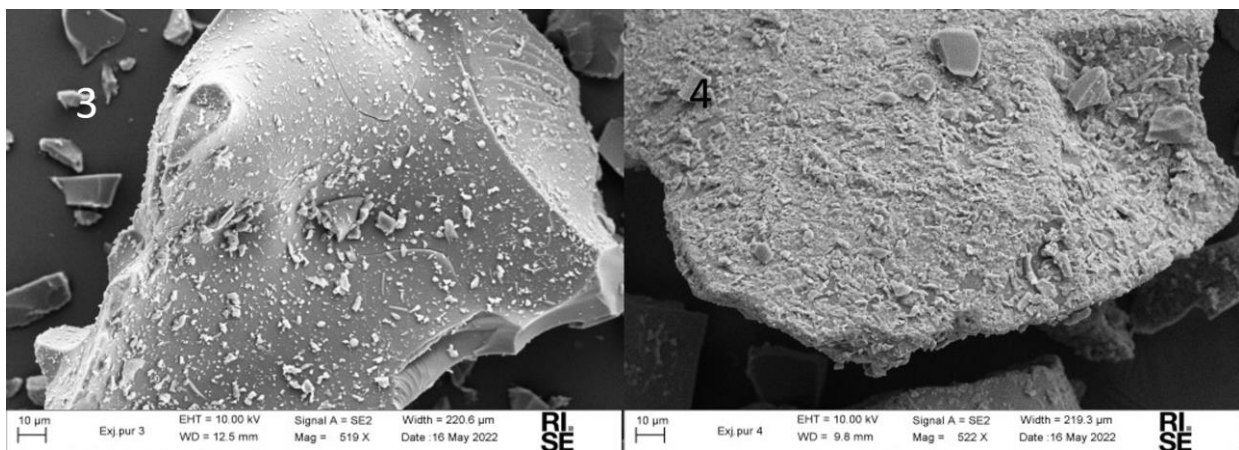


Figure 13 is showing SEM images of sample 3 and sample 4.

