

Carbon Dioxide Adsorption on Carbonized  
Cigarette Filters

---

A Thesis presented to the Faculty of the Graduate School  
at the University of Missouri-Columbia

---

In Partial Fulfillment  
of the Requirements for the Degree  
Master of Science

---

by

CHUN LI

Dr. Sheila Baker, Thesis Supervisor

MAY 2018

The undersigned, appointed by the Dean of the Graduate School, have examined the thesis entitled:

Carbon Dioxide Adsorption on Carbonized Cigarette Filters

Presented by Chun Li,

A candidate for the degree of Master of Science,

And hereby certify that, in their opinion, it is worthy of acceptance.

---

Dr. Sheila Baker

---

Dr. Bret Ulery

---

Dr. Hao Li

## ACKNOWLEDGEMENTS

First of all, I would like to express sincere gratitude to my academic advisor Dr. Sheila Baker for the continuous support of my graduate studies and research, for her precious advice and patient instructions. Her guidance helped me in all the time of research and writing of this thesis.

My sincere thanks also go to Dr. Bret Ulery in the Department of Chemical Engineering and Dr. Hao Li from Mechanical & Aerospace Engineering department for their kind willingness to be my committee members, their guidance and enthusiasm are greatly appreciated.

Besides, I would like to thank Nathan Bays for his kind help in the lab. I would like to thank all of the members in Dr. Baker's group, for their encouragement and companion.

Last but not least, I would like to thank my beloved parents, for always giving my support.

# TABLE OF CONTENTS

ACKNOWLEDGEMENTS.....	ii
TABLE OF CONTENTS.....	iii
TABLE OF FIGURES.....	vi
LIST OF ABBREVIATIONS.....	vii
ABSTRACT.....	viii
CHAPTER 1 .....	1
INTRODUCTION .....	1
1.1 Climate Change .....	1
1.2 Methods for CO <sub>2</sub> Capture.....	2
1.2.1 Introduction .....	2
1.2.2 Overview .....	2
1.2.3 Porous Solid Adsorbents .....	3
1.2.4 Modification of Porous Carbon Materials .....	5
1.3 Cigarette Filters .....	7
1.3.1 Overview .....	7

1.3.2 Utilization of the Cigarette Filters .....	8
CHAPTER 2 .....	9
EXPERIMENTAL SECTION .....	9
2.1 Materials.....	9
2.2 Preparation of Porous Carbon .....	9
2.3 Materials Characterization .....	10
CHAPTER 3 .....	12
RESULTS AND DISCUSSIONS .....	12
3.1 BET Characterization.....	12
3.2 CO <sub>2</sub> Adsorption-Desorption Tests .....	13
3.2.1 CO <sub>2</sub> Capture and Desorption Process .....	13
3.2.2 CO <sub>2</sub> Loading .....	15
3.2.3 Regeneration.....	17
3.2.4 CO <sub>2</sub> Capacity .....	20
CHAPTER 4 .....	24
CONCLUSIONS AND FUTURE WORK .....	24

4.1 Conclusions .....	24
4.2 Future Work .....	24

## TABLE OF FIGURES

<b>Figure 1</b> Illustration of CO <sub>2</sub> capture and desorption process with porous carbon. ....	13
<b>Figure 2</b> CO <sub>2</sub> adsorption over time profile for samples carbonized at 700 °C and tested at 45 °C. ....	15
<b>Figure 3</b> CO <sub>2</sub> adsorption over time profile for samples carbonized at 550 °C and tested at 45 °C. ....	16
<b>Figure 4</b> CO <sub>2</sub> adsorption over time profile for samples tested at 65 °C.....	16
<b>Figure 5</b> Desorption over time profile for samples carbonized at 700 °C and tested at 45 °C. ....	18
<b>Figure 6</b> Desorption over time profile for samples carbonized at 550 °C and tested at 45 °C. ....	19
<b>Figure 7</b> Desorption over time profile for samples tested at 65 °C.....	19
<b>Figure 8</b> CO <sub>2</sub> sorption capacities of each sorbent studied in series tests under 45 °C. ....	22
<b>Figure 9</b> CO <sub>2</sub> sorption capacities of each sorbent studied in series tests under 65 °C. ....	23

## LIST OF ABBREVIATIONS

CO <sub>2</sub>	Carbon Dioxide
N <sub>2</sub>	Nitrogen
MOFs	Metal-Organic Frameworks
BET	Brunauer-Emmett-Teller
TGA	Thermogravimetric Analyzer
M	mol/L

## ABSTRACT

Nowadays, the world is facing tremendous challenges due to increase in greenhouse gas emissions (mainly carbon dioxide), which causes a major global warming problem.

CO<sub>2</sub> release into the atmosphere is mainly due to burning of fossil fuels such as coal, petroleum and natural gas. Various methods are developed to reduce CO<sub>2</sub> emissions. Of all the ways, porous carbon is attractive because of its low energy consumption and higher adsorption capacity. Discarded cigarette filters, in the form of cigarette butts, are currently a major waste disposal and environmental pollution hazard because cellulose acetate is not biodegradable. Given that they are mainly composed of cellulose acetate, which contain a high degree of carbon atoms and can potentially be the precursor for porous carbon. The incorporation of nitrogen-containing groups into carbon has been proposed as an effective way to enhance the interaction between CO<sub>2</sub> molecules and surfaces of sorbents, which may further improve CO<sub>2</sub> adsorption capacity and CO<sub>2</sub>/N<sub>2</sub> selectivity.

In this work, to understand the relationship between nitrogen content in porous carbon/ carbonization temperature for samples and their CO<sub>2</sub> capacities, a series of nitrogen

doped porous carbons were synthesized, from cigarette filters as carbon precursor and urea as nitrogen source, by varying the urea concentration and carbonization temperature investigating their CO<sub>2</sub> adsorption capacities. Through TGA test, the sorbent 12M700C was found to have the largest CO<sub>2</sub> capacity.

# CHAPTER 1

## INTRODUCTION

### 1.1 Climate Change

Climate change is a change in the statistical distribution of weather patterns when that change lasts for extended period of time.<sup>[1]</sup> The current warming trend is of particular significance because most of it is extremely likely to be the result of human activity and proceeding at a rate that is unprecedented over decades to millennia.<sup>[2]</sup>

Most climate scientists agree that the main cause of the current global warming trend is human expansion of the “greenhouse effect”.<sup>[2]</sup> Gases that contribute to the greenhouse effect include: water vapor, carbon dioxide, methane, nitrous oxide and chlorofluorocarbons.

