POST-COMBUSTION CARBON DIOXIDE (CO₂) CAPTURE WITH BIOMASS DERIVED ACTIVATED CARBON

BİYOKÜTLEDEN ELDE EDİLEN AKTİF KARBONUN YANMA SONRASI KARBONDİOKSİT (CO₂) YAKALAMADA KULLANIMI

AYŞE SEVER AKDAĞ

PROF. DR GÜLEN GÜLLÜ

Supervisor

Submitted to
Graduate School of Science and Engineering of Hacettepe University

As a partial Fulfillment to the Requirements

For the Award of the Degree of Doctor of Philosophy

in Environmental Engineering

2021
ABSTRACT

POST-COMBUSTION CARBON DIOXIDE (CO₂) CAPTURE WITH BIOMASS DERIVED ACTIVATED CARBON

Ayşe SEVER AKDAĞ

Doctor of Philosophy, Department of Environmental Engineering

Supervisor: Prof. Dr. Gülen GÜLLÜ

Co-Supervisor: Dr. Maria Covadonga PEVIDA GARCIA

February 2021, 192 pages

The carbon dioxide (CO₂) capture and storage are indispensable for reducing greenhouse gas emissions. Post-combustion capture is one of the most promising technologies to capture CO₂ because it can be retrofitted to any facility with an acceptable footprint. Adsorption-based technologies are appealing for CO₂ capture mainly due to the ease of the regeneration and the benign character of solid sorbents. To date, the greatest research efforts have aimed at improving efficient adsorbents with higher working capacity for CO₂, higher selectivity, and better impurity tolerance. Among the alternative methodologies in adsorbent production, valorization of agricultural residues is an efficient way in terms of a sustainable circular economy. Besides, valorizing the agricultural residues in porous carbon materials contributes to the reduction of the overall cost of carbon capture since they are ubiquitous and inherently of low-cost. It may also provide a further benefit for more cost-effective waste management. In addition, in order
to scale-up the adsorption based CO$_2$ capture technology, cyclic adsorption processes are being designed and tried to be optimized. Especially, the temperature swing adsorption (TSA) processes are gaining more and more attention because they only require thermal energy, offering an additional advantage over pressure/vacuum swing adsorption (PSA/VSA) processes.

In post-combustion CO$_2$ capture literature, there are many studies that address the use of waste materials as precursors of adsorbents; the thesis study puts for the first time on evaluating the performance of hazelnut shells. The first aim of this dissertation is to develop activated carbon from hazelnut shells with suitable textural development in terms of microporosity and surface area to enhance the adsorption capacity, and to investigate its potential use for CO$_2$ capture under post-combustion capture conditions with particular emphasis on the thermal energy requirements for regeneration. The second aim is to evaluate the performance of the hazelnut shell based activated carbon under dynamic conditions in a fixed-bed reactor over consecutive adsorption–desorption cycles. For that, the maximum CO$_2$ capture capacities were determined from breakthrough curves in CO$_2$/N$_2$ binary mixture at different temperature and partial pressure conditions (14% and 30% CO$_2$ at 30°C and 50°C) which close to the real ones encountered in an industrial process. The last aim is to design different TSA processes providing higher product (CO$_2$) purity, recovery, productivity and lower specific energy consumption and to compare these processes performances with the ones obtained in VSA processes, which were also tested in the current study.

The results obtained in this dissertation revealed that it is possible to develop highly microporous carbonaceous adsorbent using hazelnut-shells and the higher separation factor of CO$_2$ over N$_2$ observed at low CO$_2$ partial pressure makes the adsorbent a good candidate for CO$_2$ capture from post-combustion flue gases. According to evaluation of adsorption capacity under static conditions, the net theoretical CO$_2$ uptake of the hazelnut-shells derived activated carbon (HS-AC) would be up to 0.064 kg CO$_2$/kg adsorbent. Secondly, the dynamic evaluation of CO$_2$ capture capacity of HS-AC with breakthrough experiments in a fixed-bed showed that HS-AC has a fast adsorption and desorption kinetics, which is very crucial in rapid swing adsorption processes. Lastly,
novel TSA configurations, which were not experimented in literature before, were proposed and they resulted in CO₂ purities of 93% and 89% with recoveries of 71% and 87%, respectively (with feed condition of 30% CO₂ at 30°C, and regeneration at 120°C). The thermal energy requirements of TSA configurations were calculated between 1.06 – 2.35 MJ/kg- CO₂ (46.6 – 103.4 kJ/mol-CO₂) depending on the feed condition and cycle configuration, which are lower than the energy requirement of amine absorption, which is the mature technology of CO₂ post-combustion capture. The CO₂ recovery and purity of optimal VSA configuration were found 100% and 92%, respectively pressure at 0.05 kPa for 7 min evacuation and 10 mL/min N₂ purging (with feed condition of 30% CO₂ at 30°C). The comparison of the best results among the two methods, TSA and VSA, illustrated that the cyclic performance parameters are slightly lower when TSA is used; however, considering the possibility of using available waste heat sources in the real applications, the utilization of TSA process is a promising method for capturing CO₂ from post-combustion flue gases.

**Keywords:** Biomass, Activated Carbon, CO₂ Capture, Temperature Swing Adsorption, Vacuum Swing Adsorption
ÖZET

BİYOKÜTLEDEN ELDE EDİLEN AKTİF KARBONUN YANMA SONRASI KARBONDIOKSİT (CO₂) YAKALAMADA KULLANIMI

Ayşe SEVER AKDAĞ

Doktora, Çevre Mühendisliği Bölümü
Tez Danışmanı: Prof. Dr. Gülen GÜLLÜ
Eş Danışman: Dr. Maria Covadonga PEVIDA GARCIA

Şubat 2021, 192 sayfa

Sera gaz emisyonlarının azaltımı için karbondioksit (CO₂) yakalama ve depolama vazgeçilmezdir. Yanma sonrası yakalama, CO₂'yi yakalamak için en umut verici teknolojilerden biridir, çünkü herhangi bir tese kabul edilebilir bir ayak izi ile sonradan eklenebilir. Adsorpsiyon temelli teknolojiler, esas olarak katı sorbentlerin uygun karakteristik özellikleri ve rejenerasyon kolaylıklarını sayesinde CO₂ yakalama için caziptir. Bugüne kadar, araştırmalar, CO₂ için daha yüksek çalışma kapasitesi, daha yüksek seçicilik ve daha iyi safsızlık toleransına sahip etkili adsorbanları geliştirmeyi amaçlamışlardır. Adsorban üretimi için tarımsal kalıntıların değerlendirilmesi, sürdürülebilir döngüsel ekonomi açısından verimli bir yoldur. Ayrıca, gözenekli karbon malzeme üretiminde tarımsal kalıntıların kullanılması, bu kalıntıların her yerde bulunmaları ve doğaları gereği düşük maliyetli olmaları nedeniyle, toplam karbon yakalama maliyetinin azaltılmasına katkıda bulunur. Bu durum, daha uygun maliyetli atık yönetimi için de fayda sağlayabilir. Ek olarak, adsorpsiyon temelli CO₂ yakalama
teknolojilerini sanayi ölçeklerine taşıyabilmek için döngüsel adsorpsiyon süreçleri tasarlamanmakta ve optimize edilmeye çalışılmaktadır. Özellikle, sıcaklık salınımılı adsorpsiyon (TSA) süreçleri, sadece termal enerjiye ihtiyaç duyduklarından ve bu durum basınç / vakum salınımılı adsorpsiyon (PSA / VSA) işlemlerine göre ek bir avantaj sunduğundan giderek daha fazla dikkat çeker.

Yanma sonrası CO₂ yakalama ile ilgili literatürde, atık malzemelerin adsorban öncüleri olarak kullanımını ele alan birçok çalışma vardır; bu tez çalışması ise ilk kez fındık kabuklarının performansı değerlendirilmiştir. Bu tezin ilk amacı, fındık kabuklarından, adsorpsiyon kapasitesinin artması gözlemlenen mikro gözeneklilik ve yüzey alanı açısından uygun dokusal gelişime sahip aktif karbon geliştirmek ve rejenerasyonu için termal enerji gerekşimlerine özel vurgu yaparak özellikle yanma sonrası yakalama koşulları altında CO₂ yakalama için potansiyel kullanımını araştırılmaktır. İkinci amacı, dinamik koşullarda, sabit yatak bir reaktörde arka arkaya adsorpsiyon-desorpsiyon döngüleri boyunca fındık kabuğu bazlı aktif karbonun performansını değerlendirmektir. Bunun için, maksimum CO₂ yakalama kapasiteleri geçiş eğrileri ile, endüstriyel bir süreçte karşılaşılan gerçek koşullara yakın olan farklı sıcaklık ve kısmi basınç altında (30°C ve 50°C'de % 14 ve % 30 CO₂) değerlendirilmiştir. Son amaç, daha yüksek ürün (CO₂) saflığı, geri kazanımı, üretkenliği ve daha düşük spesifik enerji tüketimi sağlayan farklı TSA süreçleri tasarlamak ve bu süreçlerin performanslarını mevcut çalışmada da test edilen VSA süreçlerinde elde edilenlerle karşılaştırırmaktır.

Bu tezden elde edilen sonuçlar, fındık kabukları kullanılarak oldukça mikro gözenekli karbon bazlı adsorban geliştirilmenin mümkün olduğunu göstermiş ve düşük CO₂ kısmi basıncında gözlemlenen CO₂ gazının, N₂ gazına göre daha yüksek ayırma faktörüne sahip olması, geliştirilen adsorbmanın yanı sıra baca gazlarından CO₂ yakalamada kullanım için iyi bir aday olduğunu ortaya koymuştur. Statik koşullarda adsorpsiyon kapasitesinin değerlendirilmesi ile, biyokütlüden elde edilmiş bu aktif karbonun (HS-AC) net teorik CO₂ yakalama kapasitesinin 0,064 kg-CO₂/kg-adsorban olabileceğini ortaya konmuştur. İkinci olarak, sabit bir yatakta yapılan HS-AC’nin CO₂ yakalama kapasitesinin dinamik değerlendirilmesi, HS-AC’nin, hızlı salınımlı adsorpsiyon işlemlerinde çok önemli olan, hızlı bir adsorpsiyon ve desorpsiyon kinetiğine sahip.
olduğunu göstermiştir. Son olarak, daha önce literatürde deneysel olarak denenmemiş yeni TSA konfigürasyonları tasarlanmış ve sırasıyla %71 ve %87 geri kazanımı ve %93 ve %89 CO₂ saflıkları elde edilmiştir (30°C'de %30 CO₂ gaz besleme koşulunda ve 120°C'de rejenerasyon sıcaklığında). TSA konfigürasyonlarının ısıl enerji gereksinimleri, besleme durumuna ve döngü konfigürasyonuna bağlı olarak 1.06 - 2.35 MJ/kg-CO₂ (46.6 - 103.4 kJ/mol-CO₂) arasında hesaplanmıştır ve bu, yanma sonrası CO₂ yakalamada ana teknoloji olan amin absorpsiyonunun enerji ihtiyacından düşüktür. Optimum VSA konfigürasyonunun ise, 0.05 kPa basınç altında, 7 dakika süren rejenerasyon ve 10 mL/dakika N₂ süpürme gazı ile CO₂ geri kazanımı ve saflığı sırasıyla % 100 ve % 92 bulunmuştur (30°C'de %30 CO₂ gaz besleme koşulunda). TSA ve VSA konfigürasyonları arasındaki en iyi sonuçların karşılaştırılması, TSA kullanıldığında döngüsel performans parametrelerinin biraz daha düşük olduğunu göstermiştir; fakat, gerçek uygulamalarda mevcut atık ısı kaynaklarının kullanılması olması göz önüne alındığında, TSA teknolojisi yanma sonrası baca gazlarından CO₂'nin yakalanması için umut verici bir yöntemdir.

**Anahtar Kelimeler:** Biyokütle, Aktif Karbon, CO₂ Yakalama, Sıcaklık Salmımlı Adsorpsiyon, Vakum Salmımlı Adsorpsiyon
ACKNOWLEDGEMENTS

Firstly, I would like to express my deepest gratitude to my supervisor Dr. Gülen Güllü for her guidance and unflagging support during this study.

I would like to thank my co-supervisor Dr. Covadonga Pevida for believing in me and giving me the opportunity to pursue a PhD at Nacional del Carbón (INCAR), CSIC in Spain under her Energy Processes and Emission Reduction (PrEM) Group, and for all the guidance, cooperation and support. I am thankful to her to let me follow my ideas and providing her expertise to develop them. I deeply thank her for giving me the time for discussions whenever needed in her very busy schedule.

I am thankful to the examining committee members Dr. Özkan Murat Doğan, Dr. Nurşen Altuntaş Öztaş, Dr. Merih Aydinalp Köksal, and Dr. Fatma Oztürk for their valuable suggestions and comments.

I would like to thank Ines and Nausika for sharing their knowledge during my experiments and being available for the subject discussions. I want to thank Alma for helping me getting along with this new country in my stay. I wish also thank to Roberto and Pilar for their friendship throughout my research at INCAR.

I would like to thank my colleagues Ece and Pinar for their help and support during my thesis writing time.

I am very thankful to The Scientific and Technological Research Council of Turkey (TUBITAK) for the financial support (2214A-fellow) giving me the opportunity to implement my PhD thesis at Instituto Nacional del Carbón (INCAR), CSIC in Spain.
I would like to thank Hacettepe University, Scientific Research Projects Coordination Unit for the thesis project financial support (FDK-2018-17156).

I am highly grateful to my sister Aylin and my little Tuna for their unconditional love. Lastly, I owe my sincere gratitude to my husband Osman for him incessant love, care and support throughout my life. Without his understanding and support, it would not be possible to finish this study.
# TABLE OF CONTENT

ABSTRACT .................................................................................................................................................. i

ÖZET ......................................................................................................................................................... iv

ACKNOWLEDGEMENTS ............................................................................................................................. vii

TABLE OF CONTENT ................................................................................................................................. ix

LIST OF FIGURES ........................................................................................................................................ xii

LIST OF TABLES ............................................................................................................................................ xvi

1. INTRODUCTION ....................................................................................................................................... 1

2. THEORETICAL BACKGROUND .............................................................................................................. 6

2.1. Global Warming and Carbon Dioxide (CO₂) Emissions ................................................................. 6

2.2. “Carbon Capture and Storage (CCS)” in a Nutshell ..................................................................... 10

2.2.1. Pre-Combustion ......................................................................................................................... 11

2.2.2. Oxy-fuel Combustion ................................................................................................................. 12

2.2.3. Post-Combustion ....................................................................................................................... 12

2.3. Post-combustion Carbon Dioxide Capture Technologies ............................................................. 13

2.3.1. Absorption ............................................................................................................................... 13

2.3.2. Membranes .............................................................................................................................. 14

2.3.3. Cryogenic Distillation and Air Separation .............................................................................. 15

2.3.4. Adsorption ............................................................................................................................... 15

2.4. Current Situation of CCS Technologies in the World .................................................................. 16

2.5. Adsorption Phenomena ............................................................................................................... 17

2.6. Adsorption Equilibrium ............................................................................................................... 21

2.6.1. Pure Gas Adsorption Equilibrium Models ......................................................................... 24

2.6.2. Multicomponent Gas Adsorption Equilibrium Models ...................................................... 27

2.7. Adsorbent Materials Applied to “CO₂ Capture” and Literature Studies .................................. 29

2.7.1. Activated Carbons (ACs) ........................................................................................................ 32

2.7.2. Textural Characterization of ACs .......................................................................................... 36

2.7.2.1. Pure N₂ and CO₂ Isotherms ............................................................................................... 36
2.7.2.2. Surface Area ........................................... 36
2.7.2.3. Micropore Volume ................................... 38
2.7.2.4. Pore Size Distribution ................................ 40
2.8. Adsorption Processes ...................................... 42
   2.8.1. Fixed Bed Column Dynamics .......................... 44
   2.8.2. Cyclic Adsorption Processes ........................ 48
   2.8.3. Configurations of Adsorption Cycles .............. 50
   2.8.4. Characteristic Parameters of CO₂ Adsorption Processes 52
   2.8.5. Literature on Cyclic Adsorption Processes for CO₂ Capture 53
3. MATERIALS AND METHODS .................................. 60
   3.1. Raw Material ............................................ 60
   3.2. Optimization of Single Step Activation Conditions in Thermogravimetric Analyser ............................................ 60
   3.3. Production of Hazelnut Shell Based Activated Carbon (HS-AC) and Experiments of CO₂ Uptake Capacity ........................................... 62
   3.4. Characterization of HS-AC ................................ 64
      3.4.1. Single Component Adsorption Isotherm .............. 64
      3.4.2. Multi-Component Adsorption Isotherm ............... 66
      3.4.3. Isosteric Heat of Adsorption ......................... 67
      3.4.4. Determination of Densities and Porosities ........... 67
      3.4.5. Scanning Electron Microscopy (SEM) .................. 69
      3.4.6. Specific Heat Capacity ................................ 70
   3.5. Dynamic Adsorption Experiments of HS-AC in a Fixed Bed ............ 70
      3.5.1. Fixed Bed Experimental Set-up ....................... 70
      3.5.2. Binary CO₂/N₂ Breakthrough Experiments .......... 72
      3.5.3. Cyclic CO₂ Adsorption Experiments .................. 76
         3.5.3.1. Temperature Swing Adsorption (TSA) Configurations ....... 77
         3.5.3.2. Characteristic Parameters of TSA Configurations ........ 81
         3.5.3.3. Vacuum Swing Adsorption (VSA) Configurations ......... 82
         3.5.3.4. Vacuum Temperature Swing Adsorption (VTSA) Configuration .... 87
         3.5.3.5. Characteristic Parameters of VSA/VTSA Configurations ..., 87
4. RESULTS and DISCUSSIONS ................................... 89
4.1. Thermal Characterization of Raw Material and Production of HS-AC............. 89
4.2. Textural Characterization of the Produced HS-AC .................................... 94
  4.2.1. Pore Size Distribution of HS-AC .................................................. 97
  4.2.2. Scanning Electron Microscopy (SEM) of HS-AC ............................... 99
4.3. Single Component CO₂ and N₂ Adsorption on HS-AC .............................. 100
  4.3.1. Single Component Adsorption Isotherms ......................................... 100
  4.3.2. Isosteric Heat of Adsorption ......................................................... 101
4.4. Multi-Component Adsorption Isotherms ................................................. 103
4.5. Specific Heat Capacity (Cp) of HS-AC .................................................. 107
4.6. Calculation of Thermal Energy Requirement ........................................... 108
4.7. Calculation of “net” CO₂ Capture Amount ............................................ 109
4.8. Dynamic Adsorption Experiments ......................................................... 111
  4.8.1 Binary CO₂/N₂ Breakthrough Experiments ...................................... 111
  4.8.2 Cyclic Adsorption Experiments ....................................................... 116
    4.8.2.1. Temperature Swing Adsorption (TSA) Cycles ............................ 117
    4.8.2.2. Energy Requirements of the TSA Configurations and Comparative
    Assessment of Cycle Performances ............................................. 135
    4.8.2.3. Vacuum Swing Adsorption (VSA) Cycles ................................ 141
    4.8.2.4. VTSA Configuration for the Adsorption Condition of 30% CO₂ at
    50°C .......................................................................................... 164
    4.8.2.5. Comparative Assessment of VSA Cycle Performances .................. 166
5. CONCLUSION .......................................................................................... 169
6. REFERENCES ......................................................................................... 174
APPENDIX .................................................................................................. 193
  Appendix 1 – Thesis Similarity Report ..................................................... 193
  CV ........................................................................................................ 194
LIST OF FIGURES

Figure 2.1. World energy consumption. Figure based on data from BP Statistical Review of World Energy ............................................................... 7
Figure 2.2. Anthropogenic CO$_2$ emissions .......................................................... 7
Figure 2.3. Cumulative total anthropogenic CO$_2$ emissions vs temperature anomaly relative to pre-industrial ........................................... 8
Figure 2.4. Illustrative pathways in the IPCC special report on “Global Warming of 1.5°C” .................................................................................. 10
Figure 2.5. Processes of the conventional CO$_2$ capture technologies (a) pre-combustion, (b) oxy-fuel combustion (c) post combustion .................................. 11
Figure 2.6. Schematic diagram of typical amine scrubbing unit ................................ 14
Figure 2.7. Pipeline of commercial CCS facilities from 2010 to 2020: CCS capacity ................................................................. 17
Figure 2.8. World map of CCS facilities at various stages of development .............. 18
Figure 2.9. Adsorption system which illustrates the terms of adsorbent, adsorbate and adsorptive ............................................................................ 18
Figure 2.10. Adsorption Isotherms by IUPAC classification .................................... 22
Figure 2.11. Typical schematic representation of the microstructure of activated carbon ........................................................................................................... 33
Figure 2.12. Two basic modes of operation for an adsorption process; (a) fixed cyclic bed system (b) moving continuous counter current system ......................... 44
Figure 2.13. Concentration patterns in a fixed bed .................................................... 46
Figure 2.14. Breakthrough curve for adsorption in a fixed bed ................................. 46
Figure 2.15. Breakthrough curves for a fixed-bed adsorption with (a) narrow and (b) wide mass-transfer zone .......................................................... 48
Figure 2.16. Conceptual principle of cyclic adsorption processes using either pressure (PSA), temperature (TSA) or both pressure and temperature (PTSA) to regenerate the bed ......................................................... 49
Figure 2.17. One of the beds in a Skarstrom PSA cycle for CO$_2$ adsorption .............. 51
Figure 3.1. Schematic of the experimental device used to carry out physical activation ........................................................................................................ 64
Figure 3.2. Fixed bed set-up used for the experimental study ..................................... 70
Figure 3.3. Sketch of the adsorption–desorption cycle configuration in the breakthrough experiments

Figure 3.4. Areas identified in the outlet molar flow rate curve of component $i$ used for the calculation of term A

Figure 3.5. Cycle schedule for the 4 bed-4 step TSA cycles carried out in the one column adsorption unit

Figure 3.6. Cycle schedule for the 4-bed 5-step TSA cycles carried out in the one column adsorption unit

Figure 3.7. Cycle schedule for the 4-bed 6-step TSA cycles carried out in the one column adsorption unit

Figure 3.8. Steps of the VSA configurations with 3 beds evaluated.