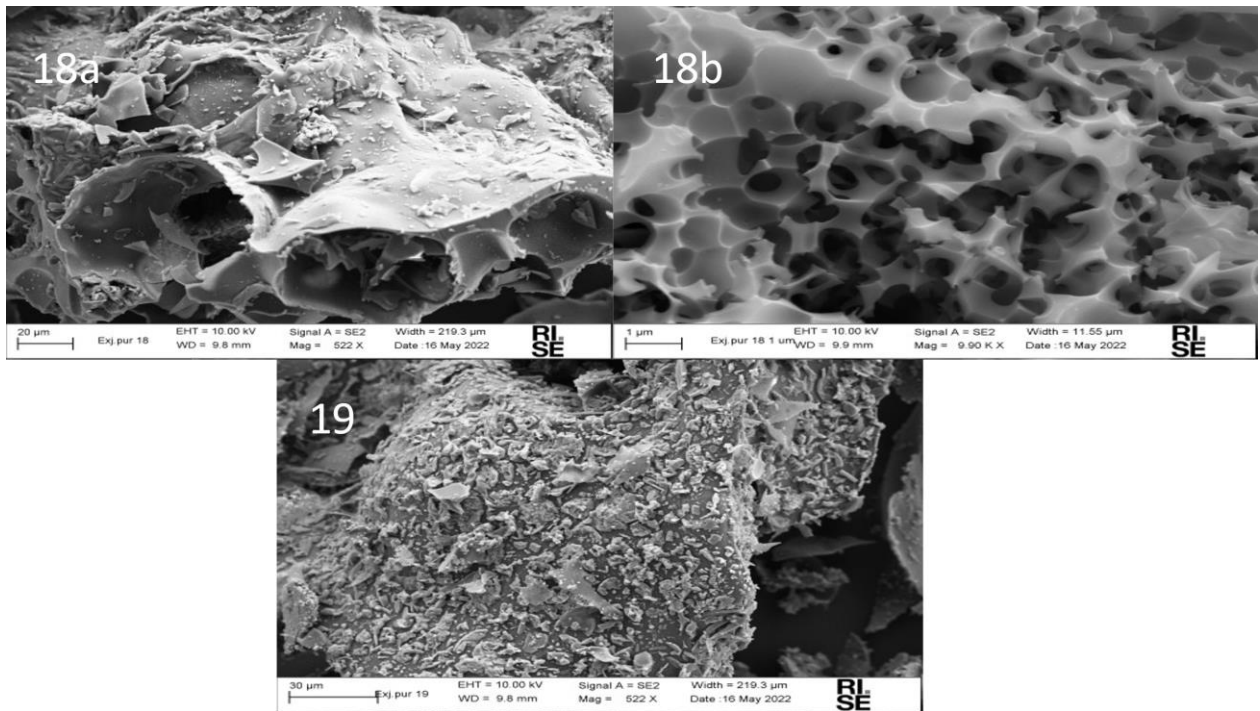


Figure 14 is showing SEM images of sample 18 and sample 19.

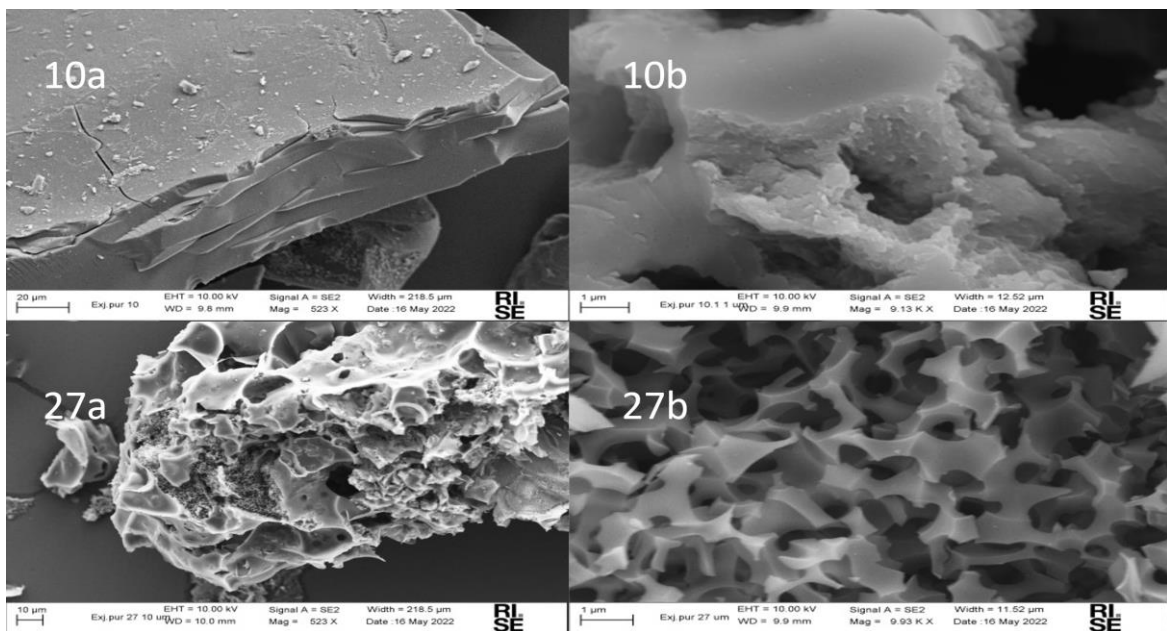


Figure 15 is showing SEM images for sample 10, sample 27.