Human activities since the beginning of the Industrial Revolution (around 1750) have produced a 40% increase in the atmosphere concentration of carbon dioxide (CO<sub>2</sub>), from 280 ppm in 1750 to 407 ppm at the beginning of 2018.<sup>[3]</sup> The vast majority of anthropogenic carbon dioxide emissions come from combustion of fossil fuels, particularly coal, oil and natural gas, with comparatively modest additional

contributions coming from deforestation, changes in land use, soil erosion and agriculture.<sup>[4]</sup> The increase in greenhouse gas (mainly carbon dioxide) causes a major warming problem. It is expected that its concentration will get doubled by 2050 if no actions are taken.<sup>[5]</sup>

## 1.2 Methods for CO<sub>2</sub> Capture

### 1.2.1 Introduction

There are growing concerns for climate change and global warming in recent years, which is mainly attributed to the emissions of CO<sub>2</sub>.<sup>[6]</sup> The lag in the development of clean and renewable sources of energy, such as wind, solar, and hydrogen, has enable fossil fuels to still remain as the main source of energy.<sup>[7]</sup> Hence, there is a need to develop technologies that allow the fossil fuel usage while reducing anthropogenic CO<sub>2</sub> emissions. Carbon dioxide capture appears to be a promising strategy to mitigate increasing CO<sub>2</sub> levels. In addition, it will buy time for cost reduction of renewable energy sources while facilitating cleaner use of fossil fuels.<sup>[8~9]</sup>

### 1.2.2 Overview

Nowadays, various approaches have been exploited for capturing CO<sub>2</sub>, including

chemisorption, physisorption and membrane sorption.<sup>[10~12]</sup> Among these approaches, the chemisorption by using alkali solution has been widely adopted for capturing CO<sub>2</sub> in industry.<sup>[13]</sup> However, the saturated chemical absorbents require enormous energy during the regeneration process and have certain intrinsic corrosiveness.<sup>[14]</sup> Membrane separation has the advantages of low energy consumption and low cost during CO<sub>2</sub> capture process, while it is inadequate for high feed flow rates, easy to get clogged up with dust, lack of economic benefit and inferior CO<sub>2</sub>/N<sub>2</sub> selectivity.<sup>[15~16]</sup> Physisorption via porous solids is identified as an efficient technology for CO<sub>2</sub> capture due to the merit of easy maintenance, low energy consumption, and excellent renewability.<sup>[17~18]</sup>

### 1.2.3 Porous Solid Adsorbents

Porous materials such as zeolites, metal-organic frameworks (MOFs), amine supported silica and carbons have been evaluated as potential candidates for CO<sub>2</sub> separation from flue gas.<sup>[19]</sup>

#### 1.2.3.1 Zeolites

Zeolites with low Si/Al ratios are probably the most promising materials for CO<sub>2</sub> capture from flue gas. They have highly favorable CO<sub>2</sub> adsorption isotherms,

corresponding to high CO<sub>2</sub> uptake (~2.5 mmol g<sup>-1</sup> at 25 °C and 0.1 bar) as well as high CO<sub>2</sub> selectivity at low pressures. This property is attributed to the presence of a large number of extra-framework alkali cations that promote CO<sub>2</sub> adsorption via strong dipole-quadrupole (electrostatic) interactions. The main drawback of zeolites is their low tolerance to moisture. They exhibit drastically decreased CO<sub>2</sub> adsorption capacities if the gas stream is not extensively dried.

#### 1.2.3.2 MOFs

MOFs have large specific surface areas and pore volumes, which give rise to remarkable CO<sub>2</sub> uptakes at high pressures (>10 bar). However, the majority of MOFs with only a few exceptions exhibit unfavorable adsorption isotherms for CO<sub>2</sub>, leading to low CO<sub>2</sub> selectivity and uptake in the low pressure range (<1.0 mmol g<sup>-1</sup> at 25 °C and 0.1 bar). Hence, most MOFs seem to be more suitable for CO<sub>2</sub> storage than for separation. The weak stability of most MOFs is another critical issue that limits their use in practical applications. New MOF materials with open metal sites or polar functional groups have been synthesized to enhance their affinity to CO<sub>2</sub> and thus the adsorption performance at low pressures and MOFs with exceptional stabilities were

also reported recently.

#### 1.2.3.3 Amine Supported Silica

Amine supported silica showed both specific selectivity toward CO<sub>2</sub> over other gases and high CO<sub>2</sub> uptake at low pressure (~1.9 mmol g<sup>-1</sup> at 25 °C and 0.1 bar). However, the strong chemical adsorption effect, as evidenced by the high CO<sub>2</sub> adsorption heat (>90 KJ mol<sup>-1</sup>), results in difficult regeneration of the sorbent and limits its use for pressure swing adsorption (PSA).<sup>[20]</sup>

#### 1.2.3.4 Carbons

Among various types of solid adsorbents have been developed for CO<sub>2</sub> capture, porous carbons is regarded as one kind promising adsorbents for CO<sub>2</sub> capture due to their extraordinary advantages such as high surface area, tunable porosity, superior thermal and chemical stability, easy regeneration and low cost.<sup>[21]</sup> Furthermore, porous carbons can be derived from several biomass and waste, which meets the need of sustainability.<sup>[22]</sup>

#### 1.2.4 Modification of Porous Carbon Materials

Incorporating alkaline nitrogen-functional groups (N-doping) into the carbon structure

can increase the adsorbent interaction with CO<sub>2</sub>. It is generally assumed that the incorporation of basic nitrogen groups into the carbon framework ensures an improved adsorption/absorption for acidic gases.<sup>[23]</sup> However, the one-to-one basic-acid interaction cannot explain the fact that in some cases a small amount of doped nitrogen leads to greatly increased CO<sub>2</sub> adsorption capacity.<sup>[20]</sup> Xing's group found that the excellent CO<sub>2</sub> capture capacity of the nitrogen-doped carbons is attributed to hydrogen-bonding interactions between hydrogen atoms (from CH and NH) on the carbon surface and CO<sub>2</sub> molecules, which is strongly facilitated by the presence of N atoms in the carbon.<sup>[24]</sup> From the study of Lee's group, they carbonized used cigarette filters under an atmosphere of NH<sub>3</sub> to dope nitrogen on carbon structure in one-step process and got improved supercapacitive performance.<sup>[25]</sup>

In this study, we inclined to use another nitrogen source and cigarette filters were firstly modified by urea to dope the nitrogen into the carbon framework. Urea can be considered as a waste product and has high nitrogen content. For use in industry, urea is produced from ammonia and carbon dioxide. Sources of ammonia are by-products from coke ovens and nitrogen fixation plants using either the cyanamide or Haber

process. Carbon dioxide is a waste product of many industries.<sup>[26]</sup>

### 1.3 Cigarette Filters

#### 1.3.1 Overview

There are 5.6 trillions of cigarette filter butts which have been produced by tobacco industries worldwide, and it is now the biggest challenge for global environmental protection every year. Cigarette filter butts are made of nearly 95% non-biodegradable cellulose acetate (plastic) which looks like cotton. Cigarette filter is disposal, toxic, and hazardous material waste thrown to the environment after usage despite its extremely slow degradation process. It has a microscopic-sized fibrous matter characterized with Y shape made of cellulose acetate. A plasticizer, glycerol triacetate, is applied to bond the fibers. Cellulose acetate is a type of polymer made of paper and similar to cotton of fiber composites in thousands of fibers.<sup>[27]</sup>

Recycling of this kind of waste material, a pending issue particularly in developed countries, can eliminate a substantial portion of purchase and disposal costs for new materials or applications. Focusing on efforts to obtain more environmentally respectful new products should be the starting point for environmental sustainability.<sup>[28]</sup>

### 1.3.2 Utilization of the Cigarette Filters

The cellulose-containing waste has been reported as a precursor for porous carbons and could be directly utilized to produce microporous or mesoporous carbon via simple carbonization at high temperature. This is of particular interest, because cellulose acetate is the principle component of the cigarette filters.<sup>[29]</sup>

Normally, the properties of porous carbons vary with the treatment temperature, soaking time, activating agents and depend on the type of precursors. To have a good understanding of the relationship between nitrogen content in porous carbon and their CO<sub>2</sub> capacities, a series of nitrogen doped porous carbons were synthesized, from cigarette filters as carbon precursor and urea as nitrogen source, by varying the urea concentration and carbonization temperature investigating their CO<sub>2</sub> adsorption capacities.