Figure 3.9. Schemes of the different VSA configurations studied experimentally according to the number of steps: (a) “3 steps”, (b) “4 steps”, (c) “5 steps”

Figure 4.1. TGA result of the raw HS sample

Figure 4.2. TG and dTG profiles of the HS-AC sample activation at 800°C for 4 hour

Figure 4.3. TG profile showing CO$_2$ uptake of the activated HS-AC800 sample at 25°C

Figure 4.4. N$_2$ isotherms at –196°C (a) and CO$_2$ isotherms at 0°C (b)

Figure 4.5. DA model fit with CO$_2$ pure adsorption isotherms at 0°C

Figure 4.6. N$_2$ adsorption QSDFT PSD of HS-AC

Figure 4.7. CO$_2$ adsorption NLDFT PSD of HS-AC

Figure 4.8. SEM images of HS-AC, the scale bars are (a) 1 mm (b) 50 µm (c) 40 µm (d) 10 µm.

Figure 4.9. Adsorption equilibrium isotherms of CO$_2$ (a), and N$_2$ (b) on HS-AC at 30, 50 and 70°C

Figure 4.10. Isosteric heats of adsorption of CO$_2$ (a) and N$_2$ (b) on HS-AC as estimated by the Clausius–Clapeyron equation

Figure 4.11. Uptake versus partial pressure of multicomponent gas adsorption equilibria at 30°C

Figure 4.12. Uptake versus partial pressure of multicomponent gas adsorption equilibria at 50°C

Figure 4.13. Uptake versus partial pressures of multicomponent gas adsorption equilibria at 70°C
Figure 4.14. Separation factor of CO$_2$ over N$_2$ at 30°C (blue), 50°C (green), and 70°C (red).

Figure 4.15. Specific heat of the HS-AC evaluated against temperature.

Figure 4.16. Example of a complete breakthrough experiment consisting of six consecutive adsorption–desorption cycles at 30°C for a mixture of 30/70 vol.% CO$_2$/N$_2$: 1- adsorption step, 2- desorption step, and 3- cooling step.

Figure 4.17. CO$_2$ (circles) and N$_2$ (diamonds) breakthrough curves of the experiments with the following CO$_2$/N$_2$ feed gas compositions: 14/86 vol.% at 30°C (a), 30/70 vol.% at 30°C (b), 14/86 vol.% at 50°C (c), 30/70 vol.% at 50°C (d).

Figure 4.18. Comparison between the capture capacities of CO$_2$ of the dynamic breakthrough experiments and the data obtained from the pure CO$_2$ adsorption isotherms at 30 and 50°C.

Figure 4.19. TSA run at 30°C with 30% CO$_2$ feed concentration.

Figure 4.20. Experimental profiles at bed exit during the TSA cycles for a feed with 14% CO$_2$ feed at 30°C. (a), (b), (c), (d) concentration; (e), (f), (g), (h) molar flow rates. N$_2$ (green), CO$_2$ (blue) and bed temperature (red).

Figure 4.21. Characteristic performances of the different TSA configurations (14% CO$_2$ at 30°C).

Figure 4.22. Experimental profiles at bed exit during the TSA cycles for a feed with 30% CO$_2$ at 30°C. (a), (b), (c), (d), (e) concentration; (e), (f), (g), (h), (j) molar flow rates. N$_2$ (green), CO$_2$ (blue) and bed temperature (red).

Figure 4.23. Characteristic performances of different TSA configurations (30% CO$_2$ at 30°C).

Figure 4.24. Experimental profiles at the bed exit during the TSA cycles for a feed with 14% CO$_2$ at 50°C. (a), (b), (c), (d) concentration; (e), (f), (g), (h) molar flowrates. N$_2$ (green), CO$_2$ (blue) and bed temperature (red).

Figure 4.25. Characteristic performances of different configurations of TSA cycles (14% CO$_2$ at 50°C).

Figure 4.26. Experimental profiles at the bed exit during the TSA cycles for a feed with 30% CO$_2$ at 50°C. (a), (b), (c) concentration; (d), (e), (f) molar flowrates. N$_2$ (green), CO$_2$ (blue) and bed temperature (red).

Figure 4.27. Characteristic performances of different TSA configurations (30% CO$_2$ at 50°C).
Figure 4.28. Working capacities of the TSA configurations at each feed condition.  

Figure 4.29. Thermal energy requirements of the TSA configurations at each feed condition.  

Figure 4.30. Experimental profiles at the bed exit during the VSA cycles for a feed with 14% CO\textsubscript{2} at 30°C. (a), (b), (c), (d), (e) concentration and total pressure, (f), (g), (h), (i), (j) molar flow rates. N\textsubscript{2} (green), CO\textsubscript{2} (blue) and bed pressure (light brown).  

Figure 4.31. Characteristic performances of the different VSA configurations (14% CO\textsubscript{2} at 30°C).  

Figure 4.32. Experimental profiles at the bed exit during the VSA cycles for a feed with 30% CO\textsubscript{2} at 30°C. (a), (b), (c), (d), (e) concentration and total pressure, (f), (g), (h), (i), (j) molar flow rates. N\textsubscript{2} (green), CO\textsubscript{2} (blue) and bed pressure (light brown).  

Figure 4.33. Characteristic performances of the different VSA configurations (30% CO\textsubscript{2} at 30°C).  

Figure 4.34. Experimental profiles at the bed exit during the VSA cycles for a feed with 14% CO\textsubscript{2} at 50°C. (a), (b), (c), (d), (e) concentration and total pressure, (f), (g), (h), (i), (j) molar flow rates. N\textsubscript{2} (green), CO\textsubscript{2} (blue) and bed pressure (light brown).  

Figure 4.35. Characteristic performances of the different VSA configurations (14% CO\textsubscript{2} at 50°C).  

Figure 4.36. Experimental profiles at the bed exit during the VSA cycles for a feed with 30% CO\textsubscript{2} at 50°C. (a), (b), (c), (d) concentration and total pressure, (e), (f), (g), (h) molar flow rates. N\textsubscript{2} (green), CO\textsubscript{2} (blue) and bed pressure (light brown).  

Figure 4.37. Characteristic performances of the different VSA configurations (30% CO\textsubscript{2} at 50°C).  

Figure 4.38. Experimental profiles at the bed exit during the VTSA cycle for a feed with 30% CO\textsubscript{2} at 50°C. (a) concentration and total pressure, (b) molar flow rates. N\textsubscript{2} (green), CO\textsubscript{2} (blue) and bed pressure (light brown).
LIST OF TABLES

Table 2.1. Comparison of various post-combustion CO$_2$ capture processes ...............16
Table 2.2. Differences between physical and chemical adsorption ...........................20
Table 2.3. The general CO$_2$ adsorption capacities of the main types of adsorbents .......32
Table 2.4. Biomass-derived activated carbons with high CO$_2$ adsorption .....................43
Table 2.5. Characteristic parameters of various TSA arrangements for CO$_2$ capture from
flue gas ......................................................................................................................59
Table 3.1 Reactors and corresponding parameters used for production ...........................63
Table 3.2. Textural characterization from the physical adsorption of N$_2$ at -196°C and
CO$_2$ at 0°C ..............................................................................................................65
Table 3.3. Breakthrough experiments conditions ..........................................................74
Table 4.1. Results of proximate and ultimate analyses of raw HS sample ......................89
Table 4.2. Experimental conditions tested in TGA for activation process, calculated
response yields and corresponding CO$_2$ capture capacities .....................................92
Table 4.3. The yield and CO$_2$ uptake of the HS derived activated carbon at smaller scale
........................................................................................................................................93
Table 4.4. Overall yield and CO$_2$ uptake of the HS derived activated carbon at higher
scale ...............................................................................................................................94
Table 4.5. Textural characteristics of the HS-AC sample ..............................................97
Table 4.6. Toth and Sips parameters for the adsorption of CO$_2$ and N$_2$ on HS-AC at 30°C,
50°C, 70°C ...................................................................................................................102
Table 4.7. Thermal energy requirement for different adsorption cases .........................110
Table 4.8. “Net” CO$_2$ uptake value of each adsorption process cases ..........................110
Table 4.9. Physical properties of HS-AC and characteristics of the fixed-bed reactor.111
Table 4.10. CO$_2$ adsorption capacities and breakthrough times for the experiments at 30
and 50°C and 130 kPa, feeding binary CO$_2$/N$_2$ mixtures (14/86 and 30/70 vol.%)        115
Table 4.11. Operating conditions of the TSA configurations for the adsorption of 14%
CO$_2$ at 30°C ..............................................................................................................120
Table 4.12. Operating conditions of the TSA configurations for the adsorption of 30%
CO$_2$ at 30°C ..............................................................................................................126
Table 4.13. Operating conditions of the TSA configurations for the adsorption of 14% CO\textsubscript{2} at 50°C .............................................................. 129
Table 4.14. Operating conditions of the TSA configuration for the adsorption of 30% CO\textsubscript{2} at 50 °C .............................................................. 133
Table 4.15. CO\textsubscript{2} recovery and purity recalculation including the cooling step. ......... 142
Table 4.16. Operating conditions of the VSA configurations for the adsorption of 14% CO\textsubscript{2} at 30°C .............................................................. 143
Table 4.17. Operating conditions of the VSA configurations for the adsorption of 30% CO\textsubscript{2} at 30°C .............................................................. 150
Table 4.18. Operating conditions of the VSA configurations for the adsorption of 14% CO\textsubscript{2} at 50°C. .............................................................. 156
Table 4.19. Operating conditions of the VSA configurations for the adsorption of 30% CO\textsubscript{2} at 50°C .............................................................. 161
Table 4.20. Operating conditions of the VTSA configuration for the adsorption of 30% CO\textsubscript{2} at 50°C .............................................................. 165
Table 4.21. Characteristic performances of the VTSA configuration for a feed with 30% CO\textsubscript{2} at 50°C .............................................................. 166
1. INTRODUCTION

The average atmospheric temperatures have been recorded by World Meteorological Organization (WMO) since 1850, and it was announced that the eighteen of the twenty warmest years was measured in the past two decades. Carbon dioxide (CO₂) emissions arising from the fossil fuel combustion is known as the largest component to the increase in atmospheric CO₂ concentration; consequently, to the rise of average global temperature during the 21st century [1].

More than 100 countries have signed the Paris Agreement on the purpose of limiting the increase of global temperature less than “2°C” (aiming “1.5°C”) compared to pre-industrial levels, and accordingly, reducing the risks and impacts of climate change. Thus, diminishing the carbon emissions, especially those from large stationary sources is a must. Nevertheless, it was stated in the fifth assessment report of “Intergovernmental Panel on Climate Change (IPCC)” that most of the climate models without “CO₂ capture and storage (CCS)” are inadequate to achieve emission reduction targets. More importantly, the mitigation cost increases by about 138% according to the scenarios not including CCS. This means that introducing renewables and nuclear energy alone will not able to restrict the temperature rise “well below” 2°C; thus, CCS processes are playing a key role for achieving the target with least-cost efforts [2,3].

One of the principal CCS routes is CCS is “Post-Combustion CO₂ Capture” which separates the CO₂ from the flue gases directly and it can be extended to power stations without major system modifications [4,5]. Liquid-phase chemisorption which uses monoethanolamine (MEA) as the solvent is known as the mature process for “Post-Combustion CO₂ Capture”; nevertheless, implementation of MEA process for capturing CO₂ has been decreasing because of its high energy requirement in the regeneration step of the diluted amine solvent and environmental concern of its by-products [2,6]. Meantime, adsorption processes has started to receive great attention as an alternative process for CO₂ capture since 1990s. There has been an ongoing and growing effort to develop the adsorption based technologies especially in improving the adsorbent characteristics such as having “higher working capacity for CO₂”, “better selectivity”, and “better tolerance to impurities” [7–11]. Following this, developing methodologies to
produce low-cost adsorbents is another crucial point. Until now, a variety of solid adsorbents have been studied including “carbon materials”, “metal organic frameworks (MOFs)”, “zeolites”, “zeolitic imidazolate frameworks (ZIFs)”, “grafted and impregnated polyamine adsorbents” [10,12,13]. Here, physisorbents like carbon materials show series of advantages such as their low cost, non-toxic nature, simple storing and displacing properties and having lower sorption enthalpy (which means smaller energy penalty) [7,14,15]. Agricultural by-products are increasingly preferred as precursors in order to prepare carbon materials which fulfill all these requirements with their availability and low cost [16–19].

In addition, in order to scale-up the adsorption based CO₂ capture technology, cyclic adsorption processes are being developed and tried to be optimized. Being an adsorption based technology, "Vacuum Swing Adsorption (VSA)" has been extensively researched for “post-combustion CO₂ capture” at both the laboratory and pilot scale stages. However, only a small number of literature studies have shown effort in designing the “Temperature Swing Adsorption (TSA)” process for CO₂ capture. Hence, the pursuit of an efficient TSA configurations for “CO₂ capture” applications remains a major research goal.

Turkey is getting attention in the OECD countries because of having the highest CO₂ emissions growth over the past decade (+ 49% over 2005-2016, excluding LULUCF) and being the third biggest CO₂ emitter (425.3 million tones excluding LULUCF in 2017) in the European Union (EU) countries. Majority of the CO₂ emissions due to fuel combustion activities arise from the energy industries specifically in public electricity and heat production. Turkey’s energy supply is still highly dependent on fossil fuels (88%) and coal accounts for a large proportion (33%, 2017) of the fossil fuels used. In addition, Turkey has one of the largest coal power plant development program in the world [20,21]. Therefore, as stated in Turkey’s strategic energy plan, coal fired power will remain as an important part of the energy mix, which makes the energy industry in Turkey more carbon—and emission—intensive. Thus, for the case of Turkey, additional to the primary options, which are increasing the efficiency of energy production and renewable energy use, renovating coal-fired plants by equipping them with carbon capture and storage (CCS) systems may be the best secondary option because of the dependence of energy industry on coal fired power.
In Turkey, a great amount of agricultural by-products is produced; therefore, one of the most encouraging alternative methods for “carbon capture” is using the biomass based solid sorbents. Despite having a high amount of agricultural by-products, Turkey has neither carbon capture system in use nor laboratory-scale studies based on biomass. For instance, Turkey is the world's leading producer, producing 450 to 650 ktones per year and accounting for roughly 70% of global hazelnut supply [22]. The shells, comprising half weight of the hazelnuts, are usually used as an individual heating, without any inspection. There are many studies about carbon capture with biomass based adsorbents in literature; however, none of these studies evaluate the “hazelnut shell” as a precursor of an “activated carbon” for being used as adsorbents in “post combustion carbon dioxide capture”.

Given this background, the purpose of the dissertation is to develop an hazelnut shell based activated carbon with the focus of its textural development to enhance adsorption capacity; to investigate its potential usage for “CO₂ capture under post-combustion conditions”, to evaluate the thermal energy requirement for the adsorption capture processes; to evaluate its dynamic behavior in a fixed bed, to assess its CO₂ capture performance from simulated flue gases in cyclic operations by designing different TSA configurations aimed at achieving higher CO₂ purity, recovery, productivity and lower energy consumption and comparing them with basic VSA/VTSA configurations.

In order to fulfill these aims, the hazelnut shells-based activated carbon (HS-AC) was produced by physical activation in single step with using CO₂ as activating agent. Textural characterization of the HS-AC was accomplished through “N₂ adsorption at -196°C” and “CO₂ adsorption at 0°C”. To determine pore size distribution of the HS-AC sample, CO₂ and N₂ isotherms were analyzed by the NLDFT and QSDFT models, respectively. The pure “CO₂ and N₂ adsorption isotherms” were also measured at temperatures of 30, 50, and 70°C, and at pressures up to 120 kPa. The resulting data were fitted with the temperature-dependent Toth and Sips models. Pure component isotherm parameters were used to predict the binary adsorption data using the “Ideal Adsorbed Solution Theory (IAST)”. The isosteric heats of adsorption of CO₂ and N₂ on the HS-AC sample were calculated by fitting the “Sips equation” to pure adsorption isotherms and applying the
“Clausius–Clapeyron” equation. The thermal energy requirement was calculated by summation of “sensible heat” required to heat the adsorbent and “isosteric heat of desorption” assuming a TSA process. The dynamic performance of the HS-AC was evaluated with “breakthrough experiments” feeding a CO₂/N₂ gas mixture, with compositions representative of different post-combustion streams (14–30 % CO₂) at 30°C and 50°C in a fixed-bed adsorption set-up. Lastly, a variety of TSA/VSA/VTSA process configurations were designed, each with its own set of cycle steps and sequence, as well as operating conditions (feed gas composition, temperature), and their effects on the process performance parameters were analyzed.

This dissertation is arranged in the following order:

Chapter 2 gives brief information about the relationship between CO₂ and climate change; and describes the importance of “CO₂ capture” technologies in the climate change actions, and then gives in-depth theoretical information about the adsorption concept constituting the baseline of this study and its application to carbon capture processes.

Chapter 3 includes material and methods followed throughout the study, including characterization of adsorbent, models for CO₂ adsorption, calculations for energy requirements, and designing and optimizing temperature and the pressure-driven cyclic adsorption process.

Chapter 4 includes the assessment and discussion of the findings. Explicitly, the performance of CO₂ adsorption of produced activated carbon (HS-AC) was figured out under static conditions using a thermogravimetric analyzer. The thermal energy requirement of HS-AC was calculated with the assumption of temperature-driven regeneration. Then, HS-AC's dynamic CO₂ capture performance was tested in a fixed-bed unit in CO₂/N₂ binary mixtures over “consecutive adsorption–desorption cycles”. Thereby, its maximum CO₂ capture capacity at different CO₂ partial pressures and temperature conditions was determined. Lastly, different configurations of
TSA/VSA/VTSA were designed, and their performances were evaluated in terms of “CO₂ purity”, “CO₂ recovery”, “productivity”, and “energy consumption”.

Chapter 5 summarizes key findings and makes suggestions for future research.
2. THEORETICAL BACKGROUND

2.1. Global Warming and Carbon Dioxide (CO₂) Emissions

Global warming refers to the increase in the global average temperature given as combined temperature across both sea and land surfaces. According to “Fifth Assessment Report of the Intergovernmental Panel on Climate Change”, in 2017, the average temperature reached almost “1°C” above pre-industrial levels, and it is increasing at “0.2°C” per decade [1]. The temperature rise has led to increasing extreme weather events and sea levels. These endanger human life and ecological systems on earth directly or indirectly [23].

CO₂, which accounts for around 60% of the heat trapped in the “atmosphere”, is primary driver of “global warming” among all greenhouse gases (GHGs) [23]. Furthermore, energy consumption accounts for the largest share of anthropogenic CO₂ emissions [24].

The following graph (Figure 2.1) shows the world consumption of primary energy resources in Exajoule according to years (1 Exajole is about “2,388 Million Tonnes Oil Equivalent”). As can be interpreted from the graph, in 2019, although the share of the renewables in the energy mixed increased a lot, about “84.3%” of the world's energy consumption was supplied by nonrenewable energies (oil, gas, and coal). This releases about 34,169 million tons (~34.2 Gt) of CO₂ in 2019 (not including other greenhouse gas emissions) [25]. Figure 2.2. illustrates the total amount of anthropogenic CO₂ emissions according to years.

Carbon dioxide concentrations in the atmosphere have steadily risen from “310 to 409.8 ppm” between 1960 and 2020 [26]. Furthermore, global emissions of anthropogenic carbon dioxide (CO₂) are predicted to rise as long as fossil fuels continue to be primary energy source [23].
A historical agreement was signed in “Paris” in “December 2015” at “United Nations Climate Change Conference”. In this conference, political leaders of the world have defined three significant climate goals to reduce the worst effects of global warming. First one is “to peak carbon emissions to the atmosphere as soon as possible”, so that lower them further over the next decade. The second and third goals are “limiting the increase
in global average temperature” and “achieving a neutral carbon balance into the atmosphere”. For the second goal, the “Paris Agreement” refers to “holding the increase in global average temperature to well below 2°C above pre-industrial level”. Actually, the Paris Agreement itself recognizes that “2°C” of temperature increase would still be a bleak outcome for the planet. It emphasizes the need “to pursue efforts to limit the temperature increase to 1.5°C above pre-industrial levels” admitting that this could undoubtedly decrease the risk of “climate change”. Thus, the limit of “1.5°C” is obviously a much more desirable outcome than “2°C”. As the last goal, a neutral carbon balance is needed; furthermore, achieving the net-zero carbon emission is extremely important to meet the target of “2°C” of global temperature increase. There is only a fixed amount of carbon that the earth can emit to retain the temperature limits. It is well illustrated in Figure 2.3, provided by the “Inter-Governmental Panel on Climate Change (IPCC)”.

![Figure 2.3. Cumulative total anthropogenic CO₂ emissions vs temperature anomaly relative to pre-industrial [1].](image)

The increase in “global average temperature” since pre-industrial times is represented on the “vertical axis” of this figure. The “horizontal axis” of which displays the total amount of carbon accumulated in the atmosphere after the Industrial Revolution. With the black line, the sum of carbon we have already released into the atmosphere is shown. The other
lines display various projections for a range of global temperature increase. The relationship is almost linear. It is possible to find the maximum amount of carbon at the bottom, or the conversion to CO₂ at the top, which can accumulate in the atmosphere for a given outcome of global warming. If we take the objective of “2°C” of global warming, the maximum amount of carbon is roughly below “1000 Gigatonnes of Carbon” or “3000 Gigatonnes of CO₂”. When the maximum amount of carbon is reached, then no more carbon to the atmosphere will be emitted than it will be retaken from the atmosphere. This is 'achieving a neutral carbon balance' with 'net zero carbon emissions'.

In recent years, although the increase in renewables and energy efficiency are essential to struggle with climate change, they will not be enough to prevent the “temperature rise” well below “2°C” and achieve a neutral carbon balance. At this point, the “Carbon Capture and Storage (CCS)” technologies can play a crucial role in many ways to make sure that net-zero carbon emissions will be achieved. Firstly, “CCS” can be incorporated into “existing energy systems” without significant system modifications. Besides, “CCS” is an applicable choice for decarbonizing emission-intensive industries such as cement production. Finally, “CCS” can be used in combination with carbon-neutral bioenergy “BECCS” to produce negative emissions.