EDS

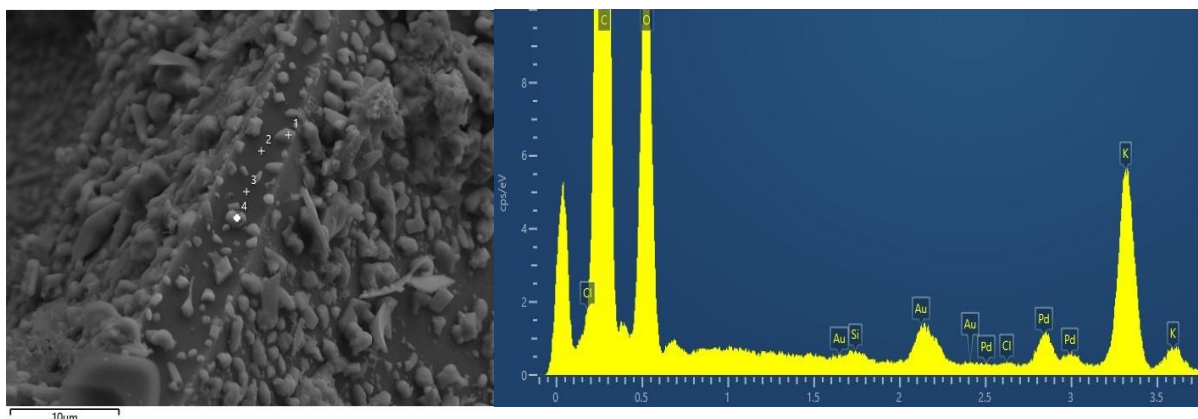


Figure 16 is showing images from SEM and EDS, proving the flakes consists of potassium.

5 DISCUSSION

5.1 Margin of error

Due to lack of time, singlets for every sample have been performed, making some inconsistent results. Doublets or triplets would have pre-empted some of the results obtained that we thought were unrealistic or confirmed some disparities that we weren't sure we could replicate.

5.2 Indirect vs Direct

When the direct and indirect activation are complete, a few differences in the char are apparent. The most distinct difference being structural, where the direct activated char is more porous and lighter. To break it down for analysis, simply crushing it in its beaker with a spoon were sufficient and it was generally easier to handle compared to the indirect activated char. This char was dense and compact, milling had to be done with a pestle and mortar for several minutes. Even then, it was difficult to get an even homogenous powder fit for analysis. This could be a reason for the inconsistent graphs given by TGA, since milling it after a poor graph sometimes improved it.

It is also noteworthy that during the washing step of the direct activated char, a thin shimmering layer formed at the top of the liquid. The layer had the appearance that of oil on water, and it is not clear what it consisted of. The indirect activated char did not have this layer, the reason behind this is not clear either. Another inconsistency in this is that sample 26, containing the most KOH of the direct samples, barley had this shimmer. It was also denser and harder to mill, thus, behaving more like the indirect samples. Sample 26 is one of the disparities that we would like to try to recreate due to it behaving differently than the other direct samples and being the one with the best adsorption capacity and should be analysed in future work.

5.3 Optimization

As previously mentioned, to decide the optimal parameters, the parameters were studied one at a time to demonstrate their influence more clearly. The activated carbon was activated at different times, temperatures, and mass ratio KOH/char. Time, temperature, and mass ratio affected the pore size and the distribution which affected the CO₂ capacities. These

parameters could affect the adsorption capacities in different ways as shown in (See table 2 and 3).

5.4 Time

According to (Deng et al., 2014), activation time had a lesser impact on the adsorption capacity than the other parameters. The results from (See table 2 and 3) show that the time does have a greater impact on the capacity. However, there is a clear difference of how time affects the capacities of direct and indirect chemically activated adsorbents. In the case of direct, the CO₂ capacity progressed as the time also increased, until it reached the 50 minute mark where it decreased from 115,48 to 53,34 mg/g. The capacity increased further until it levelled out at 90,49 mg/g. Yet, it is not as apparent in the indirect activation. It is assumed that an error at 20 minutes for indirect and 50 minutes for direct, has occurred. The times that were evaluated in the indirect and direct activation are different considering that there was an opportunity where the capacity could increase after the highest CO₂ adsorption. A clear connection between the time and the amount CO₂ adsorbed could not be established in both cases from the results that were presented and were not enough and completed.

5.5 Temperature

Activation temperature was also influential for the CO₂ adsorption of activated carbon at 25°C. When increasing activation temperatures, the CO₂ capacity increased accordingly. It is mentioned in (Deng et al., 2014), that at a certain higher temperature, the capacity would decrease, the results that are presented do not exhibit this sort of development. The temperature at 550°C was analysed mostly for economic feasibility. If the other temperatures were slightly better, then 550°C would still be the optimal temperature. The capacity levelled out at sample 18 and 24. In this case, it is assumed that these samples have reached the peak and will not notably increase. Theoretically, if the activation occurred at a higher temperature than 700°C, the capacity might have decreased.