## CHAPTER 2

### EXPERIMENTAL SECTION

#### 2.1 Materials

The Cigarette filters are from Marlboro (Philip Morris Int.), and the urea was purchased from SIGMA-ALDRICH, Co.. Carbon dioxide and nitrogen gases were obtained from Air Gas.

#### 2.2 Preparation of Porous Carbon

The coatings of unused cigarette filters were removed and the filters were soaked in urea solution of different concentrations (0M, 0.5M, 6M, 10M, 12M) for one day. Then the soaked filters were oven-dried during the night at 90 °C. After that, the filters were transferred to a tube furnace and heated up to 550 °C/700 °C with a heating rate of 10°C/min for 2 hour under continuous nitrogen (N<sub>2</sub>) flow. The as-prepared samples were labeled as XMYC, where X is the concentration of the urea solution and Y stands for the carbonization temperature. For example, the above described sample can be designated 12M700C.

### 2.3 Materials Characterization

N<sub>2</sub> adsorption-desorption isotherms were measured with a Micromeritics ASAP 2020 instrument. The Brunauer-Emmett-Teller (BET) method was utilized to calculate the specific surface area. All the samples were degassed at 110 °C under vacuum for at least 4 hours until the pressure was lower than 5 µmHg and continued for 1 hour prior to analysis. The adsorption isotherm of N<sub>2</sub> for BET specific surface area measurements were performed at -196 °C. The micropore volume analysis was obtained using “t-plot” statistical thickness method.

CO<sub>2</sub> capture/regeneration experiments were conducted using a thermogravimetric analyzer (TA Instrument Q50). For a typical procedure, a suitable amount of sorbent (5-15 mg) was placed on a platinum sample pan and transferred to the TGA instrument. At the initial stage of the test, the sorbent was heated to 100 °C under a dry nitrogen flow of 65 mL/min for 5 min in order to eliminate any moisture and extraneous adsorbed gases. The temperature was then reduced to the desired temperature (45 °C/65 °C) under nitrogen flow for 5 min. After thermal equilibrium was established, the gas was switched to CO<sub>2</sub> at the same flow rate 65 mL/min. A rapid increase in

sample mass was observed and recorded in a 15 min period which proved sufficient for each sample to reach CO<sub>2</sub> adsorption-desorption equilibrium. The regeneration of sorbent (CO<sub>2</sub> release) was implemented by reverting the flowing gas back to N<sub>2</sub> (65 mL/min) and the mass decline was recorded over time while maintaining the temperature at 45 °C/65 °C.

## CHAPTER 3

### RESULTS AND DISCUSSIONS

#### 3.1 BET Characterization

**Table 1** BET surface area and micropore volume for each sample.

Sample	BET Surface Area (m <sup>2</sup> /g)	Micropore Volume (mm <sup>3</sup> /g)
12M550C	258.11 ± 3.7	60.0
12M700C	329.15 ± 3.5	92.1
10M550C	518.86 ± 4.8	113.2
10M700C	432.58 ± 4.9	115.3
6M550C	416.48 ± 3.7	90.5
6M700C	343.41 ± 3.8	97.5
0.5M700C	527.41 ± 5.6	151.6

(BET analysis on data between P/P<sub>0</sub>=0.05-0.25)

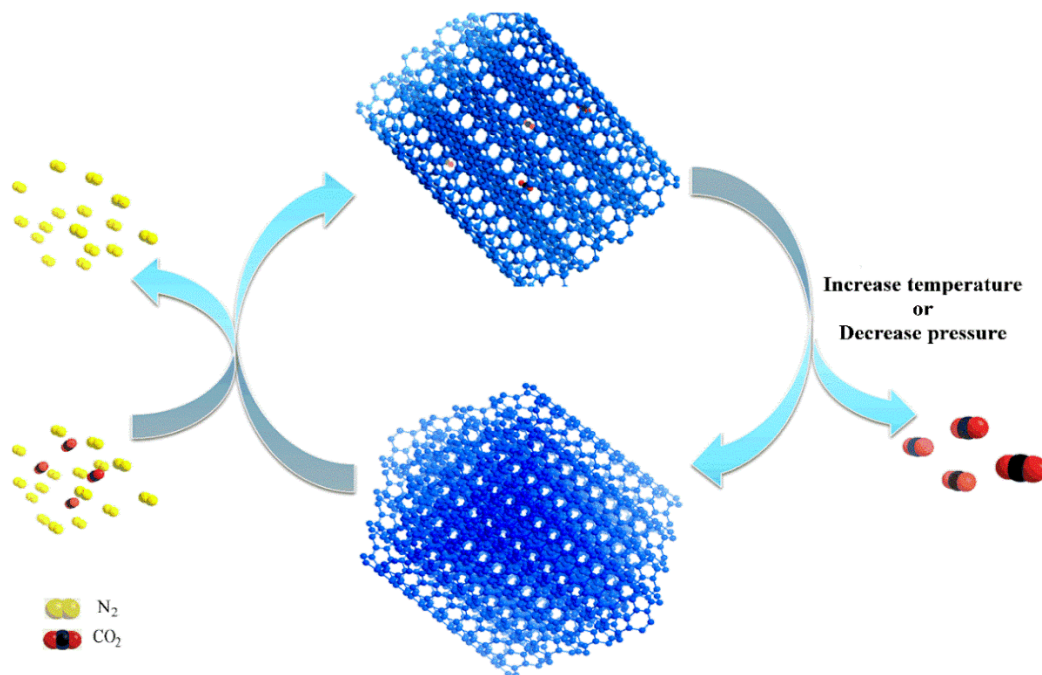
To investigate the relation between pore structure and adsorption capability, the adsorption-desorption isotherms were analyzed. According to the IUPAC classification, all isotherms were of Type IV or V, which could be classified as microporous materials hybrid with mesopores.

## 3.2 CO<sub>2</sub> Adsorption-Desorption Tests

### 3.2.1 CO<sub>2</sub> Capture and Desorption Process

The CO<sub>2</sub> capture and desorption process with porous carbon as sorbents was illustrated in Figure 1. CO<sub>2</sub> molecules in the N<sub>2</sub>/CO<sub>2</sub> gas mixture (used to simulate flue gas) were captured by the nitrogen doped porous carbon sorbents and pure N<sub>2</sub> was discharged.

After the CO<sub>2</sub> capture process, sorbents were regenerated by increasing temperature or decrease pressure so that CO<sub>2</sub> was released and sent to storage for other use. For sorbents with good regeneration ability and long life-cycle, this process could be repeated many times, thus reducing the cost related with materials for CO<sub>2</sub> capture.