The “Intergovernmental Panel on Climate Change (IPCC) Special Report” on “Global Warming of 1.5°C” display four scenarios for limiting the rise in global temperature to 1.5°C. As can be seen in Figure 2.4, three of the scenarios include “CCS”. The scenario not including “CCS” needs more drastic human behavior changes. Besides, according to a report prepared by “Organization for Economic Co-operation and Development (OECD)” and “International Energy Agency (IEA)”, “CCS will be the second largest contributor to the reduction of greenhouse gas emissions after energy efficiency improvements” in the estimated scenario for 2050 [27]. Considering the function of CCS implicit in these reports, somewhere between “350-1200 Gigatonnes (Gt) of CO₂” should be captured in this centenary. Annually about “40 Megatonnes (Mt) of CO₂” have been captured and stored until now. According to Global Status of CCS 2020 report, “this amount must be raised by at least 100-fold by 2050 to fulfill the IPCC’s scenarios” [28,29].
2.2. “Carbon Capture and Storage (CCS)” in a Nutshell

“Carbon capture and storage (CCS)” is the method of extracting carbon dioxide (CO₂) created by the combustion of fossil fuels or biomass. CCS prevents the accumulation of that gas in the atmosphere and then transport it to a storage site to isolate it permanently from the Earth's atmospheric carbon cycle, typically by injecting it at a depth of several thousands of meters into a geological reservoir, such as a depleted oil or gas field, or a saline aquifer.

As can be seen in Figure 2.5, there are three main ways of capturing carbon dioxide which are “pre-combustion”, “post combustion” and “oxyfuel-combustion”.

Figure 2.4. Illustrative pathways in the IPCC special report on “Global Warming of 1.5°C”
2.2.1. Pre-Combustion

In “Pre-Combustion Capture”, the capture of carbon dioxide takes place before combustion. Air enters an air separation unit where it is processed to be separated into its two major components, nitrogen, N₂ and oxygen, O₂. The aim here is to produce very high purity O₂ to enter the gasifier. In gasifier, the solid fuel is reacted with O₂ and steam, H₂O, in order to form a synthesis gas consisting of high pressure hydrogen, H₂ and carbon monoxide, CO (gasification). The second step after the gasification is called the water shift reaction, where H₂O is used to shift CO into CO₂ and more H₂. The syngas now consists of high pressure H₂, CO₂ and H₂O. After a drying step, the high pressure CO₂ can be captured and compressed to be transported to permanent geological storage. This leaves nearly pure hydrogen, which can be used to produce electricity without any CO₂ emissions to the atmosphere, or the hydrogen can ultimately be stored or transported away to be used as a raw material for various chemical products, or as a carbon free energy vector. The removal of CO₂ is facilitated in this technology by the fact that the absence of N₂ in the system and high gas pressure of gas stream.

The first power station with gasification and Pre-Combustion Capture, Kemper CCS facility in USA, came close to starting commercial operation in 2017.
2.2.2. Oxy-fuel Combustion

Air enters an air separation unit where it is processed to be separated into its two major components, nitrogen and oxygen. The aim here is to produce very high purity oxygen to enter the boiler of the power station, where combustion takes place, together with the fuel. When fuel is combusted with pure oxygen (in the absence of nitrogen which dilute the gases and flame), the temperature of boiler rises too much. To limit the temperature rise, a fraction of the combustion gases is diverted back to the boiler as a diluent gas. These combustion gases are inert because they have already reacted and don’t contain any fuel. The heat generated by combustion is used to drive turbines and produce electricity. The remaining part of the combustion gases leaves the boiler and enters the capture process. Because there is no nitrogen in this combustion gases, the capture unit is much smaller than which for post-combustion capture technologies. In addition, the partial pressure of CO₂ in the combustion gases is much higher, reaching up to 90% of carbon dioxide, which makes it much easier to separate. After a drying process, the separated CO₂ is compressed to be transported to permanent geological storage. It is possible to achieve capture levels very close to 100% with this technology; however, it requires to rearrange the design of power stations [30,31].

2.2.3. Post-Combustion

The flue gas, which is produced by air and fuel reaction, typically consists of N₂, CO₂, water vapor, SO₂ and particulate matter; thus, it is need to undergo some pretreatments to reduce the impurities and to cool down before capturing process. The CO₂ content in the flue gas dependents on the used fuel type; typically, it ranges from 10-30% CO₂. SaskPower (Canada) and TMC Mongstad (Norway) are the two biggest power generation facilities in the world with post-combustion carbon capture technology [24].

Since it can be easily retrofitted to existing power plants and is cost-effective, post-combustion technology is considered to provide the greatest chance of success among CO₂ capture technologies for large-scale power plants [32].
2.3. Post-combustion Carbon Dioxide Capture Technologies

The separation methods used in post-combustion processes include “absorption”, “adsorption”, “membrane separation”, “cryogenic distillation” and “air separation”.

2.3.1. Absorption

Absorption is the mature technology for the capturing of CO₂. In this method, CO₂-containing flue gas runs through an absorber unit containing amine based solvent and a chemical reaction between “carbon dioxide” and “amine based solvent” will take place due to their acidic and basic nature. Thereby, CO₂ is absorbed selectively. Then, the solvent which is rich in CO₂ is regenerated by heating in a stripper column. After that, the regenerated solvent recycled, while the extracted CO₂ is purified and compressed to be transported to permanent geological storage. The most common solvent in absorption based CO₂ capture is Monoethanoamine (MEA) due to its high affinity for CO₂, low volatility and viscosity. The reaction mechanism is as follows:

As can be seen from the reaction mechanism, carbomate is occurred during the reaction of the amines and carbon dioxide.

The main costs associated with this technique are the energy needed to transfer flue gas through the contactor and heat the regeneration solvent. The diagram of this process is demonstrated in Figure 2.6 [24,33].
2.3.2. Membranes

The gasses separation by membranes is based on the physical or chemical contact between gasses and membranes, so that a gas selectively passes through it. The separation mechanism depends on the type of membrane, whereas the pressure difference on either side of the membrane defines gas flow through the membrane. The factors that determine the behavior of the membrane are permeability and selectivity. Membranes are categorized according to the materials that make up their composition (polymeric, inorganic, carbon, alumina, silica, zeolite, hybrid, absorption, etc.) or their structure (dense, porous or supported liquid) [35].

Membranes is highly effective, particularly when there is high concentration of species that pass through the membrane. Thus, membranes are not likely to be the most effective method for “post-combustion CO₂ capture”, as “CO₂” is a minor component in the gas stream. In comparison, membranes are promising for processes involving relatively high pressure of CO₂ streams, for example for pre-combustion capture [30].
2.3.3. Cryogenic Distillation and Air Separation

This process takes advantage of the difference between the boiling points of the different compounds that make up the gas mixture. The boiling temperature of CO₂ at atmospheric pressure is -78°C, while N₂ is -195.8°C. This means that CO₂ can be separated through compression, refrigeration and expansion stages, and the subsequent distillation is applied on the liquefied gas to separate it into its different components. The key benefit of this technology is that it produces a constant stream of liquid CO₂ which is ready for transport. However, it has high energy costs [30,35].

2.3.4. Adsorption

This technology is the subject of this dissertation, thus will be explored in depth in the next section. Concisely, gas adsorption occurs between the “surface of a solid phase (adsorbent)” and “gas phase” molecules due to attractive forces (physisorption). Such interaction contributes to the accumulation of gas molecules on the solid-gas phase interface, thereby creating an adsorbed (adsorbed) phase whose density is usually considerably higher than the gaseous phase. The strength of interaction depends on the adsorbent nature as well as the adsorbate. This results in equilibrium-based selectivity, i.e. some gas molecules are preferentially adsorbed to others. This constitutes the basic concept of adsorption-based separation methods for CO₂ recovery. The adsorption equilibrium is typically described by adsorption isotherms, showing the adsorbed phase concentration vs. partial pressure. The basic modes of adsorption process operation are categorized according to their driving force for the regeneration of the adsorbent. In “Temperature Swing Adsorption (TSA)”, desorption is driven by increasing the temperature, whereas in “Pressure Swing Adsorption (PSA)” the adsorbate is moved off the solid by a decrease the pressure. When the desorption pressure is below atmospheric temperature, the term “Vacuum Swing Adsorption (VSA)” is widely used [36].

A comparison of these various “post-combustion CO₂ capture” technologies is given in Table 2.1.
Table 2.1. Comparison of various post-combustion CO₂ capture processes [31,37,38].

<table>
<thead>
<tr>
<th>Process</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Absorption</td>
<td>• High capture efficiency of &gt;90%</td>
<td>• High energy penalty for regeneration</td>
</tr>
<tr>
<td></td>
<td>• Most matured and widely applied separation process</td>
<td>• Environmental impact due to solvent degradation</td>
</tr>
<tr>
<td></td>
<td>• Moderate operating cost</td>
<td>• Corrosion problem</td>
</tr>
<tr>
<td></td>
<td>• Handle bulk amount of CO₂ stream</td>
<td>• May produce volatile compounds</td>
</tr>
<tr>
<td>Adsorption</td>
<td>• High capture efficiency of &gt;90%</td>
<td>• Process configuration is complex</td>
</tr>
<tr>
<td></td>
<td>• Lower energy consumption</td>
<td>• Relatively low CO₂ selectivity</td>
</tr>
<tr>
<td>Membrane</td>
<td>• High capture efficiency of &gt;80%</td>
<td>• Aging of membrane</td>
</tr>
<tr>
<td></td>
<td>• Low environmental impact</td>
<td>• Requirement of compression work for driving force</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• High membrane manufacturing cost</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Operational challenges such as fouling and fluxes</td>
</tr>
<tr>
<td>Cryogenic</td>
<td>• Matured separation technology</td>
<td>• High energy requirement to provide sufficient refrigeration</td>
</tr>
<tr>
<td></td>
<td>• CO₂ direct production</td>
<td>• More suitable for high CO₂ concentration, typically higher than 50%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>• Moisture must be removed from the gas mixture before cooling in order to prevent blockage caused by ice particles</td>
</tr>
</tbody>
</table>

2.4. Current Situation of CCS Technologies in the World

Figure 2.7 shows the “development of the commercial CCS facility pipeline” according to their annual CO₂ capture and storage capacity over the past decade. As it can be seen from the figure, there has been strong growth in the total capacity for the past three years [29]. The CO₂ capture and storage capacity of commercial CCS facilities which are in operational mode is about 40 Mt CO₂/year.
Furthermore, Figure 2.8 presents a world map showing the CCS facilities at various stages of development. As seen, the majority of them are located in the United States. China and Europe have the second and third highest amount of projects, respectively.

2.5. Adsorption Phenomena

The adsorption phenomena are described as sticking of fluid molecules on a solid surface. For the gas adsorption process, the number of gas molecules is increased close to the solid surface because of the attractive gas-solid interactions. The reverse process of adsorption is named as desorption where the gas molecules adsorbed solid surface transfer back to the gas phase. In these processes, the solid surface is defined as “adsorbent”. The gas molecules which is interacting with solid surface and capable of being adsorbed is referred as “adsorptive” and the gas molecules which is adsorbed on the solid and forming a separate phase is called “adsorbate” (See Figure 2.9) [39,40].
Figure 2.8. World map of CCS facilities at various stages of development (circle size is proportional to the CO₂ capture capacity of the project) [29].

Figure 2.9. Adsorption system which illustrates the terms of adsorbent, adsorbate and adsorptive [40].
If adsorbents have high “surface area” and high “porous volume”, adsorbate molecules can access the active sites of them. “The International Union of Pure and Applied Chemistry (IUPAC)” have classified the adsorbent pores: “pores of widths less than 2 nm are called *micropores*”, “that between 2 and 50 nm are called *mesopores*”, and “pores with widths exceeding 50 nm are called *macropores*”. In addition, a general distinction has been made between micropores; “width smaller than 0.7 nm are called *micropores*” [41].

Adsorption processes are categorized either chemical or physical adsorption based on strength of interactions between adsorbate and adsorbent. Strength of the bond between the “adsorbate” and “solid surface” can be estimated by the determination of heat of adsorption value. The stronger it is; the more energy is required to regeneration of the sorbent.

Both physisorption and chemisorption must be an exothermic process. It can be confirmed by the thermodynamic perspective. Since, $\Delta G = \Delta H - T \Delta S$ where; “gibbs free energy ($\Delta G$)” should be negative to be adsorption process occur spontaneously and the “entropy change ($\Delta S$)” is also negative due to the decrease in number of degrees of freedom; hence the “enthalpy change ($\Delta H$)” must be negative, indicating adsorption process is exothermic. Because of its exothermic nature, low temperature favors the adsorption; while, high temperature favors the desorption.

In chemical adsorption, a chemical bond with sharing or transferring electrons is formed between the adsorbate and the specific site on the solid surface, and high “heat of adsorption” occurs. Chemical adsorption is characterized by monolayer surface coverage only.

In physical adsorption, bonds are held by Vander Waals forces, which are arisen from long-range London dispersive forces and short-range inter-molecular repulsion. Typically, physical adsorption features low adsorption heat and hence process is fully reversible. Besides, in the physical adsorption, the adsorption equilibrium is achieved
rapidly. In addition, physical adsorption can result in more than one layer of adsorbate coverage on solid surface [39,42].

Table 2.2. list the key differences between “physical” and “chemical” adsorption.

For CO₂ capture, both chemisorption and physisorption are possible mechanisms [44]. For instance, “the heat of adsorption of CO₂ on activated carbon” with physisorption is approximately 25-30 kJ/mol; with chemisorption it can reach values between 40 and 400 kJ/mol. By taking into consideration the volume of flue gas to be handled in CO₂ capture processes, “physical adsorption” is the primary mechanism to minimize the energy requirement. In addition, in the case of “chemical adsorption” where the greater heat released during the adsorption may influence the sorbent uptake [42]. In this dissertation, a physisorbent is used and so chemisorption will not be dealt.

Table 2.2. Differences between physical and chemical adsorption [43].

<table>
<thead>
<tr>
<th>Physical Adsorption</th>
<th>Chemical Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low heat of adsorption</td>
<td>High heat of adsorption</td>
</tr>
<tr>
<td>Monolayer or multilayer</td>
<td>Monolayer only</td>
</tr>
<tr>
<td>Fast, reversible</td>
<td>Slow, irreversible</td>
</tr>
<tr>
<td>Only significant at relatively low temperatures</td>
<td>Possible over a wide range of temperature</td>
</tr>
<tr>
<td>No electron transfer, although polarization of adsorbate may occur</td>
<td>Electron transfer leading to bond formation between the adsorbate and the adsorbent</td>
</tr>
</tbody>
</table>

The adsorption separation can be determined by equilibrium and/or kinetics. The equilibrium mechanism depends on the affinities of adsorbents to the adsorbates, while the adsorption kinetics is based on diffusion rates of adsorbates in the adsorbent pores.
2.6. Adsorption Equilibrium

In an adsorption-desorption process, both the adsorption and desorption occur simultaneously and continuously. While the gas molecules are accumulating on solid adsorbent due to the gas-solid interactions and associated loss of entropy, their concentration decrease in the gas phase. During this, the rate of adsorption decreases due to the reduction of concentration differences of the gas molecules between the “gas phase” and “adsorbed phase”. As adsorption rate decreases, the desorption rate increases. When adsorption and desorption rate is equal, adsorption equilibrium is achieved and there is no more adsorbate accumulation on the solid surface.

The equilibrium relationship between the gas molecule in gas phase and adsorbed phase at a specified temperature is represented by adsorption isotherms. The adsorption isotherm represents the variation of amount of adsorbed gas molecule on adsorbent with pressure, at a constant temperature, for an adsorbate-adsorbent pair. In an adsorption isotherm, while the concentration of gas molecule in gas phase at the equilibrium is defined in partial pressure, the adsorbed phase concentration of which is expressed in mole/volume. If gas molecule is being adsorbed at below the critical temperature of it, the pressure axis in the gas isotherm is expressed in “relative pressure ($p/p^o$)”, where, “$p$ is the equilibrium absolute pressure and $p^o$ is the saturation vapour pressure of the gas component at the given adsorption temperature.” In 1985, “IUPAC” classified pysisorption isotherms in six types based on their shape, then in 2015, different subtypes have been defined. They are illustrated in Figure 2.10 [41,45].
“Type I” is given by microporous solids. It is a reversible isotherm and is limited to single layer adsorption; so it can be represented mathematically by Langmuir equation. It is concave to x-axis and approaches a limiting value. The restrictive uptake is controlled by micropore volume of the solid material rather than its internal surface area. “Type I (a)”, which has a sharp uptake at very low $p/p^o$ because of micropore filling, is obtained with materials having narrow micropores, while “Type I (b)” isotherm is given by microporous materials with a wider pore distribution (width < 2.5 nm).

“Type II” isotherms are obtained by macroporous adsorbents. Multilayer adsorption until high $p/p^o$ is reason of its shape. The inflection point indicates the starting of the multilayer coverage.

Figure 2.10. Adsorption Isotherms by IUPAC classification [45].
• “Type III” isotherm is typical of very weak adsorbate-adsorbent interactions. There is no B point, thus, monolayer formation cannot be identified.

• “Type IV” isotherm is given with adsorbents with mesoporous. Although its shape resembles Type II isotherm at a first look, due to capillary condensation at medium pressures, its shape turns towards the axis of relative pressure and gives a final saturation plateau and a hysteresis loop is observed. Pore condensation is a phenomenon states that “the gas molecules condense to a liquid like phase in a pore at a pressure, \( p \), lower than the saturation pressure, \( p^o \), of the bulk liquid”. The shape of the hysteresis loop may vary for different adsorbate-adsorbent pair and adsorption condition. Type IVb isotherm, which is much less common than Type IVa, does not show any hysteresis loop where adsorption and desorption are identical. It is observed in few mesoporous adsorbents having smaller width of pores such that silica and alumina.

• “Type V” isotherm resembles the Type III one, that includes weak adsorbate and adsorbent interactions, but there is a hysteresis loop (indicating mesoporous solids) and an inflection point at higher relative pressures in this case. The presence of the hysteresis loop is linked to filling of the pores after molecular clustering. Type V isotherm is typical of the water vapour adsorption on hydrophobic microporous (e.g. activated carbon) and mesoporous solids. Adsorption is negligible at low \( p/p^o \), and the width of the hysteresis loop is a function of pore size of the adsorbent. The narrower the pore size, the less width of the hysteresis loop [46]

• “Type VI” isotherm is a stepped isotherm associated with layer-by-layer adsorption on a non-porous solid surfaces [45, 47].
2.6.1. Pure Gas Adsorption Equilibrium Models

There are various adsorption models for the description of adsorption isotherms. The most commonly used models for single gas component adsorption processes are detailed below.

“Langmuir Model”

Langmuir model was proposed in 1918 for the description of Type I adsorption isotherm based on the monolayer adsorption [48]. The adsorption was supposed to occur on an energy homogenous surface with the identical sites for adsorption and it was assumed that there is no interaction between the gas molecule.

Langmuir's model is described by:

\[ q = q_s \frac{bP}{1 + bP} \]  
\( (Eq. 2.1) \)

Where; “\( q \) is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium, \( P \) is the partial pressure of the gas, \( q_s \) is the maximum adsorption capacity, \( b \) is the Langmuir constant and indicates the affinity between the adsorbent and adsorbate.”

“Freundlich model”

It was developed by the German mathematician, physicist and astronomer Erwin Finlay Freundlich [49]. This model is an empirical model that was originally developed by taking into account the adsorbent surface was not homogeneous. Adsorption occurs through a multilayer mechanism in which the adsorption energy decreases exponentially until the adsorption sites are complete. This model allows the adsorption capacity to be correlated with the equilibrium concentration through the following expression (Equation 2.2):
\[ q = k_f P^{1/n} \quad (Eq. 2.2) \]

Where; “\( q \) is the concentration of the adsorbed species at pressure \( P, k_f \) is the Freundlich constant, \( n \) is a dimensionless constant related to the affinity between the adsorbent and the adsorbate” (both are generally dependent on temperature).

**“Sips Model (Langmuir-Freundlich)”**

Recognizing the problem of continuous increment in amount of adsorbed species with its concentration, a new model was proposed with incorporating a finite limit when the concentration is high enough. The new model was formulated by Robert Sips in 1948 [50].

The Sips model is given in Equation 2.3. in the general form:

\[ q = q_s \frac{bP^{1/n}}{1 + bP^{1/n}} \quad (Eq. 2.3) \]

Where; “\( q \) is the concentration of the adsorbed species, \( q_s \) is the maximum adsorption capacity, \( P \) is the equilibrium pressure, \( b \) is the adsorption equilibrium constant, and \( n \) is the heterogeneity parameter of the system”. The structure and energy properties of the solid and the adsorbate may lead to the heterogeneity in the system. The “heterogeneity parameter, \( n \)” is bigger than unity, and increase of this parameter, indicates a higher degree of heterogeneity. As a first approximation, the temperature dependence of \( b \) and \( n \) were taken into consideration while temperature dependence of \( q_s \) was neglected. The calculations of adsorption equilibrium constant, \( b \), and heterogeneity parameter, \( n \), are shown in Equation 2.4 and Equation 2.5, respectively [51].
\[ b = b_0 \exp \left[ \frac{Q}{RT_0} \left( \frac{T_0}{T} - 1 \right) \right] \quad (Eq. 2.4) \]

\[ \frac{1}{n} = \frac{1}{n_0} + \alpha \left( 1 - \frac{T_0}{T} \right) \quad (Eq. 2.5) \]

Where, \( b_0, n_0, \) and \( \alpha \) are the constants; \( R \) is the universal gas constant, \( T \) is the temperature, \( Q \) is the isosteric heat at a fractional loading of 0.5, and \( T_0 \) is the reference temperature which is taken as 30 °C.” [51].

“**Toth Model**”

A variant of the Sips isotherm is the Toth equation, developed in 1971 [51]. Sips equation have a finite saturation limit, if the pressure is sufficiently high. However, Sips equation is not valid for low pressures. Toth model, however, provides a good approximation for both high and low pressure and is in the form given in Equation 2.6.

\[ q^* = q^*_s \frac{b^*P}{[1 + (b^*P)^t]^{1/t}} \quad (Eq. 2.6) \]

Where; \( q^* \) is the concentration of adsorbed species, \( q^*_s \) is the saturation capacity, \( P \) is the equilibrium pressure, \( b^* \) is the adsorption affinity, and \( t \) is the parameter specifying the heterogeneity of the system. When \( t \) is unity, the Toth equation reduces to Langmuir equation. Usually, \( t \) is less than unity, and lower \( t \) indicates a higher heterogeneity in the system. Parameters \( b^* \) and \( t \) depends on the adsorbate-adsorbant pairs” [51].