5.6 KOH

KOH/char mass ratio was as influential for the CO₂ adsorption as activation temperature. These parameters appear to show the same characteristics when it comes to how they affect the capacity. Similarly, the samples prepared at the highest mass ratio (1,5) show the highest capacity while the lower mass ratio (0,5) was inferior. Sample 0 was run to observe if the KOH had any effect on the char, the samples with KOH exhibited an improved capacity. (Ochedi, Liu and Adewuyi, 2020) mentioned that the surface area and micropore volume increased 3-fold when activated with KOH. The indirect and direct chemical activation show the same correlation towards the increase of KOH/char mass ratio. According to (Deng et al., 2014), it is stated that a mass ratio of 2 was optimal, the possibility to further increase the amount KOH could increase the capacity. Equivalently to temperature, at a certain point the capacity will not continue to increase with increasing mass ratio, it will eventually also decrease. As mentioned earlier, according to (A. R. Hemmati, A. Ghaemi., 2020), a higher concentration of KOH could lead to the formation of salts which can affect the capacity negatively.

5.7 SEM analysis

The SEM images of indirect and direct chemically activated char at different activation time, temperature, and mass ratio KOH/char were taken. Porosity can significantly affect the adsorption capacity, so SEM images were taken so the samples could be inspected

meticulously. The KOH intercalated and etched into the carbon material to form large numbers of macropores on the surface.

Sample 3 and 4 are both indirectly activated from time optimization, however, there was a fundamental difference between the adsorption capacity between these samples. In figure 13, the structure of the adsorbents is somewhat different, sample 3 has a smoother surface and some flakes, whereas sample 4 has a bristly surface which is completely covered with flakes. These flakes could be the reason for the poor adsorption capacity since they might cover the pores. A High Resolution Transmission Electron Microscopy (HRTEM) might be needed for these indirectly activated samples considering the possibility of there being micropores, which are not visible with a SEM.

Sample 18 and 19 are also from the batch of time optimization, but directly chemically activated. These samples show different surface properties in comparison to the indirectly activated adsorbents, they are more porous and not as smooth as the latter. In figure 14, sample 18 contained deep mesopores and sample 19 had a flaky surface. Which could clarify the poor CO₂ adsorption.

The differences in the surface properties between indirect and direct chemically activated char becomes more apparent at Sample 10 and 27. These samples were leading in terms of CO₂ adsorption. In figure 15, sample 10 showed a smoother surface with obscured pores, whereas sample 27 was covered with pores in different sizes. The adsorption capacity is, however, noticeably similar. The indirectly activated sample may have micropores which are not visible with a SEM.

The flakes that are present, mostly in the indirect samples, affect the adsorption quality to some certain degree. To determine what these flakes consisted of an EDS was used. As shown in figure 16, the surface and flakes consist of Carbon, Oxygen, and Potassium. The presence of potassium could indicate that KOH is still present on the char, it should not be. This could indicate that the char was not washed out thoroughly with HCl.

5.8 Future directions

To continue research on indirect activation a few problems would have to be solved addressing the inconsistent results it yielded. Whether that would be more thorough milling or washing are to be evaluated in the future. Washing sample 4 and 19 to see if they yield comparable results, it would also be interesting to conduct an elemental analysis on the shimmier during the washing step. For a more thorough evaluation of the dispersion and size of the produced pores, HRTEM should be utilized, especially on the indirect activated samples.

6 CONCLUSIONS

It is safe to say that there are major differences in morphology concerning indirect and direct chemical activation. Direct activation, especially with higher proportions of KOH, are showing more distinct pores which explains why it is more porous and lighter. It was also shown that there are no distinct differences in CO₂ adsorption capacity between indirect and direct chemical activation during optimum conditions, being 650°C with a mass ratio of 1,5 KOH. Regarding time, 40 min was chosen for direct and 30 for indirect activation. Time altered by a little but had sample 4 not been coated in potassium it might had been comparable to sample 3. The indirect activated carbons seemed to have more problems with the potassium coating than the direct activated ones, the reason for this are still unclear.

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