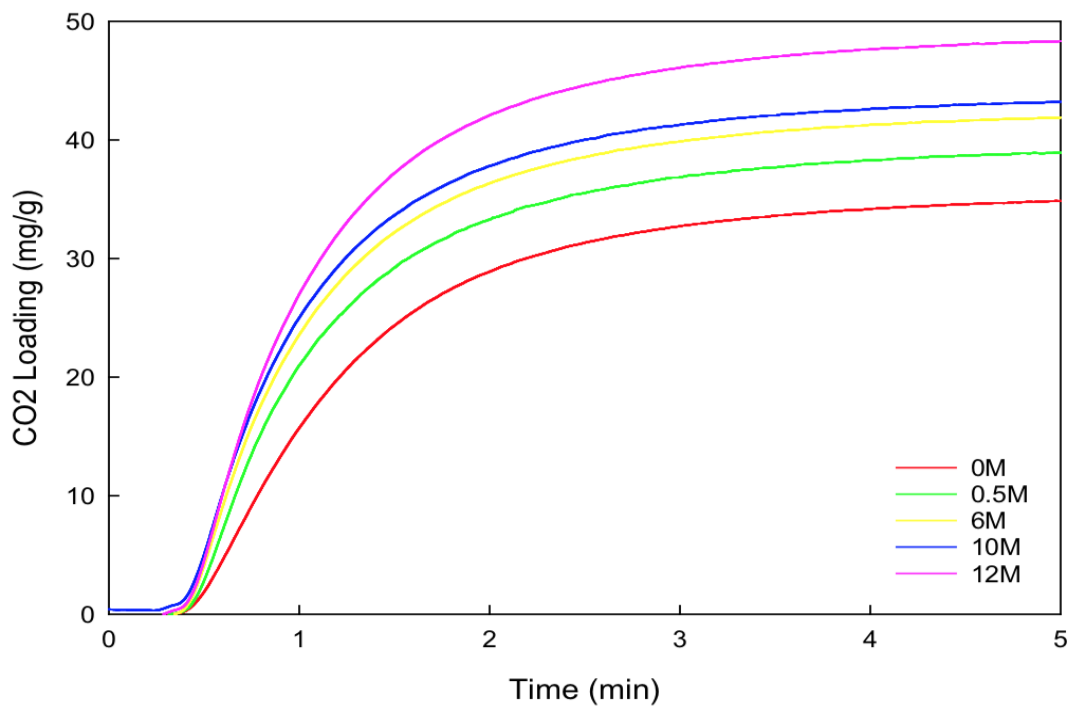
**Figure 1** Illustration of CO<sub>2</sub> capture and desorption process with porous carbon.

The CO<sub>2</sub> adsorption behaviour by our sorbents is expected to involve 3 steps. First of all, as CO<sub>2</sub> flows through the chamber, its molecules diffuse from the bulk stream to the outer surface of our samples holding by a platinum pan. When the flow rate of CO<sub>2</sub> stream is high enough, it could be assumed that its concentration near the sorbent surface ( $C_{surface}$ ) is exactly identical to the concentration in the bulk stream ( $C_{bulk}$ ). Hence, this step is not the rate limiting step of the overall process. The molecular diffusion of CO<sub>2</sub> from the outer surface of sorbents to the inner parts of them through the porous channels is usually relatively slow step and depends on the viscosity and concentration. Finally, CO<sub>2</sub> molecules will either be captured by micropores or form carbamate with the nitrogen-containing groups in the porous structures. Desorption is the reverse process of adsorption where interaction between CO<sub>2</sub> molecules and micropores or nitrogen-containing groups are first weakened as a results of increase in temperature or decrease in pressure, etc. Hence, CO<sub>2</sub> molecules are released and diffuse from the inner structure of sorbents back to the outer surface and further back to the bulk gas. In most cases, the rate of desorption is limited by the step weakening chemical bonds or physical interaction between CO<sub>2</sub> molecules and micropores or nitrogen-

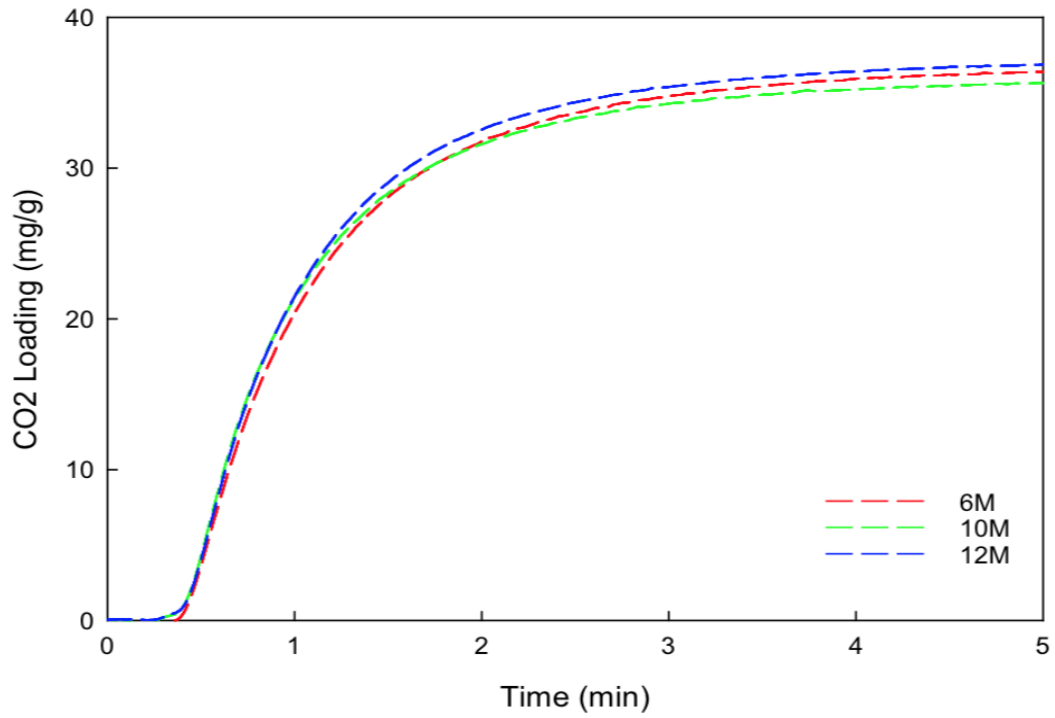
containing groups and the mass diffusion in the porous structure.