Similar to the Sips equation, the variation of the equilibrium parameters with temperature must be known in order to extrapolate or interpolate to equilibrium at other temperature
and calculate the isosteric heat. The temperature dependence of parameter $t$ is defined as in Equation 2.7 [51].

$$t = t_0 + \alpha^* \left(1 - \frac{T}{T_0}\right) \quad (Eq. 2.7)$$

Where, “$t_0$ and $\alpha^*$ are the constants. For Toth model, the same relation given in Equation 2.4 is used for describing the dependence of $b^*$ on temperature; however, this time, $Q$ is the heat of adsorption at zero fractional loading”.

### 2.6.2. Multicomponent Gas Adsorption Equilibrium Models

In the case of gas mixtures composed of more than one adsorbate (as representative of real applications) with different affinity towards the adsorbent surface, there is competition between them to bind to the solid. The model of “Ideal Adsorbed Solution Theory (IAST)” is generally used to assesses the “adsorption equilibrium”.

“The Ideal Adsorbed Solution Theory (IAST)”

The “Ideal Adsorbed Solution Theory (IAST)” was suggested by “Myers and Prausnitz” [52]. This theory is on the basis of “the thermodynamic equivalence of the surface tension of each adsorbate in equilibrium”, and it allows predicting the adsorption of the gas mixture by using the “adsorption isotherms” of each individual adsorbate.

For a gas component $i$ in an ideal solution with molar fraction in the adsorbed phase $x_i$:

$$p_i = P y_i = P_i^g(\pi)x_i \quad (Eq. 2.8)$$

$$\sum_{i=1}^{n} x_i = 1; \quad \sum_{i=1}^{n} y_i = 1 \quad (Eq. 2.9)$$
Where; “$p_i$ is the partial pressure of component $i$ in the gas phase, $P$ is the total pressure of the gas phase, $y_i$ is the mole fraction of component $i$ in the gas phase, and $p_i^0$ is the pressure of each pure component $i$ at the same surface pressure of the mixture”. The surface pressure per unit area, $\pi$, is related to $p_i^0$ of each component $i$ by means of the Gibbs adsorption isotherm (See Equation 2.10):

$$\pi A = RT \int_0^{p_i^0} \frac{q_i(p_i)}{p_i} dp_i = \text{constant} \quad (Eq. 2.10)$$

Where; “$A$ is the surface area per unit mass of adsorbent and $q_i(p_i)$ is the adsorption isotherm of the pure component $i$, represented by any isotherm model that fits the experimental data.”

The adsorbed amount can be calculated by Equation 2.11, where $q_t$ is the total amount of adsorbed species:

$$\frac{1}{q_t} = \sum_{i=1}^{n} \frac{x_i}{q_i^0} \quad (Eq. 2.11)$$

$$q_i = q_t x_i \quad (Eq. 2.12)$$

Applying “IAST” on the “Sips model” for gas mixtures, the analytical expression which is given Equation 2.13 is obtained:

$$q_i = \frac{q_t b_i y_i P (\sum_{k=1}^{n} b_k y_k P)^{(i/n)-1}}{1 + (\sum_{k=1}^{n} b_k y_k P)^{(i/n)}} \quad (Eq. 2.13)$$
Where; “i represents the component of interest, y is the mole fraction of each component in the mixture (denoted by the subscript i or k) in the gas phase, and N is the total number of components in the gas mixture.”

2.7. Adsorbent Materials Applied to “CO₂ Capture” and Literature Studies

In CO₂ adsorption processes, selecting the proper adsorbent is critical. The most important attributes of an adsorbent for this application are [10,11]:

(i) High CO₂ adsorption capacity: Amount of carbon dioxide that can be retained in unit mass of adsorbent is known as adsorption capacity. The “adsorption capacity” is directly proportional to “specific surface area”, “pore volume” and “average pore size distribution” of the adsorbent; furthermore, the affinity of CO₂ for a given adsorbent. The “slope of the adsorption isotherm” at “low relative pressure” can be used to deduce this details. It is desired that “CO₂ adsorption isotherm” of an adsorbent have steep slope at low CO₂ partial pressure, corresponding to high uptake. A less steep slope indicates lower CO₂ affinity. The high CO₂ adsorption capacity reduces the amount of sorbent used and so the size of the adsorption unit.

(ii) Fast Kinetics: A fast adsorption/desorption kinetics for CO₂ is needed in a fixed bed adsorption process to have a reasonable cycle time.

(iii) High CO₂ selectivity: The ratio between adsorption capacity of adsorbent for CO₂ and that for other gas component is known as selectivity. Selectivity parameter is the simplest way to describe multicomponent equilibrium. The CO₂ selectivity of adsorbent is related to the product purity; thus, adsorbents should possess a “high selectivity” for CO₂ in comparison to the “other gas components” present in a flue gas.
(iv) Mild condition for regeneration: It is proportional to the value of “heat of adsorption” of solid material. The “heat of adsorption” must be substantially small to ease regeneration of the adsorbent; thereby, to decrease process cost.

(v) Stability: The stability of adsorbents during long cycling effects the frequency of their replacement in the unit. Thus it is also a critical property because it directly effects the economics of process.

(vi) Low cost: The cost should be taken into consideration in the evolvement of any adsorbent for being used in CO₂ capture.

The adsorbents used in CO₂ capture processes can be characterized based on their adsorption mechanism, i.e. physisorbents and chemisorbents.

Chemical adsorbents are operated at higher process temperatures (i.e. 573 K–673 K) and target gas is bind to certain cites on these adsorbents strongly with covalent chemical reactions and so with much higher “heat of adsorption”. Metal oxides, such as calcium oxide, hydrotalcites and supported amine adsorbents, such as organically supported amines (OSA), covalently tethered amines (CTA) are the main chemical adsorbents used especially for CO₂ capture [30].

The most commonly used physical solid adsorbents in CO₂ capture processes are “carbon based materials”, “mesoporous silica”, “zeolites”, and recently “metal organic frameworks (MOFs)”.

“Zeolites” are microporous structures, made up SiO₄ and AlO₄ linked by oxygen atoms, causing rather complex polyhedral structures that enclose cavities of different sizes. Zeolites, in particular, have very high “CO₂ adsorption capacities” at “low pressures” and at “room temperature”, due to a strong quadrupole-ion interaction, but require very high regeneration energies [54].
“Metal-Organic Frameworks (MOFs)” are built by three-dimensional structures of metal ions joined by organic bridges. They are currently studied in wide range due to their large “CO₂ adsorption capacity” and “selectivity”. However, they have the disadvantage of having preferential adsorption of water [30,42].

Activated carbon (AC) is made up of an amorphous structure and a microcrystalline structure that resembles graphite and forms a series of slit-shaped channels. ACs can be obtained from any carbonaceous materials by heat treatment (carbonization), and then physical/ or chemical activation. Principally, any organic material containing a significant amount of carbon is capable of being converted into activated carbon. Natural materials (“wood, peat, coal, lignite” etc.) and industrial or agricultural end products (“slag, sludge, fly ash, saw dust, coconut shells, olive stones” etc.) are utilized for activated carbon production [55].

Activated carbons (ACs) are very competitive among the physisorbents due to [11,56–58]:

- Its acceptable high CO₂ adsorption capacity (around 10-12% by mass at 1 bar and 30°C).
- Its completely reversible CO₂ adsorption mechanism.
- Its preferential adsorption of “CO₂” over “CH₄” and “N₂”. Because the higher “polarizability” and “quadrupole moment” of “CO₂” among the other gases, it interacts with carbon lattice, and CO₂ can enter the pores of ACs more easily.
- Its polar structure; thus hydrophobic nature (no necessary to stringent moisture removal).
- Its lower “heat of adsorption” (25 – 40 kJ / mol) and so less energy requirement for regeneration.
- Its wide availability and relatively low preparation cost.

In particular, CO₂ adsorption is limited to narrow micropores (below 1 nm) at sub-atmospheric pressure. The field of adsorption potential of the opposite walls of the
micropores are overlapped each other and dispersion forces are arised. This creates high adsorption potential. Thereby, ACs which have high volume of micropores are engaging adsorbents for efficient “post-combustion CO₂ capture” applications, where the CO₂ “partial pressure” is small [59].

The main adsorbents studied in the “post-combustion CO₂ capture” literature with their adsorption capaties and working temperature are reviewed in Table 2.3.

Table 2.3. The general CO₂ adsorption capacities of the main types of adsorbents

<table>
<thead>
<tr>
<th>Adsorbent type</th>
<th>Adsorption Temperature (°C)</th>
<th>Adsorption pressure (bar)</th>
<th>CO₂ adsorption capacity (mmol/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon based</td>
<td>≤80</td>
<td>1</td>
<td>≤₃.5</td>
<td>[60–66]</td>
</tr>
<tr>
<td>Zeolite based</td>
<td>≤100</td>
<td>1</td>
<td>≤₄.9</td>
<td>[67–73]</td>
</tr>
<tr>
<td>MOF based</td>
<td>≤100</td>
<td>1</td>
<td>≤₄.5</td>
<td>[74–83]</td>
</tr>
<tr>
<td>Alkali metal carbonate based</td>
<td>≤120</td>
<td>1</td>
<td>≤₉.4</td>
<td>[84–89]</td>
</tr>
<tr>
<td>Amine based</td>
<td>≤60</td>
<td>1</td>
<td>≤₅.5</td>
<td>[90–96]</td>
</tr>
</tbody>
</table>

2.7.1. Activated Carbons (ACs)

In general, an activated carbon is made up an elemental microcrystalline structure and presents a highly disordered structure. Its random arrangement of the layers and the interlinking between them prevents the rearrangement of the structure and giving graphite structure, even if it heats to very high temperatures (~ 3000°C). The hexagonal sheets, or graphenes are folded leaving voids of different sizes, generally between 0.5 and 2 nm, which contributes to develop highly porous structure. (See Figure 2.11). However, because of the high activity of carbon atoms located at the edge of the plane, they are not saturated with carbon atoms and have free electrons. Therefore, the surface of activated
carbons may have also heteroatoms such as oxygen, hydrogen or nitrogen which increase its surface polarity slightly [97].

In general, activated carbons have an essentially microporous structure with slit-shaped pores, the pore diameter of which are defined as the distance between the walls. In addition, they can be in different forms, the most common ones: granular (with particle sizes $> 0.177$ mm), powdery (with particle sizes $< 0.02$ mm).

**Preparation of Activated Carbon**

Activated carbons are obtained in two fundamental ways: “chemical” or “physical” activation.

During “chemical activation”, a precursor material with a chemical activating agent is pyrolysed. The most used activating agents are: NaOH, KOH, H$_3$PO$_4$, ZnCl$_2$ and, H$_2$SO$_4$. Firstly, the chemical solution is mixed homogeneously with the precursor and allowed to act for a certain time, at a temperature below 100°C which is called impregnation. The activating agent can also be mixed with the precursor in solid state, without the need for impregnation. After, a pyrolytic process is applied under an inert atmosphere, where carbonization and activation take place in a temperature range between 400 and 900°C. In this stage, dehydration occurs with increasing the degree of aromatization of the carbonaceous matrix and creating a rigid three-dimensional porous structure, favored by the crosslinking of the carbonaceous matrix. Subsequently, the pyrolyzed product is
cooled and washed to eliminate excess activating chemicals on it. The environmental impact of these chemicals and the prices are considered as the main drawbacks of this activation mechanism [33,56].

Physical activation, which is considered more environmentally friendly, is usually accomplished in two stages: (1) pyrolysis of the carbonaceous raw material under inert atmosphere, (2) gasification of the produced char in the atmosphere containing CO₂, O₂ or steam which are activating agents.

In the first step, precursor material is carbonized under inert gas in order to get rid of the volatile matters and impurities. Then, it yields carbon enriched material which is called char. During devolatilization, most of the heteroatoms on the precursor material, such as O, H and N, are released as volatile matters and the char is generated. This incipient porous structure, which has very low adsorbent capacity, should be activated further to improve its porosity. This carbonization step under inert atmosphere is often conducted at temperature lower than 800°C.

In the activation step, produced char is activated in presence of activating agents that consumes the surface carbon atoms at elevated temperature between 800 - 1000°C. The pores that were initially closed or blocked are opened during this step which leads to desired texture development. The degree of activation, the type of activating agent and the conditions for activation have a direct effect on the properties of the resulting activated carbon. The degree of activation, also referred to as % burn-off, can be considered as percentage of mass loss of carbon precursor during the activation step.

The gasification reaction with CO₂, called “Boudouard” reaction, is an endothermic reaction, so it requires an external contribution of energy. In addition, the reaction between the carbonaceous materials and H₂O is also endothermic. They are simplified in Equation 2.15 - Equation 2.16 [33].
The activation with O\textsubscript{2} is an exothermic process as can be seen in Equation 2.17- Equation 2.18, and thus, the energy for the activation process can be saved with using O\textsubscript{2} as an activating agent. Moreover, O\textsubscript{2} is cheap and available everywhere (air). However, the control of this process is difficult because of high reactivity nature of O\textsubscript{2} \cite{59,100,101}.

\begin{align*}
C + CO\textsubscript{2} &\rightarrow 2CO \quad \Delta H = +173 \ \frac{kJ}{mol} \quad (Eq. \ 2.15) \\
C + H\textsubscript{2}O &\rightarrow CO + H\textsubscript{2} \quad \Delta H = +132 \ \frac{kJ}{mol} \quad (Eq. \ 2.16)
\end{align*}

Among these oxidizing agents, CO\textsubscript{2} activation is most suitable for the CO\textsubscript{2} adsorption process because of its tendencies to form narrow micropores (for instance, the use of stem is prone to formation of mesopores) and its simple nature and low cost \cite{102,103}.

\begin{align*}
C + O\textsubscript{2} &\rightarrow CO\textsubscript{2} \quad \Delta H = -395 \ \frac{kJ}{mol} \quad (Eq. \ 2.17) \\
C + \frac{1}{2} O\textsubscript{2} &\rightarrow CO \quad \Delta H = -111 \ \frac{kJ}{mol} \quad (Eq. \ 2.18)
\end{align*}

As explained, physical activation generally takes place in two steps; however, it can also be conducted in a single step with carrying out the activation directly. It was discovered that “single-step CO\textsubscript{2} activation” without a carbonization step results in microporosity and surface area that is comparable to or greater than that of conventional two-step procedure. In addition, it has lower operation and instillation cost \cite{16,59,104}.

The methodologies with their underlying theories in order to characterize ACs are given in the following section.
2.7.2. Textural Characterization of ACs

Using gas adsorption data is a well-known technique for determining the texture of porous solids. From the analysis of “gas adsorption isotherms”, the informations of “surface area”, “pore-size distribution”, “pore volume” can be obtained.

2.7.2.1. Pure N₂ and CO₂ Isotherms

The most used adsorptive gases for textural characterization of carbonaceous materials are “N₂ at -196°C” and “CO₂ at 0°C”. Although “kinetic diameters” of “N₂ (0.36 nm)” and “CO₂ (0.33 nm)” are similar, the adsorption behaviour of these two adsorptives is quite different. For instance, N₂ adsorption isotherms for characterization of narrow microporous is limited due to the restriction of diffusion rate at such a low temperature. The low rate diffusion prevents the entry of N₂ into the narrow micropore (<0.4 nm). Contrarily, CO₂ adsorption at 0°C is an accepted process for analysing the narrow micropores of the studying carbonaceous material. Because at “0°C”, the “saturation vapour pressure” of “CO₂” is about “3.5 MPa”, which is very high value (the saturation pressure of N₂ at 77 K is about 0.1MPa); therefore, the pressure needed for analyses of micropores is in the moderate range. Through the higher pressure and temperature, diffusion is faster and CO₂ is able to access the smaller pores [45]. As a side note, because of its microporosity structure, the adsorption of the gases (CO₂, N₂) on ACs can be explained by Type –I isotherm.

2.7.2.2. Surface Area

“Brunauer–Emmett–Teller method” is the procedure that is applied widely for evaluating the surface area of porous materials [105]. It is built on the indirect determination of the number adsorbate moles that complete a monolayer ($n_m$) of an adsorbent. The application of the BET method involves two stages. Firstly, the physisorption isotherm data are transformed into linear ‘BET plot’ and the BET monolayer capacity, $n_m$ is obtained. Secondly, by using the $n_m$ the “BET-area” is determined.

The linear form of “BET equation” is given below:
\[
\frac{p}{n \times (p^o - p)} = \frac{1}{n_mC} + \frac{C - 1}{n_mC} \times \frac{p}{p^o} \quad (Eq. 2.19)
\]
Although the BET equation is a quick and easy technique for determination of the materials’ surface area, it can underestimate the total surface area of ACs with high proportion narrow microporous. Therefore, the surface area obtained by this technique for microporous materials is generally called as “apparent surface area” or “BET specific area” [45].

2.7.2.3. Micropore Volume

When the “physisorption isotherm” is “Type I” and the platform is nearly horizontal, the micropore capacity can be determined by measuring the gas’s limiting uptake at the specified temperature temperature, simply. In order to convert micropore capacity into the “micropore volume”, the pores are supposed to be filled with a homogeneous, bulk like liquid. The theory of pore-volume filling proposed by Dubinin in 1965. The Dubinin's theory is common way of evaluating the microporous volume. This adsorption model takes into account the different adsorption energies level that differentiate it from BET theory. For this reason, for microporous solids, the concept of pore volume makes more sense than that of surface area [45,97].

The fundamental expression of DR equation as follows [106]:

\[
\ln W = \ln W_0 - \left(\frac{RT}{\beta E_0}\right)^2 \ln^2 \left(\frac{p^0}{p}\right) \quad (Eq. 2.22)
\]

Where; “W (cm³/g) is the volume of adsorbate condensed in the micropores at temperature T and relative pressure p/p°; W₀ (cm³/g) is the total micropore volume in which adsorbate can access; β is the adsorbate-adsorbent affinity factor with respect to benzene, which is 0.34 in the case of N₂ and 0.36 for CO₂; E₀ is the characteristic adsorption energy.”

According to the Dubin-Radushkevich equation (DR), a plot of \ln W against \ln^2(p^0/p) is linear if the size of micropores has “Gaussian distribution”. The line intersection with the
ordinate axis gives the micropore volume. From the slope of the line, the value of $E_0$ can be obtained which also gives the knowledge on the average width of the pores. The “adsorption” isotherms of “N$_2$ at -196°C” and “CO$_2$ at 0°C” can be incorporated in DR equation for determination of microporous and narrow microporous volume of the carbonaceous adsorbent.

When the microporous adsorbent is very heterogeneous in terms of surface chemistry and texture, the DR equation often fails to linearize the data. To resolve these limitations in the original DR equation, Dubinin and Astakhov (DA) suggested a more general equation [107]. They put a heterogeneity factor, $n$, in the equation instead of the exact value of 2 which indicates homogeneous microporosity. The $n$ value decreases as the width of the micropores increases.

Stoeckli and Ballerini [108] proposed an empirical equation (See Equation 2.23) that relates the characteristic energy ($E_0$) and average micropore width ($L_0$) by the following formula:

$$L_0 (nm) = \frac{10.8}{E_0 (kJ \text{ mol}^{-1}) - 11.4} \quad (Eq. 2.23)$$

In addition, for slit-shaped micropores (the most common in activated carbons) the corresponding surface area ($S_{mi}$) is determined by the Equation 2.24:

$$S_{mi} (m^2 g^{-1}) = 2000 \frac{W_0 (cm^3 g^{-1})}{L_0 (nm)} \quad (Eq. 2.24)$$

Lastly, the “total pore volume” ($Vp$) is assessed by using “N$_2$ adsorption isotherm at -196°C”. It is derived from the N$_2$ adsorbed amount at $p/p^o$ around 0.99.
2.7.2.4. Pore Size Distribution

In addition to knowledge of the volume of pores, their size distribution is the other most important thing for characterization of a carbonaceous material.

For the decision on “pore size distribution” of porous materials, Seaton et al. in 1989 [109] proposed the use of the density functional principle with N₂ adsorption isotherms. Then, the porous carbon network of individual slit-shaped graphitic pores was simulated as a continuous size distribution by Lastoskie et al. [110]. Thereafter, our understanding of liquid behavior and their phase changes restricted by walls, capillaries and slits has significantly improved. This model is further adapted for a variety of porous materials and was eventually accepted as a “standard method” for determining the “pore size distribution” of porous materials using gas adsorption [111,112].

Density functional theory utilizes the interactions of gas-gas and gas-solid to determine the distribution of pore sizes based upon equations of the statistical mechanical model. A serious of individual pore isotherms are theoretically developed in this model. The theoretically developed isotherms which fit the experimental data are used to calculate the “pore size distribution” based on individual pores [113].

The relationship between the experimental and theoretical isotherms of a porous material are interpreted as an equation called a “Generalized Adsorption Isotherm (GAI)” as follows: [45].

\[
N \left( \frac{P}{P_0} \right) = \int_{W_{\text{min}}}^{W_{\text{max}}} N \left( \frac{P}{P_0}, W \right) f(W) dW \quad (\text{Eq. 2.25})
\]

Where; “\(N(P/P_0)\) is experimental adsorption data which is the amount adsorbed at relative pressure \(P/P_0\); \(W\) is pore width; \(N(P/P_0, W)\) is the isotherm on a single pore of width \(W\) and \(f(w)\) is the pore size distribution function.”
Because the NLDFT model considers that the pore walls are infinite in size and they also do not present surface irregularities, false maximum can be seen in the obtained distributions. For example, in the case of slit-type pores defined as two parallel and infinite layers, there would be a favored N₂ adsorption in pores of 1 nm (in this size 3 molecules of N₂ would be accommodated), which causes an apparent maximum in the pore size distribution around at this size.

To avoid this problem, the Quantachrome company developed a new model based on the same DFT theory, called “Quenched Solid Density Functional Theory (QSDFT)” [114]. This model defines the pores with the consideration of the effects of the surface heterogeneity. This minimizes the artifact indicated above and increases reliability of the analysis.

In this dissertation, due to these potentials of ACs and their chance for being able to produce by low cost single step activation methodology mentioned before, biomass based activated carbon were decided to be produced for further adsorption experiments to accomplish adsorption of CO₂ in different gaseous streams. Physical activation in a single step by using carbon dioxide as an activating agent were chosen as the main methodology to produce activated carbon and the agricultural by-products of hazelnut shells were chosen as the precursor of this activated carbon. The first reason of the consideration of the hazelnut shells (HS) from the Turkish food industry as a promising carbonaceous precursor to develop activated carbon is its huge amount and local availability in Turkey. Because, Turkey is the first world hazelnut producer which covers approximately 60-70% of the world’s production (hazelnut production in the world is reached to about 1 million tons/year). For instance, 670 ktone and 515 ktone hazelnut was produced in Turkey in the years 2017 and 2018, respectively and the large amount of shell residue arises from hazelnuts production since it constitutes the half weight of the hazelnut [115]. Secondly, there are many studies about carbon capture with biomass based adsorbents in literature; however, none of these studies evaluate the hazelnut shell as a “precursor” of an “activated carbon” for being used as “CO₂ adsorbent” material in post combustion carbon dioxide capture. Lastly, the shells are usually used as an individual heating, without any
inspection in Turkey and evaluating them as a CO\textsubscript{2} adsorbent may contribute the sustainable waste management.

Case in point, the some of the literature studies evaluating the adsorbents prepared from biomass wastes with CO\textsubscript{2} activation with high CO\textsubscript{2} adsorption performance is presented in Table 2.4.

### 2.8. Adsorption Processes

“Fixed-Bed” and “Moving-Bed” adsorption systems are the two separation systems used in large-scale adsorption processes. In a “fixed bed”, firstly the adsorbent is saturated, then it is regenerated in a cyclic manner (See Figure 2.12 (a)). In “moving bed” systems as shown in Figure 2.12 (b), the adsorbent and the feed are contacting each other continuously [42].

In adsorption of a “fixed bed”, one of the beds is fed by the gas, while the other is being regenerated. When adsorbate gas concentration in the exit gas stream exceeds a certain point, the feed gas starts to pass into the second fresh bed while the saturated bed is being regenerated [123].

In moving bed adsorber, adsorbent is circulated from adsorption bed to regeneration bed. The benefit of moving bed adsorbers is that they reduce the pressure drop observed mostly in fixed beds. In addition, adsorbent which is at equilibrium with feed leaves the bed such that the efficiency of mass-transfer zone is increased. However, in addition to the sorbent attrition problem, the system design is more complex.
In this dissertation, the evaluation of the adsorbent was conducted in a “laboratory scale fixed bed system”. Therefore, the fundamentals of adsorption dynamics of fixed bed process were explained in the following sections.

Table 2.4. Biomass-derived activated carbons with high CO$_2$ adsorption

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Activating agents</th>
<th>Temp. (°C)</th>
<th>P (bar)</th>
<th>Surface area (m$^2$/g)</th>
<th>Pore vol. (cm$^3$/g)</th>
<th>CO$_2$ uptake (mmol/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Almond shell</td>
<td>CO$_2$</td>
<td>25</td>
<td>1</td>
<td>1090</td>
<td>0.5</td>
<td>2.7</td>
<td>[116]</td>
</tr>
<tr>
<td>Grass cuttings</td>
<td>CO$_2$</td>
<td>0</td>
<td>0.10</td>
<td>841</td>
<td>0.38</td>
<td>1.45</td>
<td>[117]</td>
</tr>
<tr>
<td>Rice husk char</td>
<td>CO$_2$</td>
<td>25</td>
<td>1</td>
<td>1097</td>
<td>0.34</td>
<td>3.1</td>
<td>[118]</td>
</tr>
<tr>
<td>Olive stone</td>
<td>CO$_2$</td>
<td>25</td>
<td>1</td>
<td>1079</td>
<td>0.5</td>
<td>2.4</td>
<td>[119]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coconut shell</td>
<td>CO$_2$</td>
<td>0</td>
<td>1</td>
<td>1327</td>
<td>0.65</td>
<td>5.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>25</td>
<td>0.15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[120]</td>
</tr>
<tr>
<td>Food waste</td>
<td>CO$_2$</td>
<td>25</td>
<td>1</td>
<td>830.3</td>
<td>0.49</td>
<td>4.36</td>
<td>[121]</td>
</tr>
<tr>
<td>Palm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kernel Shell</td>
<td>CO$_2$</td>
<td>25</td>
<td>1</td>
<td>367.8</td>
<td>0.22</td>
<td>2.13</td>
<td>[122]</td>
</tr>
</tbody>
</table>
2.8.1. Fixed Bed Column Dynamics

The change in CO$_2$ concentration in a fixed bed as a function of bed position and time is shown in “Figure 2.13” for a CO$_2$-selective adsorption process. Here, “C” and “C$_0$” are the “CO$_2$” concentrations in fluid phase and gas inlet, respectively. The patterns of the
step-shaped concentration profile of CO$_2$ in a fixed bed are explained below in detail [124]:

(i) Initially (t = 0) the bed contains no adsorbate (CO$_2$) (fresh bed) and the gas stream with a given adsorbate concentration (C$_0$) feeds the bed containing solid adsorbent.

(ii) At first (t = t$_1$), the majority of mass transfer occurs near the bed's entrance, where the feed first comes into contact with the solid material. As consequence of adsorption, the concentration of “CO$_2$” in the fluid phase decreases exponentially with distance ultimately to zero.

(iii) At (t = t$_2$), near the inlet, the adsorbent is nearly saturated where the adsorbed concentration equal to the feed concentration. The majority mass transfer occurs away from “the inlet” and concentration gradient takes on a S form. The region in which the mass-transfer takes place is referred as “Mass Transfer Zone (MTZ)” with typical boundaries on “C/C$_0$” to “0.95 to 0.05”.

(iv) The MTZ moves down the bed with time. At the time, in which MTZ reaches the bed outlet (t = t$_3$), adsorbate begins to be detected at the outlet stream. It is known as the breakthrough point at which the gas inlet should be diverted to a regenerated bed in an industrial practice.

The curve in Figure 2.14. which is a graphical representation of the changes of concentration of exit gas as a “function of time” is called “breakthrough curve”. As seen in this figure, the adsorbate concentration is practically zero between the time at adsorption starts and the breakthrough point (t$_3$). In case of continuing to feed the gas stream to the bed beyond the breakthrough point, the outlet concentration gradually escalates until it reaches the feed concentration of adsorbate. At point (t = t$_5$), the bed is fully saturated.
Figure 2.13. Concentration patterns in a fixed bed [56,124,125].

Figure 2.14. Breakthrough curve for adsorption in a fixed bed.
The residence time of the gas in a bed is given by the relationship between the volume of the bed and the volumetric feed flow rate. The choice of “residence time” is the key in the adsorption processes since, if the time is too short, there will be no significant adsorption. Reducing the “feed flow”, increasing the “bed volume”, or adjusting the “feed pressure” may all be used to extend the time.

Dynamic adsorption processes are being investigated by the breakthrough curve; thus, the curve influences the process design. Ideally, a breakthrough curve has vertical shape indicating ideal adsorption. However, in the real systems, some factors which are explained below make its shape more dispersive and less sharp [126]:

- “Shape of the adsorption isotherms”: the breakthrough curves in the case of a favorable isotherm (Langmuir Type) appear to have a uniform pattern, becoming self-sharpening as they progress down the column's length (see Figure 2.15. (a)). In the case of an unfavorable isotherm, the breakthrough curves, on the other hand, do not sharpen but rather become stretched as they progress down the column's length (see Figure 2.15. (b)). If the isotherm is linear, the form of the breakthrough curve remains unchanged, as does the mass-transfer zone.

- “Resistance to diffusion inside the porous structure of the adsorbent”: the curve that has steep slope implies a narrow “mass transfer zone”, and is linked to rapid mass transfer which is desirable. On the opposite, if the “ratio of the mass transfer zone width to the bed length” is higher (distended breakthrough curve), there is a significant resistance in the system to the mass transfer, which slows down the process of adsorption.

- “Axial dispersion of the adsorption column”: because of the different interstitial fluid concentrations, the mixing in the fluid phase along the axial direction is obtained. The shape of the “breakthrough curve” is quite dispersed and the efficiency of the separation process is reduced.
2.8.2. Cyclic Adsorption Processes

Adsorption processes are operated by cycling manner through a given sequence of steps in a fixed bed column to simulate a continuous process. At least one adsorption and one desorption step should be involved in the cycle, to return the solid adsorbent precisely to its previous state and allow it to sustain performance for a long period:

1. In the adsorption step, the matter that is preferentially adsorbed is retained on the adsorbent.

2. Desorption stage, frequently referred to as regeneration stage, during which the adsorbate is released from the adsorbent.

The volume of gas adsorbed increases as the temperature decreases because of “exothermic nature” of adsorption process. In addition, with increased pressure, the adsorbed gas amount increases to maximum capacity. Because of the “high temperature” and “pressure” dependence of gas adsorption, gas adsorption processes have been designed around cyclic temperature or pressure changes, depending on the energy type used to regenerate the bed [42]. These are named as “Pressure/Vacuum Swing Adsorption (PSA/VSA)”, “Thermal Swing Adsorption (TSA)” and combination of two, “Pressure-Temperature Swing Adsorption (PTSA)” and illustrated in Figure 2.16.
TSA takes advantage of the disparity in equilibrium adsorbed amount at various temperatures. As seen in Figure 2.16., the bed is fed at \( T_{\text{ads}} \), \( P_{\text{ads}} \), and then regenerated by heating to \( T_{\text{des}} \), thereby; the adsorbed gases are recovered (from point A to C). In PSA process, the bed is loaded at slightly high pressure, at \( T_{\text{ads}} \), \( P_{\text{ads}} \), then the bed is regenerated by the reduction of pressure to \( P_{\text{des}} \) (from point A to B) (it should be noted that the pressure even after the reduction is still higher than atmospheric pressure). As alternative to PSA process, “vacuum swing adsorption (VSA)” is used where the adsorption takes place at “ambient pressures” and the “desorption pressure” level is below atmospheric pressure. It is also possible to carry out the regeneration of the bed by combining both methods, then being called PTSA or VTSA. Simultaneously increasing temperature and decreasing pressure results in better regeneration, as seen in Figure 2.16 when moving from point A to D.

The steps of the swing adsorption cycles are explained in more detail focusing on the removal of \( \text{CO}_2 \) (heavy component) from \( \text{N}_2 \) (light component) in the sub-section 2.9.3.
2.8.3. Configurations of Adsorption Cycles

Multiple columns are normally operated in parallel to allow an adsorption based process to treat continuous feed and produce a product continuously.

*Pressure Swing Adsorption (PSA)*

In 1960, the basic cycle configuration of PSA system was first defined by Skarstrom [43]. Skarstrom cycle consist of two columns that are subject to “adsorption”, “blowndown”, “purging” and “pressurization” with an arrangement which ensures a continuous flow of the exit gases. The basic steps mentioned for one of the beds in his cycle are illustrated in Figure 2.17. and they are explained below in detail.

1. *Pressurization (step A)*: The bed is pressurized with raffinate product and enriched with the less strongly adsorbed species (N\(_2\)). At the end of the step, the bed is ready for adsorption step. The column is ready to be adsorbed ending of the step.

2. *Adsorption (step B)*: The gas mixture (CO\(_2\) and N\(_2\)) is feeding from bottom of the bed and “adsorption” occurs where CO\(_2\) are retained in the different layers of adsorbent. Raffinate product (N\(_2\)) leaves at the top of the bed. This step ends before CO\(_2\) begins to be detected at the outlet gas stream (breakthrough point); in other words, before the adsorbent reaches saturation.

3. *Blowdown (step C, depressurization)*: The bed is regenerated by reducing the operating pressure. With the pressure reduction, “CO\(_2\)” is partially desorbed from the column and “CO\(_2\)-rich gas” (extract product) is produced. The depressurization step ends when the flow rate of N\(_2\) lean-CO\(_2\) rich gas decreases.

4. *Purge (step D)*: After evacuation step, the bed still has CO\(_2\) both in adsorbed and gas phase. To decrease the strongly adsorbed component in both phases, a “purge step” is carried out in “counter-current” direction. In this step, a part of the raffinate product (N\(_2\)) is recycled to get rid of CO\(_2\) from the voids and to desorb
most of the CO$_2$ molecules that have been trapped in the solid. Thereby, CO$_2$-rich gas stream is produced and more efficient separation can be achieved.

Figure 2.17. One of the beds in a Skarstrom PSA cycle for CO$_2$ adsorption, which is subjected to: (A) pressurization, (B) adsorption of CO$_2$ and production of N$_2$, (C) blow down with production of CO$_2$ and (D) purge with production of CO$_2$.

In the context of carbon capturing, in order to improve PSA cycle efficiency, other PSA processes which include additional steps such as bed pressure equalization and product purge (rinse) have been developed:

- *Product purge (rinse):* After the “adsorption step”, a part of the extract product (e.g. CO$_2$) is introduced to the column in the direction of the feed in order to flushes out N$_2$. This step increases the purity of the component that is strongly adsorbed over the component that is weakly adsorbed.
• *Pressure equalization:* a bed at high pressure is depressurized connecting with another that is at low pressure, until an intermediate pressure value is reached in both. This step reduces the energy consumption associated with pressure variation and allows to improve recovery.

**“Vacuum Swing Adsorption (VSA)”**

VSA shares the common principle with PSA. The only difference is that the regeneration step is conducted at below atmospheric pressure. This vacuum recovery of CO₂ is promising technology with a dual bed configuration to separate CO₂ from flue gases [127–129].

**“Temperature Swing Adsorption (TSA)”**

In the same way as the Skarstrom cycle, the basic TSA cycle has four steps. In this case, product recovery is obtained by with heating and cooling steps instead of pressure changing steps. After the adsorbent and CO₂ in the gas phase have reached equilibrium, the temperature of the column is raised either “directly” using a hot purge or “indirectly” using an external heat exchanger. Then, a cooling step is added after regeneration step.

**“Vacuum-Temperature Swing Adsorption (VTSA)”**

Another alternative technology that is called VTSA would allow a broad regeneration of the solid material and, thus a greater recovery by combination of vacuum and regeneration by temperature increase. The VTSA may have even lower energy requirements than the VSA since slight heating can reduce the level of vacuum necessary to carry out regeneration.

**2.8.4. Characteristic Parameters of CO₂ Adsorption Processes**

There are different parameters that allow characterizing the operation of cyclic adsorption/desorption processes. The main performance indicators of the processes are:
• **Purity (%)**: it can be calculated for both the raffinate and the extract product. It is the ratio of concentration of the adsorbate and the concentrations of all gases at the outlet stream of the bed. In the case of raffinate, the purity is determined from the gas stream leaving the bed during non-productive step (i.e., adsorption step), while for the extract product, it is determined from the gas stream leaving bed during regeneration step.

• **Product recovery (%):** it is defined as the ratio of amount of adsorbate which is desorbed in the regeneration step to the “total amount” of adsorbate which is fed to the column in the “adsorption step”.

• **Productivity (mol /kg-h):** it is the ratio of moles of product recovered versus the cycle time in total and the adsorbent mass. It is beneficial for determining of the size of the adsorption unit and therefore the capital cost.

• **Working capacity (mol/kg):** it is the difference in adsorption capacity of the adsorption step and the desorption step.

• **Energy requirement (MJ/mole):** it represents the total energy required against the moles of product recovered. An estimate of the operating costs of the adsorption process is provided by this indicator.

To achieve a desired level of separation specifications and efficiencies, it is necessary to optimize the cyclic adsorption process configuration for each application and adsorbent.

**2.8.5. Literature on Cyclic Adsorption Processes for CO₂ Capture**

There are many challenges in designing an adsorption based CO₂ capture process. A standard “post combustion flue gas” is at about 40–200°C and 1 bar, it is a mixture consisting of approximately 4–30% CO₂ and mostly N₂. The “low CO₂ concentration” in the “flue gas” brings the main complexity in “CO₂ capture process” because of the high
CO₂ purity and recovery (both above 90%) targets set by various regulatory bodies for capturing CO₂. In addition, the amount of emissions from “existing power plants” are huge; for instance, coal-fired power plant with a capacity of 500 MW produces about “10,000” tons of CO₂/day. This makes CO₂ productivity and the equipment size key elements of adsorption based CO₂ capture process design. Thus, shorter cycle times are required to enhance CO₂ productivity and reduce plant size [130].

The standard cycle configurations including high pressure or low temperature (stripping cycles) feed step aim to achieve pure light product. In the case of using these configurations in CO₂ capture, the purity of “heavy component” (i.e. CO₂) cannot be satisfied because the column contains a huge amount of light gas component before the adsorption step and also purge gas is utilized. Therefore, standard configurations for adsorption-based cyclic processes are not applicable for capturing CO₂ [131].

The design of cyclic adsorption processes to recover heavy components at high purity remains a concern of the recent scientific research. The current design of the cyclic processes focusing on the “recovery of heavy product” with “Pressure/ Vacuum Swing Adsorption (PSA/VSA)” and, then “Temperature Swing Adsorption (TSA)” are summarized in the following paragraphs.

During the last decade, different cycle configurations for VSA/PSA have been investigated by a series of studies for the recovery of the heavy product. In these studies, both the cycle configuration and operating conditions have been optimized considering the separation performance and/or separation specifications.

Some key steps were pointed to achieve “high purity” and “recovery” of CO₂ with the studies conducted by different researchers [130,132–135]. These are: (1) a blowdown step which is introduced before the main evacuation step and decrease the pressure to an intermediate level; (2) a recycling step which is applied after the adsorption step and returns a steam including heavy product to the column; (3) another recycling step which returns a stream with high amount of light product to the beginning of the cycle [131].
To decrease the energy requirement of the pressure driven adsorption processes, “pressure equalization” step was introduced to the basic “Skarstrom configuration” by “ESSO Research group” [136]. In the step, two pressurized beds at different levels were placed with a connection in-between. In that way, the energy requirement for the pressure adjustment was decreased. Agarwal et al. demonstrated the importance of pressure equalization steps in cycle configurations in optimizing the energy consumption of process [137]. Haghpanah et al. represented that while the pressurization of a counter-current light product is important for achieving higher performance, the introduction of a step to recycle the stream enriched in heavy product jeopardized the productivity as well as energy consumption [138]. Contrarily, Reynolds et al. demonstrated that recycling a heavy product could result in higher productivity for some cases [132].

VSA configurations aimed at recovering CO₂ by using various adsorbents have also been published. Shen et al. examined the impact of different operational parameters using activated carbon beads in a single-bed VSA cycle [139]. They achieved a modest performance of 54% “CO₂ purity” and 66% “CO₂ recovery” with a “productivity” of “1.59” mol CO₂ /kilogram-hour with a cycle sequence including “feed pressurization, adsorption, evacuation and light reflux” steps. “Nikolaidis et al.” simulated a “two-bed six-step VSA configuration” including “light product pressurization” step using zeolite, AC and MOF as adsorbents [140]. Although 90% “CO₂ purity” and 90% “CO₂ recovery” were obtained after optimization, they stated that the optimum process efficiency metrics and operating conditions of the various adsorbents were not explicitly connected.

The effect of vacuum pressure on total defined power consumption was studied by Chaffee et al. [141]. For the case studied, the optimum vacuum pressure was specified at 0.04 bar. “Haghpanah et al.”, designed a simple “four-step VSA cycle” with “light product pressurization step” and a lower vacuum pressure of 0.03 bar to recover “CO₂” from 15 vol.% “CO₂” gas stream [142]. In this study, 90% “purity of CO₂” and 90% “recovery of CO₂” were accomplished with an “energy consumption” of 131 kWh/t.

Zhang et al. designed “3-bed VSA” cycles with 6 and 9 steps to discuss the effects of “feed gas temperature”, “evacuation pressure” and “feed concentration” on process
performance both by simulation and experimentation [129]. Krishnamurthy et al., conducted a pilot-scale research based on a “4-step VSA” cycle including “light product pressurization” with “zeolite 13X” as the adsorbent. “95 % purity” and “90% recovery” were obtained with an “energy consumption” of 475 kW/tone [143]. Webley et al., developed a new 4-bed VSA cycle including two “pressure equalization steps” after the CO₂ “rinse step” and got to reduce “specific power consumption” [144].

As aforementioned, various process configurations were investigated by changing their step sequence, operating conditions, type of adsorbent etc. The results reveal that there is “trade-off” between the “separation performance” and “energy efficiency” of the cyclic adsorption process. Furthermore, there is not a consensus about the optimum cycle configurations rendering both high “separation performance” and “energy efficiency”. Therefore, the design of the cyclic processes for “CO₂ capture” purposes is still an active research topic.

For “CO₂ capture” from “post-combustion gas streams”, VSA/PSA processes have been widely studied in the last decade, while the application of TSA for CO₂ capture is in its infancy [145,146]. The first reason for the lagging behind the development of “TSA processes for CO₂ capture” is the use of direct hot non-adsorbing purge gas for the regeneration of bed in conventional applications, like removal of “volatile organic compounds” from the air. However, it causes to a significant dilution problem in CCS applications which require high pure CO₂ recovery. The second reason is that conventional TSA cycles need long heating/cooling times causing lower productivity for a given bed volume [147].

To overcome the drawbacks of TSA processes for CO₂ capture, indirect heating and cooling have been tested by insertion of heating elements or coils with heat transfer fluids wrapped around the adsorber which require modifying the geometry of the column [134,148–150].

TSA processes have some advantages over PSA/VSA for CO₂ capture. Firstly, the large volume of flue gas released near ambient pressure does not need to be pressurized or vacuumed as in PSA/VSA [151]. Secondly, waste heat of power-plants can be utilized.
for supplying the energy required by TSA [152]. Moreover, the ΔT values for the regeneration and adsorption steps in TSA is reported as 30°C to 150°C [131]. Consequently, the combination of low temperatures needed for thermal regeneration and the ability to use waste heat may reduce operating costs and promotes the utilization of TSA processes for “capturing CO₂ from post-combustion gas streams”.

Developing more efficient TSA processes is currently a hot topic in adsorption based CO₂ capture studies. The synthesis of tailor-designed materials, the design of columns which transfer heat effectively and the cycle configuration design are three main topics of ongoing research. The latter is the focus of the present study; therefore, an overview and the recent developments in TSA cycle design are summarized in the following paragraphs.

The first studies dealing with indirectly heated TSA processes were reported in the early 2000’s [153,154]. A novel three-step cycle design, focusing on maximizing the purity of CO₂, was presented by Walton and LeVan [155]. In their design, purge gas was not used for regeneration and the bed was cooled down before the adsorption step. “Grande et al.” and “Ntiamoah et al.” proposed the utilization of a “hot CO₂ product rinse step” to improve the product purity of the product [156,157].

Clausse et al., evaluated the sensitivity of indirectly heated TSA to variations in “desorption temperature” and “purge flow rate” by using a numerical model, and found that for a “desorption temperature” below “130°C”, the productivity was higher at low purge flow rate; although, high flow rate increased the productivity at higher desorption temperatures [149].