### 3.2.2 CO<sub>2</sub> Loading

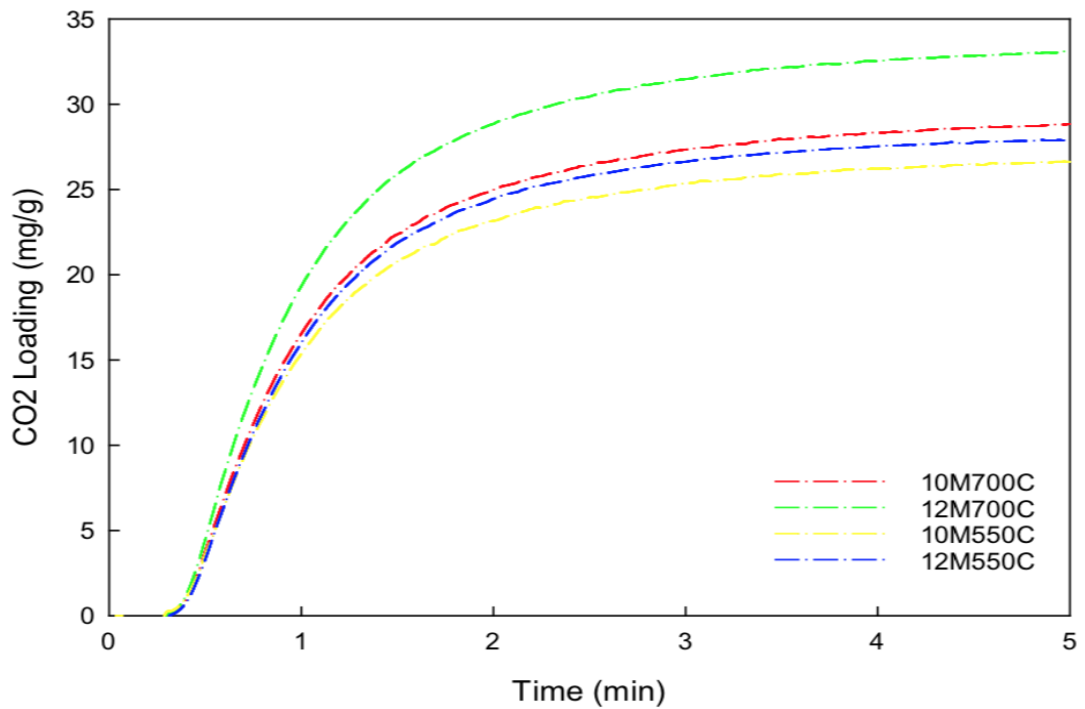
Figure 2 and 3 illustrated the time dependent CO<sub>2</sub> adsorption behavior of samples under 45 °C with carbonized temperatures of 700 °C and 550 °C. Figure 4 shows the behavior of samples under 65 °C. 5 minutes was used as the upper limit of the time profile since the adsorption-desorption equilibrium was almost well-established for each sample.



**Figure 2** CO<sub>2</sub> adsorption over time profile for samples carbonized at 700 °C and tested at 45 °C.



**Figure 3** CO<sub>2</sub> adsorption over time profile for samples carbonized at 550 °C and tested at 45 °C.



**Figure 4** CO<sub>2</sub> adsorption over time profile for samples tested at 65 °C.

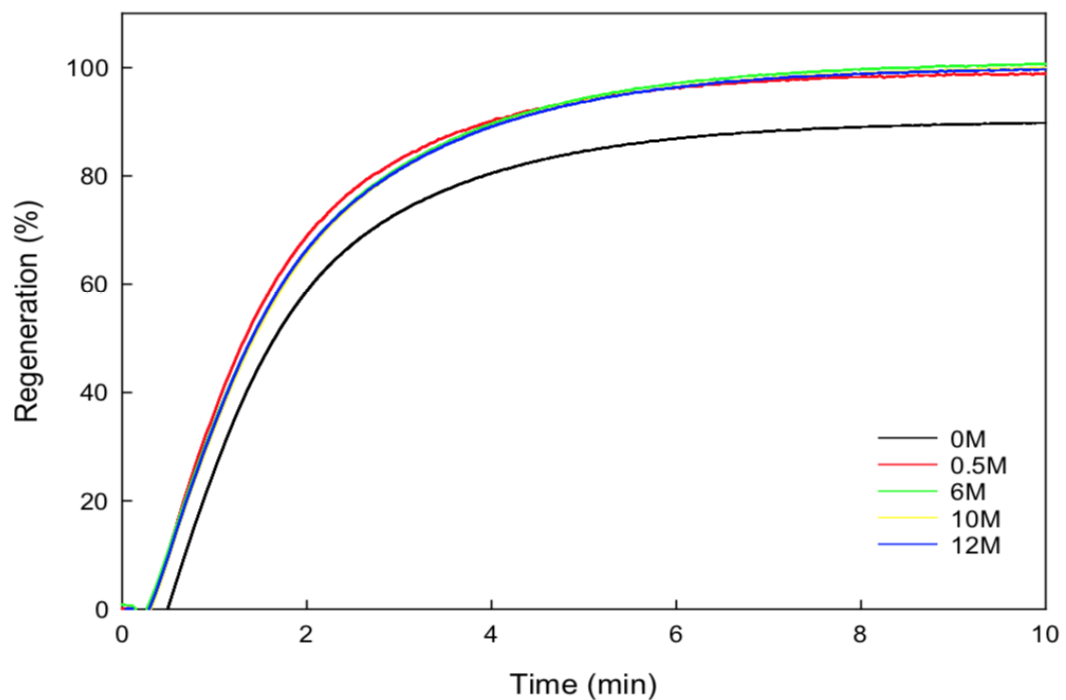
From Figure 2, 3 and 4, it was clear that the 12M700C urea doped porous carbon had the best performance under 45 °C and 65 °C in terms of CO<sub>2</sub> capacity and kinetics.

From Figure 2, it can be seen that the capacity of non-doped carbon 0M was lower than 0.5M, 6M, 10M and 12M. Hence, it was effective to increase the capacity of porous carbon sorbent by soaking the carbon precursor (cigarette filters in our experiments) in solutions containing nitrogen sources (urea solution in our experiments). Moreover, the higher was the concentration of urea concentration (under 12M for urea solution in our experiments), the better sorbents performed. Compared with Figure 3, the samples carbonized under 700 °C adsorbed more CO<sub>2</sub> in 5 minutes than the ones burned under 550 °C, which could be explained as the higher temperature was able to give samples higher degree of carbonization on the basis of that the higher carbonization temperature resulted in larger micropore volume seen from the BET characterizaiton section.

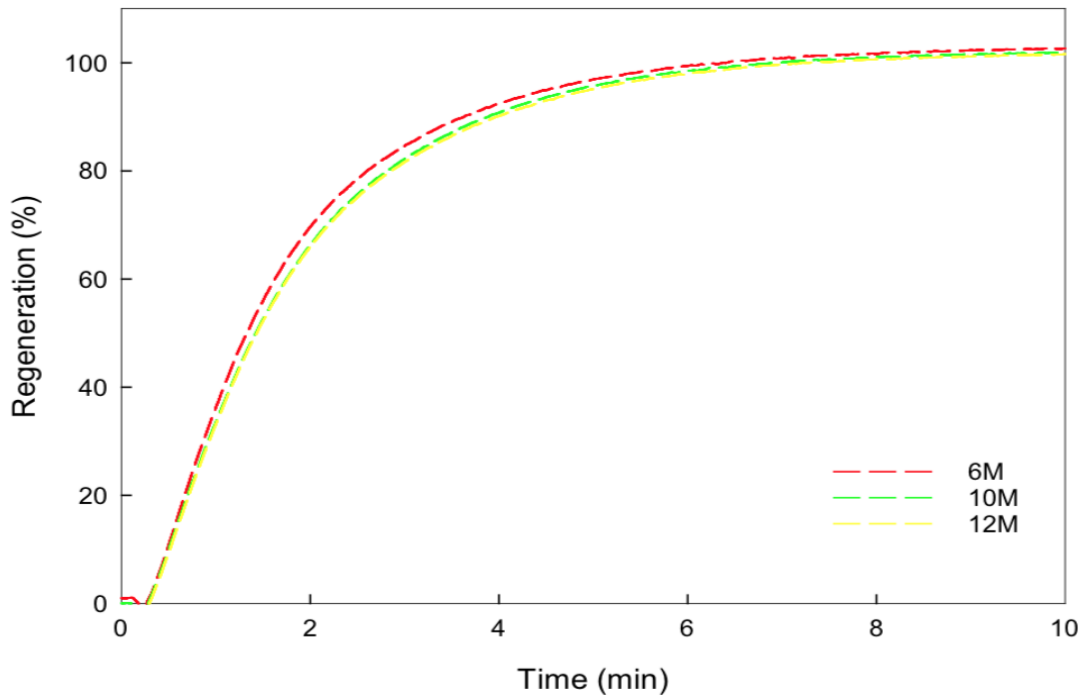
### 3.2.3 Regeneration

In addition to high adsorption capacity, regeneration of sorbents is another key issue that must be taken into consideration in real industry. Sorbents with better regeneration ability require lower energy input during the regeneration process, thus reducing the

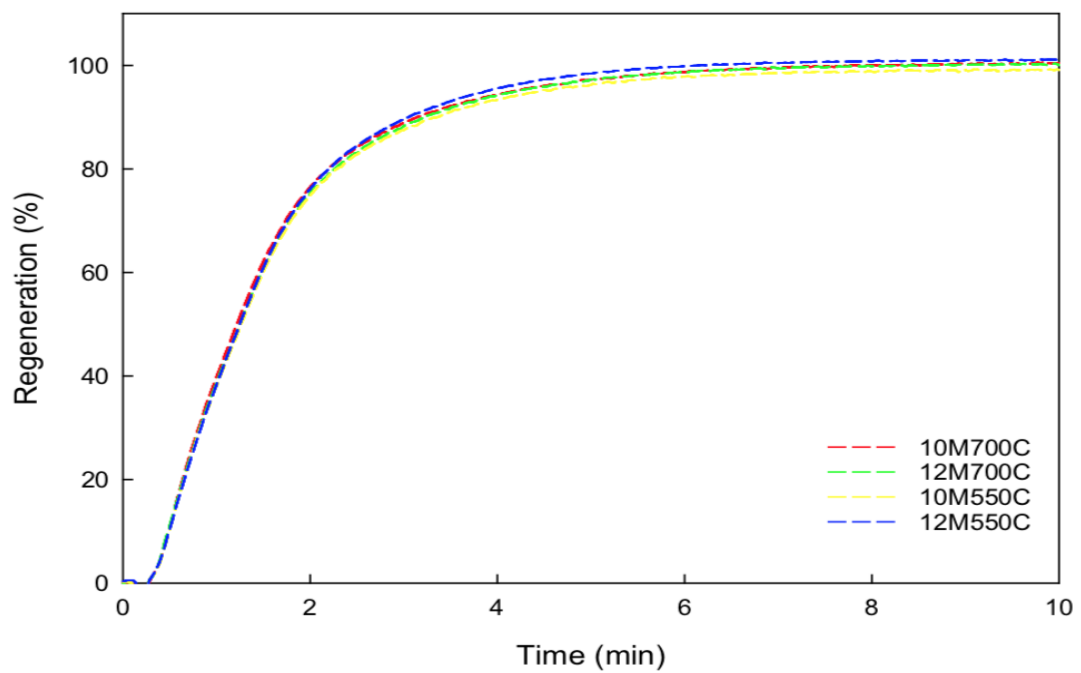
overall cost for CO<sub>2</sub> capture and are more favorable from the economics side. As we did in our previous report, the regeneration process was carried out under N<sub>2</sub> gas at a flow rate of 65 mL/min and at the same temperature for CO<sub>2</sub> adsorption process to investigate the regeneration ability of our sorbents without energy input. The weight loss was tracked by TGA and the desorption over time profiles for samples burned at 700 °C/ 550 °C and tested at 45 °C/ 65 °C were shown in Figure 5, 6 and 7.



**Figure 5** Desorption over time profile for samples carbonized at 700 °C and tested at 45 °C.



**Figure 6** Desorption over time profile for samples carbonized at 550 °C and tested at 45 °C.



**Figure 7** Desorption over time profile for samples tested at 65 °C.

From Figure 5 and 6, it was clear that the 6M700C and 6M550C possessed the best regeneration ability and reached almost 100% regeneration after 10 min under N<sub>2</sub> flow at 45 °C. 10M700C, 12M700C, 10M550C and 12M550C also showed good regeneration. As discussed in the previous part, the 12M samples had the best adsorption performance. Under 45 °C, the regeneration time is 10 min and 7.3 min for 12M700C and 12M550C. Under 65 °C, their regeneration time is 8.5 min and 6.2 min. As the concentration of urea solution increases, sorbents required more time to reach equilibrium. Compared with the regeneration of 700 °C carbonized sorbents tested under 45 °C in Figure 5, the 550°C carbonized ones approached equilibrium faster and had higher % desorption. In addition, at elevated test temperature shown in Figure 7, the % desorption for the samples increased and the time required to get equilibrium decreased.

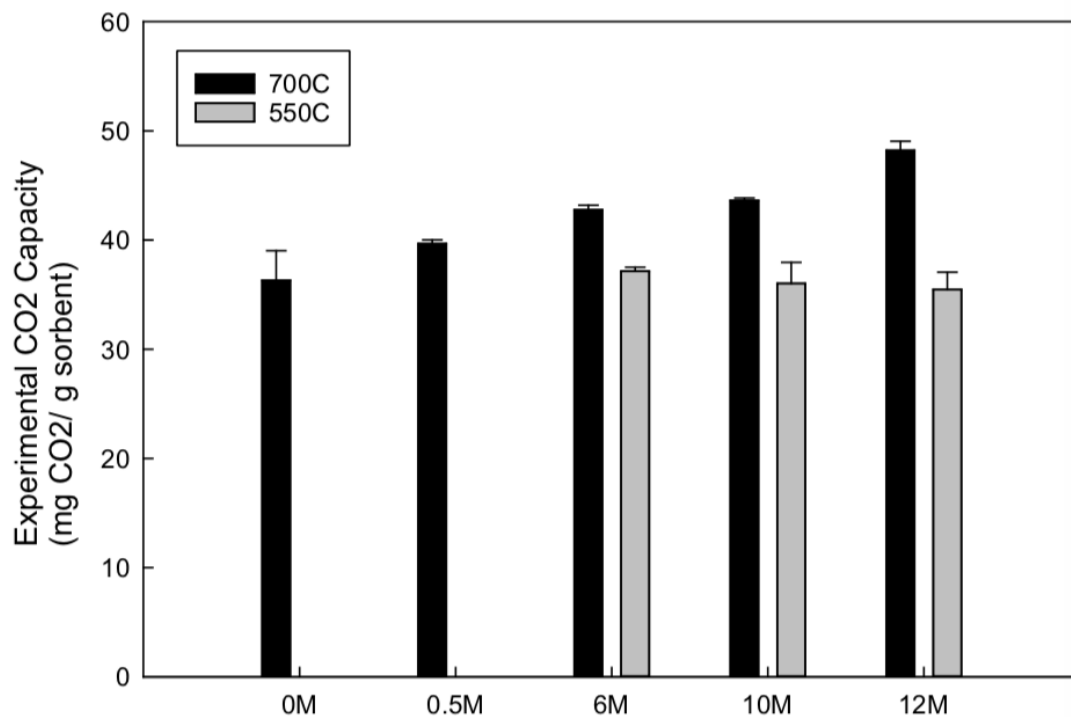
### 3.2.4 CO<sub>2</sub> Capacity

The CO<sub>2</sub> sorption capacities for each sorbent studied were summarized in Figure 8 and 9. At 45 °C, the capacities for 0M700C, 0.5M700C, 6M700C, 6M550C, 10M700C, 10M550C, 12M700C and 12M550C were found to be 36.33, 39.68, 42.77, 37.16, 43.64,