Tlili et al. noted that recovery levels are limited when the bed heating was only used as a regeneration step without any means to decrease CO₂ “partial pressure” in the bed. Thus, hot “N₂ gas” was served as a purge gas after the product flow had stopped in the heating step. CO₂ purity is reduced by dilution in proportion to the volume of N₂ gas used, but
additional recovery was gained. Furthermore, “pressure equalization” step, which requires more than two columns, could enhance the “CO₂ purity” [147].

Table 2.5. summarizes the other most relevant literature on CO₂ capture by TSA.

As seen from the literature review, a broad variety of cycles have been proposed to optimize various aspects of the overall process. The results reported in the literature reveal that no “plug-and-play solution” in the design of cycles for CO₂ separation exist. Cycle configurations are designed according to the specific adsorbent properties and the envisioned separation targets for a particular application.
Table 2.5. Characteristic parameters of various TSA arrangements for CO₂ capture from flue gas.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>CO₂ (vol.%)</th>
<th>T&lt;sub&gt;low&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;high&lt;/sub&gt; (°C)</th>
<th>Purity (%)</th>
<th>Recovery (%)</th>
<th>Productivity (kg/m&lt;sup&gt;3&lt;/sup&gt;h)</th>
<th>Energy (MJ/kg-CO₂)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolite 13 X</td>
<td>10</td>
<td>15</td>
<td>150</td>
<td>n.a.</td>
<td>56</td>
<td>39</td>
<td>7.9</td>
<td>[159]</td>
</tr>
<tr>
<td>Zeolite 5A</td>
<td>12.5</td>
<td>25</td>
<td>210</td>
<td>99</td>
<td>79</td>
<td>n.a.</td>
<td>n.a.</td>
<td>[147]</td>
</tr>
<tr>
<td>Zeolite 5A</td>
<td>10</td>
<td>15</td>
<td>150</td>
<td>94</td>
<td>74</td>
<td>37</td>
<td>6.0</td>
<td>[150]</td>
</tr>
<tr>
<td>Zeolite 13 X</td>
<td>10</td>
<td>15</td>
<td>150</td>
<td>94</td>
<td>65</td>
<td>25</td>
<td>8.8</td>
<td>[150]</td>
</tr>
<tr>
<td>AC</td>
<td>17</td>
<td>30</td>
<td>100</td>
<td>43</td>
<td>40</td>
<td>30</td>
<td>n.a.</td>
<td>[160]</td>
</tr>
<tr>
<td>Zeolite 5A</td>
<td>10</td>
<td>20</td>
<td>160</td>
<td>95</td>
<td>81</td>
<td>42</td>
<td>3.23</td>
<td>[149]</td>
</tr>
<tr>
<td>Zeolite 13X-APG</td>
<td>15</td>
<td>25</td>
<td>170</td>
<td>92</td>
<td>78</td>
<td>69</td>
<td>n.a.</td>
<td>[134]</td>
</tr>
<tr>
<td>HMCFC</td>
<td>13</td>
<td>25</td>
<td>125</td>
<td>95</td>
<td>20</td>
<td>n.a.</td>
<td>n.a.</td>
<td>[161]</td>
</tr>
<tr>
<td>Zeolite APG IIA</td>
<td>15</td>
<td>25</td>
<td>150</td>
<td>79</td>
<td>77</td>
<td>60</td>
<td>4.8</td>
<td>[162]</td>
</tr>
<tr>
<td>Polymer-supported amine</td>
<td>13</td>
<td>35</td>
<td>120</td>
<td>90</td>
<td>82</td>
<td>n.a</td>
<td>n.a</td>
<td>[163]</td>
</tr>
<tr>
<td>hollow fiber: zeolite, NaUSY</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>[157]</td>
</tr>
<tr>
<td>Mg-MOF-74</td>
<td>15</td>
<td>30</td>
<td>125</td>
<td>96.22</td>
<td>86.5</td>
<td>64</td>
<td>2.39</td>
<td>[164]</td>
</tr>
<tr>
<td>Zeolite 13X</td>
<td>12</td>
<td>30</td>
<td>150</td>
<td>96</td>
<td>90</td>
<td>35</td>
<td>5.1</td>
<td>[58]</td>
</tr>
<tr>
<td>Zeolite 13X</td>
<td>12</td>
<td>25</td>
<td>150</td>
<td>93.9</td>
<td>91.9</td>
<td>96</td>
<td>2.85</td>
<td>[165]</td>
</tr>
<tr>
<td>MOF-Mn</td>
<td>19</td>
<td>25</td>
<td>150</td>
<td>&gt;96</td>
<td>&gt;90</td>
<td>32-59</td>
<td>3.1-5.8</td>
<td>[166]</td>
</tr>
<tr>
<td>Zeolite 13X</td>
<td>12</td>
<td>30</td>
<td>170</td>
<td>95</td>
<td>90</td>
<td>23.55</td>
<td>4.86</td>
<td>[167]</td>
</tr>
<tr>
<td>Polyaniline</td>
<td>15.03</td>
<td>35</td>
<td>110</td>
<td>47.65</td>
<td>92.46</td>
<td>n.a.</td>
<td>n.a.</td>
<td>[168]</td>
</tr>
</tbody>
</table>

59
3. MATERIALS AND METHODS

3.1. Raw Material

Hazelnut shells (HS) from Turkish food industry were used as the carbon based material in the activated carbon production. The hazelnut shells were ground and sieved between 1-3 mm particle size for further treatments. Firstly, the proximate and ultimate analyses were conducted on the raw samples by using “LECO CHN-2000” and by “LECO VTF-900”. Then, in order to specify possible activation conditions, thermogravimetric analysis (TGA) was performed on the raw adsorbent.

3.2. Optimization of Single Step Activation Conditions in Thermogravimetric Analyser

As a more environmentally friendly approach, the single step physical activation procedure was used to produce activated carbon. Hazelnut shells (HS) were activated with mixture of CO$_2$ and N$_2$ gases in a single step physical activation by using the Setaram TGA92 in order to produce low-cost and sustainable carbon based adsorbents. The optimum activation conditions were specified for maximizing the formation of narrow size-microspores which are highly desired for achieving high CO$_2$ adsorption capacity.

The thermo gravimetric analyser consists of three part: an upper head part through which the gases are introduced; a central part where the graphite heat resistance locates to heat the device, and, a lower head part, through which the furnace gases exit. The gas flow inside the device is in axial direction, since the gas is introduced through the upper part of it and exits through its lower part. The sample is located in a grid crucible and suspended on a wire, both of platinum. Inside the furnace there is a thermocouple close to the crucible position to measure the temperature of the sample.

Before each activation process, approximately 40 mg of sample was dried for 30 minutes at “100°C” under N$_2$ flow. Then, the single step activation process was started by heating the samples to selected activation temperatures (800°C, 850°C and 900°C) with 15°C min$^{-1}$ heating rate and providing a mixture of N$_2$ and CO$_2$ gases at 20 mL/min and 50
mL/min flow rates, respectively. The residence time of the sample in the TGA was determined considering the target solid yields in each experiment which are about 15% and 20% in this dissertation. The solid yields were calculated by dividing the sample mass at the end of the activation process by the mass of the dried sample at the beginning of the activation process as follows:

\[
\text{Yield (\%)} = \frac{m_fA}{m_o} \times 100 \quad (Eq. 3.1)
\]

Where; “\(m_fA\) is the final mass at the end of the activation process and \(m_o\) is the mass of the sample at the end of the drying step.”

The CO\(_2\) uptake performance of produced ACs were evaluated at “25°C” and “atmospheric pressure” in the same TGA feeding a gas stream (50 mL/min flow rate) with 100% vol. CO\(_2\) and 10% vol. CO\(_2\) (balance N\(_2\)). Before the measurements of CO\(_2\) adsorption, the activated sample was dried for 90 minutes at 150°C under 50 mL/min pure N\(_2\) flow. After the drying phase, the sample temperature is decreased to 25°C under the “N\(_2\) flow”. The N\(_2\) flow with 50 mL/min was sustained for about 1h after the mass of the sample becomes constant. Then, the inlet gas was turned to CO\(_2\) with “50 mL/min” to start the adsorption. For the 10% vol. CO\(_2\) adsorption case, “5.6 mL/min” CO\(_2\) flow rate and “50 mL/min” N\(_2\) were used. The CO\(_2\) gas was supplied to the system until there is no change in the “mass of the sample”. The CO\(_2\) “adsorption capacity” is calculated by using the mass gain of the sample during the adsorption process as described below.

After drying step at 150°C, no gas is assumed to be adsorbed on the sample. Then, at 25°C, after the cooling step, the adsorbed N\(_2\) amount is calculated by:

\[
q_{N_2}(\%, \text{mass}) = \frac{m_{TRN_2} - m_{150^°CN_2}}{m_{150^°CN_2}} \times 100 \quad (Eq. 3.2)
\]
Where; \( m_{150^\circ C,N_2} \) is the sample mass at the end of the drying step and \( m_{T,N_2} \) is the mass at temperature \( T \), at the end of the cooling step under \( N_2 \) atmosphere."

Then, similarly, the total \( \text{CO}_2 \) and \( \text{N}_2 \) adsorbed at the adsorption temperature is determined by:

\[
q_{N_2+CO_2}(\% \text{ mass}) = \frac{m_{T,(N_2+CO_2)} - m_{150^\circ C,N_2}}{m_{150^\circ C,N_2}} \times 100 \quad (Eq. 3.3)
\]

Where; \( m_{T,(N_2+CO_2)} \) is the mass of the sample at the end of the adsorption step at temperature \( T \)."

Then, the difference between "\( q_{N_2+CO_2}(\% \text{ mass}) \)" and "\( q_{N_2}(\% \text{ mass}) \)" gives the \( \text{CO}_2 \) adsorption capacity "\( q_{CO_2}(\% \text{ mass}) \)".

The both procedures for activation and \( \text{CO}_2 \) capture were conducted in triplicate for each condition to check the reliability of the data.

### 3.3. Production of Hazelnut Shell Based Activated Carbon (HS-AC) and Experiments of \( \text{CO}_2 \) Uptake Capacity

Once the optimal activation conditions were defined by TGA study, hazelnut shell based activated carbon (HS-AC) were produced in a vertical tubular furnace with sufficient quantity for their characterization and evaluation as \( \text{CO}_2 \) adsorbent.

The procedures described below were done firstly in a small reactor and once the product quality was ensured, the final production stage was handled in a larger reactor. The reactor size, the amounts of samples used and activating agent flow rates are given in Table 3.1.
The dried raw hazelnut shells were placed in the vertical tubular kiln inside a double jacketed quartz reactor which is demonstrated in Figure 3.1. A porous plate was inserted at the bottom of the tube; it holds the solid sample and the tars. The inlet gas was introduced into the reactor via the upper section of the outer jacket. A gas exit was placed at the top of the inner reactor to ensure the discharge of the exhaust gases. Bronkhorst High Tech mass flow controllers were used for adjusting the flow rate and concentration of the feed gas. The air inside the system was removed by supplying CO$_2$ to the reactor for 10 minutes. The vertical tubular kiln was preheated to the specified activation temperature prior to the activation process and “at time zero”, the reactor with dried samples was placed into the furnace, and the CO$_2$ flow with 100 mL/min in small reactor, 370 mL/min in big reactor was started. The activation stage was finished when the targeted carbon yields achieved (15% and 20%) and the reactor allowed cooling down in the kiln. A sample-contact thermocouple was used to monitor the temperature during activation, in order to avoid thermal runaway. The production procedure was performed for three times and then the produced samples were well mixed before the characterization and CO$_2$ adsorption performance assessment, which was being conducted at 25°C under 100% and 10% CO$_2$ molar flow ratio in the same TGA again.

<table>
<thead>
<tr>
<th>Reactor</th>
<th>Inner diameter (cm)</th>
<th>Length (cm)</th>
<th>Raw sample amount (g)</th>
<th>CO$_2$ flow rate (mL min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small</td>
<td>2</td>
<td>45</td>
<td>7</td>
<td>100</td>
</tr>
<tr>
<td>Big</td>
<td>3.8</td>
<td>50</td>
<td>70</td>
<td>370</td>
</tr>
</tbody>
</table>

The dried raw hazelnut shells were placed in the vertical tubular kiln inside a double jacketed quartz reactor which is demonstrated in Figure 3.1. A porous plate was inserted at the bottom of the tube; it holds the solid sample and the tars. The inlet gas was introduced into the reactor via the upper section of the outer jacket. A gas exit was placed at the top of the inner reactor to ensure the discharge of the exhaust gases. Bronkhorst High Tech mass flow controllers were used for adjusting the flow rate and concentration of the feed gas. The air inside the system was removed by supplying CO$_2$ to the reactor for 10 minutes. The vertical tubular kiln was preheated to the specified activation temperature prior to the activation process and “at time zero”, the reactor with dried samples was placed into the furnace, and the CO$_2$ flow with 100 mL/min in small reactor, 370 mL/min in big reactor was started. The activation stage was finished when the targeted carbon yields achieved (15% and 20%) and the reactor allowed cooling down in the kiln. A sample-contact thermocouple was used to monitor the temperature during activation, in order to avoid thermal runaway. The production procedure was performed for three times and then the produced samples were well mixed before the characterization and CO$_2$ adsorption performance assessment, which was being conducted at 25°C under 100% and 10% CO$_2$ molar flow ratio in the same TGA again.
3.4. Characterization of HS-AC

3.4.1. Single Component Adsorption Isotherm

“Textural characterization” of the produced HS-AC samples was accomplished by means of physical “N$_2$ adsorption at -197°C” in “Micromeritics ASAP 2010” and “CO$_2$ adsorption at 0°C” in “Micromeritics TriStar 3020” In this equipments, “the volume of gas adsorbed at equilibrium pressure” is calculated as the difference of the volume of gas introduced and that required to fill the dead space of the tube. Supplying successive gas flow and allowing enough time to reach equilibrium, the “isotherm” is constructed “point by point” in the evaluated pressure range. Note that the samples were first degassed “overnight” at “100°C” and “under vacuum”.

“CO$_2$ adsorption at 0°C” and “sub-atmospheric pressure” is limited to pores width below 1 nm; while, the “N$_2$ adsorption at -196°C” has constraints on the diffusion of the adsorbate in the narrower pores; thus, it covers wider pore sizes. Therefore, the N$_2$ and CO$_2$ adsorption isotherms at these conditions give extensive information on the porous texture of activated carbons. A summary of the methodology used to characterize the
porous texture of the HS-AC is shown in Table 3.2. The models and equations used to determine the textural parameters of adsorbent have been described in Chapter 2 of Theoretical Background.

Table 3.2. Textural characterization from the physical adsorption of N₂ at -196°C and CO₂ at 0°C.

<table>
<thead>
<tr>
<th>Physical adsorption of N₂ at -196°C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total pore volume $V_p$</td>
<td>The adsorbed amount of N₂ at a relative pressure of 0.99</td>
</tr>
<tr>
<td>Specific surface area BET</td>
<td>Brunauer-Emmett-Teller equation [105]</td>
</tr>
<tr>
<td>Micropore volume $W_{0,N₂}$</td>
<td>Dubinin-Radushkevich Equation (DR) assuming the density of the adsorbed phase of 0.808 cm³ g⁻¹, the cross-sectional area of 0.162 nm² and the affinity coefficient of 0.34 [106]</td>
</tr>
<tr>
<td>Micropore surface area $S_{DR,N₂}$</td>
<td></td>
</tr>
<tr>
<td>Characteristic energy $E_{0,N₂}$</td>
<td></td>
</tr>
<tr>
<td>Average micropore width $L_{0,N₂}$</td>
<td>Stoeckli-Ballerini Equation [108]</td>
</tr>
<tr>
<td>Pore size distribution PSD</td>
<td>QSDF (Quenched Solid Density Functional Theory) model assuming slit pores.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Physical adsorption of CO₂ at 0°C</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Narrow micropore volume $W_{0,CO₂}$</td>
<td>Dubinin-Radushkevich (DR) and Dubinin-Astakhov (DA) Equations with assuming the density of the adsorbed phase of 1.023 cm³ g⁻¹, the cross-sectional area of 0.187 nm² and the affinity coefficient of 0.36 [106,169]</td>
</tr>
<tr>
<td>Narrow micropore surface area $S_{DR,CO₂}$</td>
<td></td>
</tr>
<tr>
<td>Characteristic energy $E_{0,CO₂}$</td>
<td></td>
</tr>
<tr>
<td>Average narrow micropore width $L_{0,CO₂}$</td>
<td>Stoeckli-Ballerini Equation [108]</td>
</tr>
<tr>
<td>Pore size distribution PSD</td>
<td>NLDFT (Nonlocal Density Functional Theory) model assuming slit pores</td>
</tr>
</tbody>
</table>

65
Furthermore, the “pure adsorption isotherms” of “N₂” and “CO₂” were determined at sub-atmospheric pressures and at “three different temperatures (30, 50 and 70°C)” in the TriStar 3020 volumetric device to evaluate adsorption capacity of the adsorbent in the possible conditions of flue gases from power plants. During the analysis, the temperature was controlled by “Thermo Haake thermostatic bath” and the samples again were first degassed overnight “under vacuum” and at “100°C” before the measurements. Then, the equilibrium of pure adsorption isotherms was described by Sips and Toth models (described in detail in Chapter 2 of Theoretical Background) at the three temperatures up to atmospheric pressure: after recording the experimental data, fitting of the models on the “experimental results” was performed. The best fit on the “experimental data” was sought by minimizing the difference between the adsorption amounts measured in experiments and calculated in the models at all temperatures. For that, “the Solver” tool of “Microsoft Excel” was used by utilizing the sum of the “squared relative errors (SSE)” as an objective function, which is calculated as in Equation 3.4:

\[
SSE \% = \sqrt{\frac{\sum [(q_{e,i} - q_{p,i})/q_{e,i}]^2}{N - 1}} \times 100 \tag{Eq. 3.4}
\]

Where, “q_{e,i} and q_{p,i} are the measured and calculated amounts adsorbed, respectively, and N is the total number of data.” Therefore, lower the SSE, better the fit of the model to the particular adsorbate-adsorbent system.

### 3.4.2. Multi-Component Adsorption Isotherm

“Ideal Adsorbed Solution Theory (IAST)” of Prausnitz and Myers [52] was used in order to estimate the multicomponent adsorption of the “binary mixture of CO₂ and N₂” from the pure component isotherm parameters obtained experimentally. IAST model is based on thermodynamics and it specifies the relation between the gaseous and adsorbed phases by assuming an ideal behavior similar to “Raoult’s law” for the “vapor-liquid equilibrium”. For the prediction of multicomponent CO₂ and N₂ adsorption, the MATLAB code, IAS, which utilizes IAST and developed by Do was used [170].
3.4.3. Isosteric Heat of Adsorption

In the development of an adsorption-based separation process, the significant temperature changes caused by the exothermic process of adsorption must be taken into consideration. To include the effect of this heat, “isosteric heat of adsorption”, which is defined as the variation of energy in the infinitesimal number of molecules during their phase change from gaseous to adsorbed phase at a certain “temperature”, “pressure”, and specific adsorbate loading, is used [171].

In this dissertation, for both “Sips and Toth” isotherm models, the “isosteric heat of adsorption” of CO₂ on HS-AC was calculated by using the “Clausius–Clapeyron” equation, which defines the change of pressure with varying temperature due to the isosteric heat for constant adsorbed quantity. The Clasius Clapayron equation is given in Equation 3.5 [172]:

\[
\frac{Q_{st}}{RT^2} = \left( \frac{\partial \ln P}{\partial T} \right)_{n^*} = \frac{\ln P}{P_0} = -\frac{Q_{st}}{RT} \left( \frac{1}{T} - \frac{1}{T_0} \right) \quad (Eq. 3.5)
\]

Where; “n* denotes the specific amount adsorbed at a specific pressure and temperature.”

3.4.4. Determination of Densities and Porosities

Real Density (Helium Density)

The real density is “the ratio of the mass of adsorbent to its particle volume”, without considering “interparticle void volume” and “internal pore volume”. A gas, that is not being adsorbed, is used to fill the pores completely with increasing pressure. Thus, Helium is the most appropriate gas to carry out this measurement, due to its small molecular size and its inert nature.

To obtain the real density of the HS-AC sample, the Micromeritics Accupyc 1330 Pycnometer equipment was used at 35°C. The sample was degassed before the measurement to remove adsorbed gases and moisture on it.
**Apparent Density**

The “apparent density” is “the ratio between the mass and the apparent volume of the sample” including the “interparticle void volume” and “internal pore volume”. The apparent volume is always higher than the real one (particle volume) for porous solids. The calculation of the apparent density is carried out by mercury porosimetry. At atmospheric pressure, mercury does not able to penetrate into the pores of adsorbent due to its high surface tension. Pressure must be increased to penetrate the mercury into that pores.

The apparent density measurement of HS-AC sample was carried out with Micromeritics Autopore IV 9500 at 100°C, for about 10 h., after degassing of the HS-AC sample under vacuum.

**Porosity**

Being a characteristic parameter of a packed bed, porosity types are used in the calculations of the fixed bed experiments.

The particle porosity of HS-AC ample was calculated by:

\[
\varepsilon_p = 1 - \left( \frac{\rho_p}{\rho_r} \right) \quad (Eq. 3.6)
\]

Where; “\( \rho_p \) is the apparent density that was determined by mercury porosimetry at 0.1 MPa, and \( \rho_r \) is the real density, determined by helium pycnometry.”

When the adsorbent is used in fixed beds, the bed porosity (external void fraction), \( \varepsilon_b \), is taking into interest. It is the fraction of the bed not occupied by the solid material analogous to fixed bed volume. It was calculated by the following equation for the HS-AC sample and fixed bed used in this study:
\[ \varepsilon_b = 1 - \left( \frac{\rho_b}{\rho_p} \right) = 1 - \left( \frac{m_{ads}}{\rho_p V_b} \right) \quad (Eq. 3.7) \]

Where; “\( \rho_b \) is the bed density (ratio of adsorbent mass, \( m_{ads} \), to bed volume \( V_b \)).” The bed density depends on both the intrinsic density of the material and its packing.