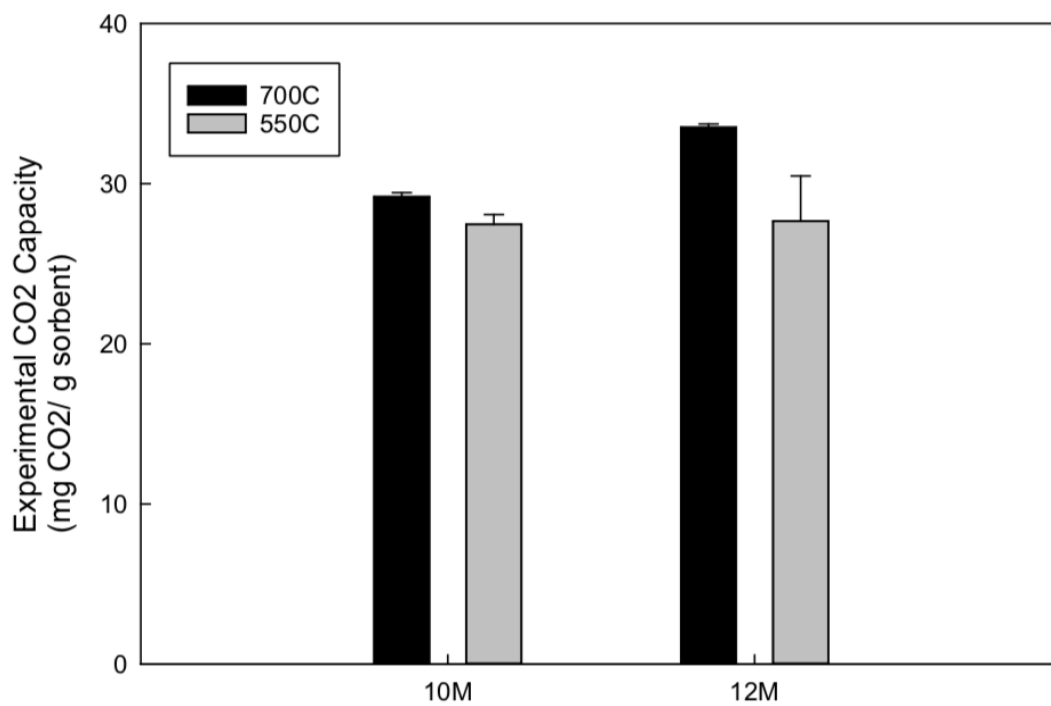
36.04, 48.22, 35.5 mg CO<sub>2</sub> / g sorbent respectively. When temperature was increased to 65 °C, the capacities of 10M700C, 10M550C, 12M700C and 12M550C were 29.19, 27.48, 33.53 and 27.67 mg CO<sub>2</sub> / g sorbent. Among all the samples, 12M700C had the highest CO<sub>2</sub> sorption capacity. Both the two figures indicated that the CO<sub>2</sub> capture capacity rises with the increase of urea solution concentration. At the same time, we can see that the 700 °C carbonized samples have larger values of capacities than the 550 °C carbonized ones have. Compared with the corresponding capacities at 45 °C, the % decrease in capacities at 65 °C for 10M700C, 10M550C, 12M700C and 12M550C were calculated as 33.1%, 23.77%, 30.48% and 22.06%.

An interesting result was found for the sample 12M700C, which had the highest CO<sub>2</sub> sorption capacity, however, its specific surface area and micropore volume were both smallest among all the samples according to the BET characterization section. Meanwhile, the sample 0.5M700C had the largest specific surface area and micropore volume. Furthermore, there is no good correlation between adsorption capacity of samples and their specific surface area or micropore volume in this research, like the larger specific surface area or micropore volume samples possess, the more CO<sub>2</sub> they

adsorb. So we conjectured that the high concentration of urea solution may bring the pore blocked and the dominating factor in the CO<sub>2</sub> capture process for the samples was its nitrogen-containing groups in the porous structures.



**Figure 8** CO<sub>2</sub> sorption capacities of each sorbent studied in series tests under 45 °C.



**Figure 9** CO<sub>2</sub> sorption capacities of each sorbent studied in series tests under 65 °C.

## CHAPTER 4

### CONCLUSIONS AND FUTURE WORK

#### 4.1 Conclusions

To summarize, nitrogen-doped porous carbon sorbents were synthesized by urea modification and high temperature carbonization of pure cigarette filters. The resulting products possessed high CO<sub>2</sub> adsorption capacity and excellent regeneration ability. In this research, by varying the concentration of urea solution and carbonization temperature, further information was obtained. The conclusions show that nitrogen doping did favor the increase of CO<sub>2</sub> uptake. And with the rise of urea concentration or elevation of carbonization temperature, the sorbents exhibited better performance for CO<sub>2</sub> capture, but the changes could not benefit the renewability of the adsorbents.

#### 4.2 Future Work

In this research, we used urea as nitrogen source and obtained products with high capacity of CO<sub>2</sub>. According to the published work, many other nitrogen sources were employed, like HNO<sub>3</sub><sup>[30]</sup>, diamine<sup>[31]</sup> and so on. Besides, almost all the porous carbons with high CO<sub>2</sub> capacity were prepared by KOH activation.<sup>[21]</sup> However, due to time

limitation, the samples in this study were only modified by urea to achieve nitrogen doping.

For scale up this technology, the heating methods for carbonization are supposed to be taken into considerations. Carbonization is defined as the process by which high carbon content solid residues are formed from organic material by pyrolysis in an inert atmosphere. It is generally accepted that the process parameters which most influence the product distribution are pyrolysis temperature, heating rate, residence time and reactor pressure. Slow pyrolysis is a preferred process for carbonization since it maximizes carbon yield and is characterized by slow heating rates (typically 5-8 °C/min). The energy required to derive the process can be supplied either: (i) directly from heat produced from exothermic reactions, (ii) directly from combustion of pyrolysis fuel gases from by-products and/or feedstock, (iii) indirectly from flue gas through a heat transfer surface, or (iv) indirectly from heat carriers other than flue gases.<sup>[32]</sup> Further investigations are essential for future applications in the industry field.

## Reference

- [1] National Research Council. 2010. Advancing the Science of Climate Change. Washington, DC: The National Academies Press.
- [2] IPCC, 2014: Climate Change 2014: Synthesis Report. Contribution of Working Groups I, II and III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Core Writing Team, R.K. Pachauri and L.A. Meyer (eds.)]. IPCC, Geneva, Switzerland, 151 pp.
- [3] ESRL WebTeam (2018, April 9). Trends in Atmospheric Carbon Dioxide. Retrieved from <https://www.esrl.noaa.gov/gmd/ccgg/trends/global.html>
- [4] EPA (2018, April 11). Sources of Greengas Emissions. Retrieved from <https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions>
- [5] C. Stewart, M.-A. Hessami, A study of methods of carbon dioxide capture and sequestration—the sustainability of a photosynthetic bioreactor approach, Energy Convers. Manag. 46 (2005) 403-420.
- [6] J. Rogelj, M. den Elzen, N. Höhne, T. Fekete, H. Winkler, R. Schaeffer, F. Sha, K. Riahi, M. Meinshausen, Paris agreement climate proposals need a boost to keep

warming well below 2 °C, *Nature* 534 (2016) 631-639.

[7] X. Zhao, X. Hu, R. Bai, W. Dai, M. Fan, M. Luo, Enhancement of CO<sub>2</sub> adsorption and amine efficiency of titania modified by moderate loading of diethylenetriamine, *J. Mater. Chem. A1* (2013) 6208-6215.

[8] D.M. D'Alessandro, B. Smit, J.R. Long, Carbon dioxide capture: prospects for new materials, *Angew. Chem. Int. Ed.* 49 (2010) 6058-6082.

[9] M.G. Plaza, C. Pevida, A. Arenillas, F. Rubiera, J.J. Pis, CO<sub>2</sub> capture by adsorption with nitrogen enriched carbons, *Fuel* 86 (2007) 2204-2212.

[10] W. Xie, W. Sun, W. Chu, C. Jiang, Y. Xue, Investigation of the doped transition metal promotion effect on CO<sub>2</sub> chemisorption on Ni (111), *Appl. Surf. Sci.* 258 (2012) 6239-6245.

[11] E. Jiang, S.W. Choi, S.-M. Hong, S. Shin, K.B. Lee, Development of a cost-effective CO<sub>2</sub> adsorbent from petroleum coke via KOH activation, *Appl. Surf. Sci.* 429 (2018) 62-71.

[12] X. Gao, X. Zou, H. Ma, S. Meng, G. Zhu, Highly selective and permeable porous organic framework membrane for CO<sub>2</sub> capture, *Adv. Mater.* 26 (2014) 3644-3648.

- [13] Y. Li, H.P. Wang, C.Y. Liao, X. Zhao, T.L. Hsiung, S.H. Liu, S.G. Chang, Dual alkali solvent system for CO<sub>2</sub> capture from flue gas, *Environ. Sci. Technol.* 51 (2017) 8824-8831.
- [14] H.R. Radfarnia, A.Sayari, A highly efficient CaO-based CO<sub>2</sub> sorbent prepared by a citrate-assisted sol-gel technique, *Chem. Eng. J.* 262 (2015) 913-920.
- [15] E. Favre, Carbon dioxide recovery from post-combustion processes: can gas permeation membranes compete with absorption?, *J Membr. Sci.* 294 (2007) 50-59.
- [16] J.Y. Lim, J.K. Kim, C.S. Lee, J.M. Lee, J.H. Kim, Hybrid membranes of nanostructural copolymer and ionic liquid for carbon dioxide capture, *Chem. Eng. J.* 322 (2017) 254-262.
- [17] A.D. Wiheeb, Z. Helwani, J. Kim, M.R. Othman, Pressure swing adsorption technologies for carbon dioxide capture, *Sep. Purif. Rev.* 45 (2015) 108-121.
- [18] G. Yin, Z. Liu, W. Wu, Q. Liu, Dynamic adsorption of CO<sub>2</sub> over activated carbon- Error analysis and effect of N<sub>2</sub>, *Chem, Eng. J.* 219 (2013) 380-384.
- [19] C. Goel, H. Kaur, H. Bhunia, P.K. Bajpai, Carbon dioxide adsorption on nitrogen enriched carbon adsorbents: Experimental, kinetics, isothermal and thermodynamic

studies. *CO2 Utilization*, 16 (2016) 50-63.

[20] Y. Zhao, X. Liu, K.X. Yao, L. Zhao, Y. Han, Superior capture of CO<sub>2</sub> achieved by introducing extra-framework cations into N-doped microporous carbon. *Chemistry of Materials*, 24(2012) 4725-4734.

[21] L. Yue, Q. Xia, L. Wang, L. Wang, H. DaCosta, J. Yang, X. Hu, CO<sub>2</sub> adsorption at nitrogen-doped carbons prepared by K<sub>2</sub>CO<sub>3</sub> activation of urea-modified coconut shell. *Journal of Colloid and Interface Science*, 511(2018) 259-267.

[22] S. Zhang, J. Liu, P. Huang, H. Wang, C. Cao, W. Song, Carbonaceous aerogel and CoNiAl-LDH@CA nanocomposites derived from biomass for high performance pseudo-supercapacitor. *Science Bulletin*, 62(2017) 841-845.

[23] G. Hao, W. Li, D. Qian, A. Lu, Rapid synthesis of nitrogen-doped porous carbon monolith for CO<sub>2</sub> capture. *Advanced Materials*, 2010, 22, 853-857.

[24] W. Xing, C. Liu, Z. Zhou, L. Zhang, J. Zhou, S. Zhuo, Z. Yan, H. Gao, G. Wang, S.Z. Qiao, Superior CO<sub>2</sub> uptake of N-doped activated carbon through hydrogen-bonding interaction. *Energy Environ. Sci.*, 2012, 5, 7323-7327.

[25] M. Lee, G. Kim, H.D. Song, S. Park, J. Yi, Preparation of energy storage material

derived from a used cigarette filter for a supercapacitor electrode. *Nanotechnology*, 25(2014) 345601.

[26] N.W. Krase, V.L. Gaddy, Synthesis of urea from ammonia and carbon dioxide. *Ind. Eng. Chem.*, 1922, 14(7) 611-615.

[27] Y. Hamzah, L. Umar, Preparation of creating active carbon from cigarette filter waste using microwave-induced KOH activation. *Journal of Physics: Conf. Series* 853(2017) 012027.

[28] R. Maderuelo-Sanz, V.G. Escobar, J.M. Meneses-Rodríguez, Potential use of cigarette filters as sound porous absorber. *Applied Acoustics* 129(2018), 86-91.

[29] T.S. Blankenship, R. Mokaya, Cigarette butt-derived carbons have ultra-high surface area and unprecedented hydrogen storage capacity. *Energy Environ. Sci.*, 2017, 10, 2552-2562.

[30] X. Ma, M. Cao, C. Hu, Bifunctional HNO<sub>3</sub> catalytic synthesis of N-doped porous carbons for CO<sub>2</sub> capture. *J. Mater. Chem. A*, 2013, 1, 913.

[31] A. Grondein, D. Bélanger, Chemical modification of carbon powders, *Fuel* 90(2011), 2684-2693.

[32] C.R. Lohri, H.M. Rajabu, D.J. Sweeney, C. Zurbrügg, Char fuel production in developing countries – a review of urban biowaste carbonization. *Renewable and Sustainable Energy Reviews*, 59(2016) 1514-1530.