The calculation of bed volume is carried out by using the general formula which is for the calculation of a cylinder volume: by taking the bed height as the average of the adsorbent height value at the beginning and at the end of the experiments, \( h_f \).

\[ V_b = \pi r^2 h_f \quad (Eq. 3.8) \]

Lastly, the total porosity of the bed, \( \varepsilon_T \), was calculated from [173]:

\[ \varepsilon_T = \varepsilon_b + (1 - \varepsilon_b)\varepsilon_p \quad (Eq. 3.9) \]

3.4.5. Scanning Electron Microscopy (SEM)

“Scanning Electron Microscopy (SEM)” makes it possible to obtain two-dimensional images of the surface of a material. The solid surface is swept by means of a programmed scan with a high-energy electron beam. One part of the primary beam which collide with the sample rebounds (backscattered electrons) and another part plucks electron from the sample (secondary electrons). The emitted secondary electrons are picked by the detector, providing an image of the surface morphology of the sample. The resolution is being a few nanometers.

The morphology of the HS-AC adsorbent was assessed by “Field Emission Scanning Electron Microscopy (FESEM)” in a “Quanta FEG 650”. SEM images were taken at a “magnification” of 1500 and at 25 kV. The “backscattered electron images” were analysed by “Energy Dispersive X-ray microanalysis (EDX)” to detect the scarce inorganic matters.
3.4.6. Specific Heat Capacity

“Specific heat capacity” of an adsorbent is the amount of heat that is required to increase the temperature of one-gram sample by 1°C. It is measured in J/g°C. The “specific heat of the HS-AC” was calculated in a “Setaram C80 Calvet Calorimeter”.

3.5. Dynamic Adsorption Experiments of HS-AC in a Fixed Bed

In this dissertation, the dynamic adsorption experiments including both breakthrough experiments and “cyclic swing adsorption experiments” were conducted in a “fixed bed adsorption laboratory unit”.

3.5.1. Fixed Bed Experimental Set-up

Both breakthrough and cyclic CO₂ adsorption experiments were carried out in a “fixed-bed” experimental device designed and tuned by the PrEM Group at INCAR-CSIC. Figure 3.2 shows a simplified schematic “fixed bed experimental set-up”.

Figure 3.2. Fixed bed set-up used for the experimental study.
The adsorption bed (column) consists of a “stainless steel reactor” with 13 mm internal diameter and 133 mm height, which is placed in a vertical position. Inside the reactor, there is a porous plate with a mesh size of 20 µm (to prevent the solid flow), where the adsorbent is placed. The adsorbent in the reactor may reach a height of approximately 120 mm. The feed gas is introduced through the upper part of the column and the outlet gas leaves from the bottom part. The reactor is designed to operate under pressure of up to 230 bar and temperatures of 300°C.

A 102 mm long “K-type thermocouple” is located at a height of 46 mm above the porous plate in order to monitor the bed temperature continuously. The temperature is controlled with PID controller which has two control systems: the first one regulates the coiled electrical resistance around reactor which has 700 W power; the second activates a solenoid valve allowing the passage of a stream of compressed air for cooling.

The “pressure” in the bed is controlled by means of a “back-pressure regulator (BPR)” with a pressure range of 0 to 250 kPa (± 0.1 kPa) (WIKA, model A).

The process feed stream consists of two gas lines, flow rates of which are regulated by “mass flow controllers (Bronkhorst High-Tech)”. The range of the flow rate is in between 1 to 200 cm³/min under normal conditions. These mass flow controllers have a constant accuracy of 1% and a repeatability of 0.1% over their entire operational flow rate range. Through these gas lines, N₂ and CO₂ are fed in different ratios to prepare gas mixtures with different concentrations representing post-combustion gas streams.

A vacuum system consisting of a vacuum controller and an “electromagnetic angle valve” is connected to the experimental unit during the vacuum swing adsorption experiments through a “3-way pneumatic valve”. The vacuum level is regulated with the help of a “vacuum controller” from “Oerlikon Leybold Vacuum”, which is connected to a “Thermovac pressure transducer”.
The exit gas composition is analysed by a Varian CP-4900 “dual channel micro-gas chromatograph”, fitted with a “thermal conductivity detector” (TCD), which enables semi-continuous gas analysis. The chromatograph has a 5 Å molecular sieve column and a Hayesep A column. The TCD, is used “He” as the carrier gas. Furthermore, the mass flow rate of the exit gases is measured by a mini “CORI-FLOW meter (MFM)”.

All data described above are controlled and recorded by a “Supervisory Control and Data Acquisition (SCADA)” system.

3.5.2. Binary CO$_2$/N$_2$ Breakthrough Experiments

“Breakthrough experiments” were conducted in the “fixed bed adsorption column”, described in the previous section, feeding binary gas mixtures (N$_2$/CO$_2$) at a “flow rate of 100 mL/min” with “14 and 30 vol.% CO$_2$ (N$_2$ balance)” at two temperatures (30 and 50°C) and atmospheric pressure. These gas mixtures resemble flue gas compositions from a “coal-fired power plant” and a “cement plant”, respectively.

In the breakthrough experiments, the produced activated carbon (HS-AC) was subject to “consecutive adsorption –desorption cycles” at the each specified adsorption conditions.

Before each breakthrough experiment, HS-AC was pre-conditioned by feeding N$_2$ (“100 mL/min for 60 min at 150°C and atmospheric pressure”) to the reactor. Each cycle was consisted of the following steps: (1) cooling of the adsorbent bed in a pre-conditioning step, for 30 min., passing a flow of “100 mL/min of N$_2$” through the column; (2) adsorption step feeding CO$_2$/N$_2$ gas mixtures (14/86 % and 30/70 v/v) with a “total feed flow rate” of 100 mL/min through the pre-cleaned and pre-conditioned adsorbent bed at the selected adsorption temperature (30 or 50°C) for 30 min; and (3) desorption step switching the gas flow rate to 100 mL/min of N$_2$ and heating the adsorbent bed to 120°C, for 30 min, to fully desorb the gas components adsorbed on the bed. In all the steps, the flow rate of the feed stream was kept constant at “100 mL/min” and the total pressure in the adsorbent bed was around 140 kPa. The CO$_2$ and N$_2$ composition of the effluent gas from the adsorbent bed was continuously monitored as a function of time. Figure 3.3.
shows a sketch of the adsorption-desorption steps during the breakthrough experiments. Table 3.3. summarizes the “experimental conditions”.

In addition, to correct the gas retained in the “dead volume” of the equipment, blank experiments were carried out with filling the bed with glass beads at all the evaluated adsorption conditions.

The amount of adsorbed gas component \( i (i = \text{CO}_2, \text{N}_2) \) at equilibrium was calculated by following mass balance (Equation 3.10) to each adsorption–desorption cycle.

![Figure 3.3. Sketch of the adsorption–desorption cycle configuration in the breakthrough experiments.](image-url)
Table 3.3. Breakthrough experiments conditions

<table>
<thead>
<tr>
<th>Step</th>
<th>Time (min)</th>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
<th>Feed flow rate (mL.min⁻¹)</th>
<th>Feed composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. Drying</td>
<td>60</td>
<td>150</td>
<td>1.4</td>
<td>100</td>
<td>1.00 0.00</td>
</tr>
<tr>
<td>II. Pre-</td>
<td>30</td>
<td>30 / 50</td>
<td>1.4</td>
<td>100</td>
<td>1.00 0.00</td>
</tr>
<tr>
<td>conditioning</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>III. Adsorption</td>
<td>30</td>
<td>30 / 50</td>
<td>1.4</td>
<td>100</td>
<td>0.86 0.14</td>
</tr>
<tr>
<td>IV. Desorption</td>
<td>30</td>
<td>120</td>
<td>1.4</td>
<td>100</td>
<td>0.70 0.30</td>
</tr>
</tbody>
</table>

\[
q_i = \frac{1}{m_{adsorbent}} \left[ \frac{ts}{(A)} (F_{i,feed} - F_{i,our})dt - \frac{(B)}{\gamma_{i,feed}P_b\varepsilon_T V_b}{ZRT_b} - \frac{(C)}{\gamma_{i,feed}P_b V_d}{ZRT_b} \right] \quad (Eq. 3.10)
\]

Where; “\(q_i\) stands for the specific adsorption capacity of the adsorbent for the gas component \(i\); \(m_{adsorbent}\) is the mass of adsorbent in the bed; \(F_{i,feed}\) and \(F_{i,our}\) refer to the molar flow rates of the gas component \(i\) at the inlet and outlet of the bed, respectively; \(ts\) is the time required to reach saturation; \(\gamma_{i,feed}\) is the molar fraction of the gas component, \(i\) in the feed stream; \(P_b\) and \(T_b\) are the pressure and temperature of the bed at equilibrium; \(\varepsilon_T\) is the total porosity of the bed; \(V_b\) is the bed volume; \(V_d\) is the dead volume in the system (tubing + column); \(Z\) is the compressibility factor of the gas component \(i\) at \(P_b\) and \(T_b\); and \(R\) is the universal gas constant. The time required for the bed to become completely saturated, which means the \(CO_2\) concentration at the bed outlet is equal to the feed concentration, \(y_{CO_2, out} = y_{CO_2, in}\), is denoted by \(ts\).”

The “total porosity of the bed, \(\varepsilon_T\)” was calculated by [174]:

\[
\varepsilon_T = \varepsilon_b + (1 - \varepsilon_b) \cdot \varepsilon_p \quad (Eq. 3.11)
\]
Where; “$\varepsilon_b$ is the packed bed porosity and $\varepsilon_p$ is the particle porosity.”

In Equation 3.10, “the term (A) is the total number of moles of gas component $i$ retained in the adsorbent bed over the cycle time. Terms (B) and (C) are correction factors to account for the gas component $i$ which has accumulated in the intra particle voids and dead space of the bed, respectively”.

The determination of term A was carried out by a “graphical method that makes use of the outlet concentration of the component $i$ and the total molar flow rate at each time $t$ between 0 and $t_s$”. The procedure used is presented graphically in Figure 3.4.

![Figure 3.4. Areas identified in the outlet molar flow rate curve of component i used for the calculation of term A.](image)

Figure 3.3 shows the areas into which the breakthrough curve of component $i$ is divided to perform the calculations. The total area, $A_{total}$, is the sum of the areas under and above the curve and corresponds to the total amount of the gas component fed into the bed. It is estimated by multiplying the molar flux of the “gas component $i$” in the “feed stream” ($F_{i,in}$) by the total time of the adsorption stage ($t_{ads}$), as shown in the following expression:

$$A_{total} = F_{i,in} \cdot t_{ads} = F_{i,total} \cdot t_{ads} = A_s + A_b \quad (Eq. 3.12)$$
The area under the curve, $A_b$, corresponds to the amount of non-adsorbed gas that leaves the adsorption bed, and it is graphically calculated by the trapezoidal method. The area above the curve, $A_s$, which represents the amount of gas retained in the adsorbent bed during the adsorption stage, is determined by difference (Equation 3.13). This area stands for the integral of term A in Equation 3.10.

$$A_s = A_{total} - A_b \quad (Eq. 3.13)$$

The breakthrough times ($t_b$) of CO$_2$, meaning that CO$_2$ begins to be detected at the outlet of the bed, were also determined for each adsorption condition. A “relative concentration ($C_{i, out}/C_{i, in}$) of 0.05” was taken as the reference value to determine the breakthrough times.

### 3.5.3. Cyclic CO$_2$ Adsorption Experiments

The performance of the HA-AC adsorbent in cyclic adsorption-desorption operation was assessed by exploring the following “regeneration strategies”: “temperature swing adsorption (TSA)”, “vacuum swing adsorption (VSA)” and a “combination of both (VTSA)”. It is possible to consider any swing adsorption cycle as a series of elementary steps; the cycle configuration varies with the sequence of these steps and their execution.

In the current study, different step configurations were set in both TSA and VSA cycles and “the influence of the cycle design” on the “purity of CO$_2$” in the product stream, the “recovery of CO$_2$”, the “CO$_2$ throughput per mass of adsorbent and cycle time (productivity)”, and the energy requirement of the process were evaluated.

These experiments were conducted in the single fixed bed laboratory unit previously described, using the same feed stream conditions as in the breakthrough experiments: at 30 and 50°C with CO$_2$ contents in the feed of 14 and 30 vol.% (balance N$_2$) and at atmospheric pressure. The adsorption step of the first cycle started with a completely regenerated bed. Each cycle configuration ran for at least 30 cycles to ensure reaching cyclic steady state.
3.5.3.1. Temperature Swing Adsorption (TSA) Configurations

Different TSA configurations including adsorption, rinse with CO₂, desorption, and cooling steps were conducted in the single “fixed bed” unit. In the TSA configurations, durations of the adsorption steps were set to values close to the breakthrough times at each feed condition: “7 min.”, “5 min.”, “4.5 min.”, and “3 min” for the adsorption conditions of 14% CO₂ at 30°C, 30% CO₂ at 30°C, 14% CO₂ at 50°C and 30% CO₂ at 50°C, respectively. In all the configurations, the length of the cooling step was set equal to that of the adsorption step at the corresponding feed condition; furthermore, N₂ gas at a flow rate of “10 mL/min” was used as a sweep gas during the cooling step. Besides, to simulate an operation with a unit of 4 beds and continuous processing of the feed, the sum of the “adsorption” and “cooling” steps’ durations were set equal to that of the rinse and regeneration steps. The total “feed flow” rate was maintained at 100 mL/min. The step configurations of the TSA cycles are explained below:

4-bed 4-step TSA experiments (Configurations A)

These experiments were carried out in the “single fixed bed unit” simulating a “4-step” TSA operation with “4 columns”. This is the basic cycle configuration to determine the process parameters that can be obtained at the selected feed conditions. The results obtained served as a guide to prepare the configuration of subsequent cycles. The steps sequence was as follows: adsorption (I); rinse with pure CO₂ (II); regeneration with indirect heating (III); indirect cooling with N₂ purge (IV). The length of each step was set equal to that of the adsorption step.

Feed: total flow rate of 100 mL/min with 14% or 30% CO₂ was fed to the column at atmospheric pressure and an adsorption temperature of 30 or 50°C. This step was terminated just before the breakthrough of CO₂ in this fixed bed system at the given feed condition.

Rinse with pure CO₂: pure CO₂ gas was used to rinse the bed before the desorption step by setting the rinse to feed ratio (R: F), volume basis, at 0.5.
Regeneration: the regeneration temperature was set at 120°C. Following the rinse step, the bed was heated indirectly to the regeneration temperature by the electric jacket surrounding the fixed bed column. During regeneration, a small flow of N\textsubscript{2} gas was used as a sweep gas. The CO\textsubscript{2} product was collected during the step.

Cooling: after desorption, the bed was co-currently purged with pure N\textsubscript{2} gas at a flowrate of 10 mL/min and an external air cooling system was used to cool the bed.

The schematic diagram of the 4 step – 4 bed TSA experiments is illustrated in Figure 3.5.

![Schematic diagram of the 4 step – 4 bed TSA experiments](image)

Figure 3.5. Cycle schedule for the 4 bed-4 step TSA cycles carried out in the one column adsorption unit (A=adsorption; R=rinse with pure CO\textsubscript{2}; H= heating; C=cooling and purge with N\textsubscript{2}).

4-bed 5-step TSA experiments (Configurations B and Configurations B-I)

These experiments were carried out in the “single fixed bed unit” simulating a “5-step” TSA operation with “4 columns”. The general step sequence of the cycles was as follows:
feed (I); rinse with pure CO\textsubscript{2} (II); regeneration with indirect heating in two steps (III-IV); indirect cooling with N\textsubscript{2} purge (V). In these experiments, the conditions and duration of the adsorption and cooling steps were kept similar to Configurations A; however, the duration of the “rinse step” was shortened to account for the extension of the heating steps. Furthermore, the heating was carried out in two separate steps: the column valve at the bottom of the reactor was closed during the first heating step and it was re-opened and the target product collected during the second heating step where the temperature was set at 120°C. The rinse step in these cycles was carried out with two different R:F ratios of 0.5 (Configuration B) and/or 0.7 (Configuration B-I). The schematic diagram of the “4-bed 5-step” TSA experiments is illustrated in Figure 3.6.

Figure 3.6. Cycle schedule for the 4-bed 5-step TSA cycles carried out in the one column adsorption unit (A=adsorption; R=rinse with pure CO\textsubscript{2}; H1=first step of heating with no flow exit; H2=second step of heating with product collection; C=cooling and purge with N\textsubscript{2}).
4-bed 6-step TSA experiments (Configurations C and Configurations C-I)

All the step conditions, except for the rinse step, were the same as those of Configurations B. Here, the rinse step was performed in two stages with R:F ratios of 0.5 (Configuration C) and/or 0.7 (Configuration C-I), as in Configurations B and Configurations B-I. During the first rinse, while pure CO\textsubscript{2} was purging the bed, the temperature was maintained at the adsorption condition. However, in the second rinse, light heating indirectly applied to the reactor to raise the temperature to a mild level (80°C). The regeneration temperature was set at 120°C with two heating stages as in Configuration B.

The schematic diagram of the 6 step – 4 bed TSA experiments is shown in Figure 3.7

Figure 3.7. Cycle schedule for the 4-bed 6-step TSA cycles carried out in the one column adsorption unit (A=adsorption; R1=rinse with pure CO\textsubscript{2}; R2=rinse with pure CO\textsubscript{2} with light heating; H1=first step of heating with no flow exit; H2=second step of heating with product collection; C=cooling and purge with N\textsubscript{2}).
Finally, the desorption temperature was increased to 130°C in order to evaluate the effects of regeneration temperature on the cyclic adsorption performance of HS-AC in the fixed bed for the Configuration B, which was conducted at the feed condition of 30% CO₂ at 30°C; and, for the Configuration C-I, which was conducted at the feed condition of 14% CO₂ at 50°C. The configurations for which the regeneration temperature was set at 130°C are labelled as Configuration D.

Summary of all different configurations of TSA cycles including step durations, flowrates and step temperatures etc. for different feed conditions, which are studied experimentally in the current research, are presented in detail in the Results and Discussion section.

3.5.3.2. Characteristic Parameters of TSA Configurations

The performance of the separation process was determined with four parameters (see equations 3.14 to 3.17): (1) N₂ purity in the raffinate, (2) CO₂ purity in the product stream, (3) CO₂ product recovery and (4) CO₂ throughput per mass of the adsorbent and cycle time (productivity).

\[
N₂\text{ purity (\%)} = \frac{\int_{t_R}^{t_R + t_{\text{des}}(t)} N₂_{\text{out}} dt}{\int_{t_R}^{t_R + t_{\text{des}}(t)} N₂_{\text{out}} dt + \int_{t_R}^{t_R + t_{\text{des}}(t)} CO₂_{\text{out}} dt} \quad (Eq. 3.14)
\]

\[
CO₂\text{ purity (\%)} = \frac{\int_{t_R}^{t_R + t_{\text{des}}(t)} CO₂_{\text{out}} dt}{\int_{t_R}^{t_R + t_{\text{des}}(t)} N₂_{\text{out}} dt + \int_{t_R}^{t_R + t_{\text{des}}(t)} CO₂_{\text{out}} dt} \quad (Eq. 3.15)
\]

\[
CO₂\text{ recovery (\%)} = \frac{\int_{t_R}^{t_R + t_{\text{des}}(t)} CO₂_{\text{out}} dt}{\int_{t_R}^{t_R + t_{\text{des}}(t)} CO₂_{\text{in}} dt} \quad (Eq. 3.16)
\]

\[
\text{Productivity (mol kg}^{-1}\text{h}^{-1}) = \frac{\int_{t_R}^{t_R + t_{\text{des}}(t)} CO₂_{\text{out}} dt}{t_{\text{cycle}} \cdot m_{\text{adsorbent}}} \quad (Eq. 3.17)
\]
In Equations (3.14) – (3.17), “\( t_R \) refers to the time of the cycle at which the rinse step ends, \( t_H \) refers to the time at which the heating step is finalised, \( t_{cycle} \) refers to the full cycle time. \( F_{N_2, out} \) and \( F_{CO_2, out} \) are the molar flow rates of \( N_2 \) and \( CO_2 \) leaving the column, respectively. \( m_{adsorbent} \) is the mass of adsorbent in the bed”.

### 3.5.3.3. Vacuum Swing Adsorption (VSA) Configurations

The \( CO_2 \) adsorption cycles with vacuum regeneration were conducted experimentally in the “fixed bed unit”. Five different configurations were established and tested for a wide range of feed conditions representative of post combustion flue gas streams: 14 and 30 vol.\% \( CO_2 \) at 30°C and 50°C and atmospheric pressure.

Firstly, the VSA cycles with three steps including adsorption, rinse with pure \( CO_2 \), and blowdown were evaluated (Configuration A and Configuration B). Then, pressurization with feed and \( N_2 \) purge steps were added to the basic three step VSA configurations, thereby; four and five steps VSA configurations (Configuration C, D and E) were obtained. In the design of all these VSA configurations, the total length of the cycles for each configuration at a particular feed condition was kept constant and simulation of a 3-bed VSA operation was considered.

The different cycle configurations with three adsorbent beds arranged in parallel and investigated in the current study are shown in Figure 3.8 and Figure 3.9 based on the step numbers.
During the “adsorption step”, CO$_2$ was adsorbed on the adsorbent packed in the column as the feed gas passed through the column, while CO$_2$-lean gas stream exited the bed. In the rinse step, a flow of pure CO$_2$ fed the bed co-currently to the feed but it was not possible to recirculate part of “the product” from the “evacuation step” in the laboratory set-up. In the blowdown step, the adsorbed CO$_2$ desorbed from the bed and a “CO$_2$-rich gas” was collected by reducing the pressure to vacuum level. Finally, in the last stage of the cycle, a small N$_2$ purge fed the bed at low pressure, to recover the remaining CO$_2$ after the blowdown. In the pressurization step, the bed was directly pressurized with the feed and there was no gas flow at the exit of the column. The bed was pressurized until the pressure in the bed equaled the feed and the bed got ready for the next cycle. As can be seen in Figure 3.9, all the VSA steps were carried out co-currently to the feed.
Figure 3.9. Schemes of the different VSA configurations studied experimentally according to the number of steps: (a) “3 steps”, (b) “4 steps”, (c) “5 steps”. (P = pressurization, A = adsorption, R = rinse with product (CO$_2$), B = blowdown (evacuation), Pu = purge with raffinate (N$_2$)).
In all the cases, the feed gas was fed at a flow rate of “100 mL/min” and the step length was set at a value close to the breakthrough time of the adsorbent HS-AC, at the specified feed conditions, avoiding saturation of the bed during the adsorption step. The duration of the “adsorption step” (including pressurization with the feed) was kept constant in all the evaluated configurations. Furthermore, the vacuum pressure in the line during the blowdown step was set to 0.005 bar to ensure “dynamic vacuum” during the “evacuation step”. At industrial scale, the low-pressure purge step can be performed by recirculating a fraction of the raffinate. As mentioned before, since the experimental unit has a single bed, it is not possible to carry out recirculation and this step was conducted using a stream of 10 mL/min of N₂.

The other design parameters (duration of steps, flow rates, feed temperature, and CO₂ concentration) for each VSA configuration are detailed below:

**3-bed 3-steps VSA experiments (Configuration A and Configuration B)**

These experiments correspond to the simplest VSA configurations evaluated, consisting of three steps: adsorption, rinse, and blowdown (see Figure 3.9. (a)). In Configuration A, the lengths of each step were set equal to “7.5 min”, “5.5 min”, “5 min”, and “3.5 min” for the “adsorption” conditions of 14% CO₂ at 30°C, 30% CO₂ at 30°C, 14% CO₂ at 50°C, and 30% CO₂ at 50°C, respectively. In this configuration, the R/F ratio was set at 0.5.

The 3-step configurations were evaluated under an additional operating condition to investigate the influence of the length of the evacuation step (Configuration B). The length of evacuation step extended to “11.5 min.”, “8.5 min”, “8 min” and “5.5 min” for the feed conditions of 14% CO₂ at 30°C, 30% CO₂ at 30°C, 14% CO₂ at 50°C, and 30% CO₂ at 50°C, respectively. That duration was subtracted from the length of the rinse step not to collapse the 3-beds system configuration (new rinse step durations were as follows: “3.5 min”, “2.5 min”, “2 min”, and “1.5 min” for the feed conditions of 14% CO₂ at 30°C, 30% CO₂ at 30°C, 14% CO₂ at 50°C, and 30% CO₂ at 50°C, correspondingly). To keep the amount of CO₂ fed to the system in the rinse step similar to the previous Configuration A and make the results comparable, the CO₂ flow during the rinse step was increased to
15, 33, 17.5, and 35 mL/min for the “adsorption” conditions of 14% CO$_2$ at 30°C, 30% CO$_2$ at 30°C, 14% CO$_2$ at 50°C and 30% CO$_2$ at 50°C, respectively, in Configuration B.

3-bed 4-step VSA experiments (Configuration C)

A purge with N$_2$ step was incorporated to the previous configuration just after the evacuation step, ending in a cycle configuration with 4 steps (see Figure 3.9. (b)). The length of the purge step was subtracted from the evacuation length; thereby, the total duration of the cycle was not changed and there was no need to add any additional bed to the system. The length of the purge step was set at “3.5 min”, “2.5 min”, “2 min”, and “1.5 min” for the feed conditions of 14% CO$_2$ at 30°C, 30% CO$_2$ at 30°C, 14% CO$_2$ at 50°C, and 30% CO$_2$ at 50°C, respectively. The durations and flowrates of both adsorption and rinse steps were kept similar to Configuration B.

3-bed 5-step VSA experiments (Configuration D and Configuration E)

In Configuration D, a pressurization step was added after the purge step (see Figure 3.9. (c)), resulting in a total of five stages. The total duration of the “pressurization” and “adsorption” steps was equal to the duration of the corresponding adsorption step in previous configurations. Namely, this configuration can also maintain a continuous feed flow with three beds. During the pressurization step, the feed stream was supplied to the reactor, and the bottom valve was closed to increase the pressure inside the reactor to the adsorption level.

The 5-step cycle configuration was evaluated under different operating conditions by extending the duration of the desorption step and, consequently, decreasing the duration of the purge step (Configuration E). Therefore, the lengths of the purge steps decreased to “2.5 min”, “1.5 min”, “1 min”, and “0.5 min”; the lengths of evacuation steps increased to 9 min, 7 min, 7 min, and 5 min for the feed conditions of 14% CO$_2$ at 30°C, 30% CO$_2$ at 30°C, 14% CO$_2$ at 50°C, and 30% CO$_2$ at 50°C, correspondingly.
A summary of all the VSA configurations including step durations, flow rates, step temperatures and pressures etc. for the different feed conditions are presented in detail in Tables 4.17 - 4.21 in the Results and Discussion section.

### 3.5.3.4. Vacuum Temperature Swing Adsorption (VTSA) Configuration

Another alternative that would allow a deeper regeneration of the adsorbent bed and, therefore, a greater “recovery”, would be the combination of “thermal regeneration” and “vacuum”, namely, a “VTSA” process. To investigate this alternative, a final experiment evaluating a VTSA configuration was carried out using Configuration E as a basis, for the feed condition of 30% CO\(_2\) at 50°C. The temperature was increased to 80°C during the vacuum evacuation step.

### 3.5.3.5. Characteristic Parameters of VSA/VTSA Configurations

The characteristic parameters of “raffinate (N\(_2\)) purity”, “product (CO\(_2\)) purity” and “CO\(_2\) recovery” were estimated by the following formulas:

\[
Raftinate\ purity = \frac{\int_{t_R}^{t_R^B} FN_{2,\text{out}} dt}{\int_0^{t_R} FN_{2,\text{out}} dt + \int_0^{t_R} FC_{O2,\text{out}} dt} \quad (Eq. 3.18)
\]

\[
Product\ purity = \frac{\int_{t_R}^{t_R^B} FC_{O2,\text{out}} dt}{\int_{t_R}^{t_R^B} FN_{2,\text{out}} dt + \int_{t_R}^{t_R^B} FC_{O2,\text{out}} dt} \quad (Eq. 3.19)
\]

\[
Product\ recovery = \frac{\int_{t_R}^{t_R^B} FC_{O2,\text{out}} dt}{\int_0^{t_R} FC_{O2,\text{in}} dt} \quad (Eq. 3.20)
\]

When the raffinate purge step is introduced, the “CO\(_2\) purity and recovery” for both the blowdown and purge steps can be determined as follows:
In Equations (3.18) – (3.22), \( t_R \) refers to the time of the cycle at which the rinse step ends, \( t_B \) refers to the time at which the blowdown step is finalized, and \( t_{Pu} \) to the end time of the purge with raffinate step. \( F_{N_2,\text{out}} \) and \( F_{CO_2,\text{out}} \) are the molar flow rates of N\(_2\) and CO\(_2\) leaving the adsorber, respectively.
4. RESULTS AND DISCUSSIONS

4.1. Thermal Characterization of Raw Material and Production of HS-AC

Firstly, the proximate and ultimate analysis of the raw HS sample was conducted, and the results are given in Table 4.1. Although HS sample had a relatively high oxygen content caused by its high volatile matter content, it was mainly characterized by low ash content (0.94 wt.%) and high carbon content (52.27 wt.%), which make it a good “precursor” for development of an “activated carbon”, as reported by the other bio-waste precursors in literature [175–179].

<table>
<thead>
<tr>
<th>Proximate Analysis</th>
<th>Ultimate Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture (%)*</td>
<td>Ash (%)**</td>
</tr>
<tr>
<td>Wet Basis (%)**</td>
<td>Carbon (%)**</td>
</tr>
<tr>
<td>Volatile Matter (%)**</td>
<td>Hydrogen (%)**</td>
</tr>
<tr>
<td>Fixed Carbon (%)**</td>
<td>Nitrogen (%)**</td>
</tr>
<tr>
<td></td>
<td>Oxygen (%)**</td>
</tr>
<tr>
<td>12.73</td>
<td>52.27</td>
</tr>
<tr>
<td>75.83</td>
<td>5.69</td>
</tr>
<tr>
<td>23.23</td>
<td>0.50</td>
</tr>
<tr>
<td>0.94</td>
<td>34.85</td>
</tr>
<tr>
<td></td>
<td>6.69</td>
</tr>
</tbody>
</table>

* % by weight
** % by weight on dry basis

“Single-step physical activation with CO₂” was selected as activation method, because of its lower environmental impact and allowing to be obtain completely microporous structure, compared to chemical activation. To determine the conditions of single step activation, raw HS sample was evaluated in the “Thermogravimetric Analyzer (TGA)” under the flow of mixture of CO₂ and N₂ with the flow rates of 50 mL/min and 20 mL/min, respectively, up to 1000°C with the heating rate of 15°C min⁻¹. As seen in the Figure 4.1, the third sudden weight loss region corresponding to forming of micro-pore structure was observed at the temperature interval of 800°C – 900°C and between 80 – 95 minutes. In the light of this information, the temperatures of “800°C”, “850°C”, “900°C” with the target yield values of 15% and 20% were selected for the single step activation conditions of HS samples.
As an example, the TG and dTG profiles showing the activation process of HS sample conducted at 800°C for 4h under the flow of CO₂ and N₂ mixture is given in Figure 4.2. The first sudden mass loss observed at the temperature about 100°C, is due to the loss of moisture content of the sample. Then, the “second and third peaks” were observed between 300°C and 400°C because of the decomposition of the hemicellulose and cellulose structure in the biomass. Then, the all remaining volatile compounds containing lignin were desiccated at the end of the activation stage (here, at 800°C after 4h). The residual solid, which is also known as char, was named as HS derived activated carbon (HS-AC). Then, the “CO₂ capture capacity” of the activated carbon derived from HS at 800°C for 4 h, HS-AC800, was determined at 25°C and atmospheric pressure in the same TGA device as explained in Metarials and Method part (section 3.2) and the TG profile obtained is given in Figure 4.3. The carbon yields and corresponding CO₂ capture capacities of all HS-AC samples are presented in Table 4.2. for different activation conditions.
Figure 4.2. TG and dTG profiles of the HS-AC sample activation at 800°C for 4 hour

Figure 4.3. TG profile showing CO$_2$ uptake of the activated HS-AC800 sample at 25°C
<table>
<thead>
<tr>
<th>Heating rate $({\degree}C \text{ min}^{-1})$</th>
<th>Flowrate in activation (ml min$^{-1}$)</th>
<th>Adsorption temperature ($^\circ$C)</th>
<th>Flowrate in adsorption (ml min$^{-1}$)</th>
<th>Activation temperature ($^\circ$C)</th>
<th>Residence time (min)</th>
<th>Response yield (wt.%)</th>
<th>$\text{CO}_2$ ratio in mixture (vol.%)</th>
<th>$\text{CO}_2$ capture capacity (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 $\text{CO}_2$: 50 $\text{N}_2$: 20</td>
<td>25 $\text{CO}_2$: 50 $\text{N}_2$: 20</td>
<td>25 $\text{CO}_2$: 50 $\text{N}_2$: 20</td>
<td>120 $\text{CO}_2$: 50 $\text{N}_2$: 20</td>
<td>240 $\text{CO}_2$: 5.6 $\text{N}_2$: 50</td>
<td>120 $\text{CO}_2$: 50 $\text{N}_2$: 20</td>
<td>240 $\text{CO}_2$: 5.6 $\text{N}_2$: 50</td>
<td>240 $\text{CO}_2$: 5.6 $\text{N}_2$: 50</td>
<td>240 $\text{CO}_2$: 5.6 $\text{N}_2$: 50</td>
</tr>
<tr>
<td>$\text{CO}_2$: 50 $\text{N}_2$: 20</td>
<td>800 $\text{CO}_2$: 5.6 $\text{N}_2$: 50</td>
<td>100 $\text{CO}_2$: 50 $\text{N}_2$: 20</td>
<td>100 $\text{CO}_2$: 5.6 $\text{N}_2$: 50</td>
<td>100 $\text{CO}_2$: 5.6 $\text{N}_2$: 50</td>
<td>100 $\text{CO}_2$: 5.6 $\text{N}_2$: 50</td>
<td>100 $\text{CO}_2$: 5.6 $\text{N}_2$: 50</td>
<td>100 $\text{CO}_2$: 5.6 $\text{N}_2$: 50</td>
<td>100 $\text{CO}_2$: 5.6 $\text{N}_2$: 50</td>
</tr>
</tbody>
</table>
As can be seen in Table 4.2, for all activated samples, the CO$_2$ capture performance is higher at the yield of 15%. This can be attributed to the longer activation duration which provides more time to adsorbate for reacting with the carbon on the sample surface, resulting in the development of more microporosity.

Multiple regression and multiple range tests were applied using StatGraphics software for the determination of optimum activation conditions. Both yield and activation temperature were found as significant parameters for the CO$_2$ capture capacity. From multiple range test, two homogenous groups were identified: the activation temperature at 800°C, the activation temperatures at 850°C and 900°C, which means the activation at the “temperatures” of 850°C and 900°C are statistically indifferent. Therefore, the activation temperature of 900°C was not utilized due to the high energy demand. Considering these analyses, activating the samples at 800°C for 4 hours and at 850°C for 1.5 hours were identified as two feasible production processes in the quartz bed reactor.

The activation was performed in a small reactor (I.D. 2.9 cm) and the adsorption performances of the samples were examined (See Table 4.3). Then, keeping the superficial velocity constant, the activated “carbon production” was scaled up by using a “larger reactor (I.D. 3.9 cm)”. Then, in addition to the performance evaluation under pure CO$_2$ flow, the CO$_2$ uptake performances of these final products were also evaluated under the gas flow with 10% vol. CO$_2$ concentration, which is a representative concentration value of flue gas from “coal power plants”.

Table 4.3. The yield and CO$_2$ uptake of the HS derived activated carbon at smaller scale

<table>
<thead>
<tr>
<th>Activation Temperature (°C)</th>
<th>Activation Duration (min)</th>
<th>Carbon Yield (%)</th>
<th>CO$_2$ capture temperature (°C)</th>
<th>CO$_2$ ratio in gas mixture (%)</th>
<th>CO$_2$ Capture Capacity (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>240</td>
<td>14.78</td>
<td>25</td>
<td>100</td>
<td>9.7</td>
</tr>
<tr>
<td>850</td>
<td>90</td>
<td>14.26</td>
<td>25</td>
<td>100</td>
<td>9.6</td>
</tr>
</tbody>
</table>


Table 4.4 shows the CO\textsubscript{2} uptake performance obtained at the larger scale. The CO\textsubscript{2} uptake capacities of the HS based activated carbon samples (HS-AC) are similar to those of biomass-derived adsorbents which are reported previously [180,181].

Table 4.4. Overall yield and CO\textsubscript{2} uptake of the HS derived activated carbon at higher scale

<table>
<thead>
<tr>
<th>Activation temperature (°C)</th>
<th>Activation duration (min)</th>
<th>Carbon yield (%)</th>
<th>CO\textsubscript{2} capture temperature (°C)</th>
<th>CO\textsubscript{2} ratio in gas mixture (%)</th>
<th>CO\textsubscript{2} capture capacity (wt.%</th>
<th>CO\textsubscript{2} capture capacity (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>240</td>
<td>15.98</td>
<td>25</td>
<td>10</td>
<td>9.9</td>
<td>2.26</td>
</tr>
<tr>
<td>850</td>
<td>90</td>
<td>17.50</td>
<td>25</td>
<td>10</td>
<td>9.7</td>
<td>2.17</td>
</tr>
</tbody>
</table>

4.2. Textural Characterization of the Produced HS-AC

The “N\textsubscript{2} adsorption isotherms at -197°C” and “CO\textsubscript{2} adsorption isotherms at 0°C” of the sample are presented in “Figure 4.4 (a) and (b)”, respectively. Having a sharp elbow at very low relative pressures, N\textsubscript{2} adsorption isotherms, Figure 4.4 (a), represents the characteristics of the Type I pattern according to the classification of “International Union of Pure and Applied Chemistry (IUPAC)” [182]. Moreover, as seen in Figure 4.4 (a) and (b), the desorption curve overlaps the adsorption curve. Therefore, it can be revealed that the adsorption mechanism is “micropore filling” and the activated sample is nearly strictly microporous [183]. The samples activated at 800°C (HS-AC800) and 850°C (HS-AC850) exhibit almost the same isotherm patterns and also, their bulk densities measured at 0.1013 MPa are very close (0.64, 0.73 g ml\textsuperscript{-1}, correspondingly) that is an importing factor to determine adsorber volume. Therefore, the following experiments and analyses were done only for the samples activated at 850°C, since the production at 850°C is more cost-effective due to its shorter activation duration. Here after, HS-AC850 is called only HS-AC.
The textural parameters calculated using the isotherms obtained in the experiments are shown in Table 4.5. The nitrogen equivalent “BET surface area” was calculated as 708 m$^2$/g. The surface area obtained from CO$_2$ isotherms on the basis of Dubinin–Radushkevitch approach is 1093.78 m$^2$ g$^{-1}$ at 0°C. Both Dubinin-Radushkevitch (DR) equation and Dubinin–Astakhov (DA) equation, which is the more general expression of DR equation and applicable also for adsorption on structurally heterogeneous solids, were utilized and both models fit very well with the CO$_2$ isotherms obtained experimentally (see Figure 4.5).
The $n$ value in DA equation was calculated as 1.8, indicating a small deviation from the homogeneous micropore structure. Moreover, the presence of the slightly heterogeneous porosity can also be deduced by examining the $N_2$ adsorption graph where the plateau at high relative pressures is slightly slant (see Figure 4.4 (a)) [106]. The total pore volume and micropore volume obtained by $N_2$ adsorption isotherms shows that 92% of the entire pores are micropores. Furthermore, the narrow micropore volume calculated using $CO_2$ adsorption isotherms reveals that the micropores are mostly composed of narrow micropores. This is also evident in the close values of micropore and narrow micropore widths calculated by $N_2$ (0.72 nm) and $CO_2$ (0.59 nm) adsorption isotherms, respectively. In addition, while the characteristic energy of $N_2$ was calculated as 26.45 kJ mole$^{-1}$, which of $CO_2$ was calculated as 29.80 kJ mole$^{-1}$, showing the higher affinity of the HS-AC sample with $CO_2$.

These results are in line with the previous studies stating the single step $CO_2$ activation as an efficient process to develop microporosity in biomass based activated carbons [177,181,184–188].

**Figure 4.5.** DA model fit with $CO_2$ pure adsorption isotherms at 0°C.
4.2.1. Pore Size Distribution of HS-AC

CO₂ and N₂ isotherms of HS-AC sample were analyzed by the QSDFT (Figure 4.6) and NLDFT (Figure 4.7) models, respectively, and a major contribution of pores under "0.6 nm" was confirmed. According to the NLDFT, 52% of the total narrow micropore volume was comprised of pores with sizes below 0.36 nm, which is desirable for "CO₂ capture" under typical "post-combustion" conditions.
NLDFT model gave sharp peak in the narrower micropore sizes (between 0.16 nm and 0.18 nm) (see Figure 4.7); however, it is not realistic and an artefact. The reason is that NLDFT only considers slit shaped pores and does not take into account rugosity of the surface.

Figure 4.6. \(N_2\) adsorption QSDFT PSD of HS-AC

Figure 4.7. \(CO_2\) adsorption NLDFT PSD of HS-AC
4.2.2. Scanning Electron Microscopy (SEM) of HS-AC

To gather more insights into the characteristics of HS-AC, it was analyzed by SEM/EDX. Figure 4.8 shows the particle morphology of HS-AC. The well-developed porous structure with different pore size formed during the CO2 single stage activation can be seen in the SEM images.

In addition, EDX analysis (inset in Figure 4.8 (b)) shows high intensity carbon peak indicating there is almost no impurities on the produced activated carbon.

Figure 4.8. SEM images of HS-AC, the scale bars are (a) 1 mm (b) 50 μm (c) 40 μm (d) 10 μm.
4.3. Single Component CO$_2$ and N$_2$ Adsorption on HS-AC

4.3.1. Single Component Adsorption Isotherms

Single-gas adsorption isotherms of “CO$_2$ and N$_2$” for HS-AC sample were measured at “30°C”, “50°C” and “70°C” at “sub-atmospheric pressure” to estimate the adsorption equilibrium of “CO$_2$ and N$_2$” at the post-combustion conditions. The adsorption data were fitted by Sips and Toth models using solver tool in EXCEL. Thereby, the optimal values of the isotherm parameters for each adsorbate and each temperature were determined. Figure 4.9 represents the “single-gas adsorption isotherms of CO$_2$ and N$_2$”. As seen in this figure, both models fit well to experimental data of the sample.

First of all, Multifactor ANOVA test was conducted and it was showed that this two factors, temperature and absolute gas pressure, have a statistically significant effect on pure gas adsorption isotherms at the 95% confidence interval (p values were 0.0277 and 0.0250 which were smaller than 0.005). As stated, temperature has substantial effect on the “equilibrium adsorption capacity” at a given pressure. Furthermore, the “CO$_2$ adsorption capacity” of HS-AC is significantly greater than the N$_2$ adsorption capacity at the same “pressure” and “temperature”. This is because of the higher “quadrupole moment” of CO$_2$ that leads to a “higher affinity of the adsorbent surface for CO$_2$” [170]. The maximum adsorption amount of CO$_2$ on the activated HS-AC sample at 120 kPa reached the value of 2.9 mmol g$^{-1}$ at 30°C.

The pure isotherm parameters of the Toth and Sips models for HS-AC are presented in Table 4.6. In the calculation, the maximum adsorption capacity, $q_s$, was assumed to be independent of temperature, while the adsorption equilibrium constants, $b$ and $b^*$, and the heterogeneity factors, $t$ and $n$, were assumed to be temperature dependent. The parameters $t$ in Toth model, which is generally smaller than unity, $n$ in Sips model, which is generally more than unity, characterize the system’s heterogeneity. As the heterogeneity parameter gets close to unity, both models approach the Langmuir model, for which the system is completely homogeneous. Heterogeneity parameters of $n$ and $t$, approach the unity as the temperature increases, which indicates that the system is more homogeneous at higher temperatures. Furthermore, the “affinity parameters”, $b$ and $b^*$, increase with decreasing...
adsorption temperature. Lastly, it is worth noting that Toth model assumes zero loading in the estimation of “heat of adsorption”, “$Q$”, while Sips model calculates $Q$ at a fractional loading of 0.5, which is the underlying reason of the higher $Q$ values obtained for Toth model in Table 4.6 [170,189].

![Graphs showing CO$_2$ and N$_2$ adsorption isotherms](image)

Figure 4.9. Adsorption equilibrium isotherms of CO$_2$ (a), and N$_2$ (b) on HS-AC at 30, 50 and 70°C (Solid points represent experimental data. The solid lines show the fitting to the Toth model and the dashed lines show the fitting to the Sips model).

### 4.3.2. Isosteric Heat of Adsorption

Information about the “isosteric heat”, “$Q^\text{st}$”, is important for the design of adsorption process. The heat emitted by the adsorbate as it transitions from the gaseous to the adsorbed phase is partially absorbed by the solid adsorbent, which leads to an increase in temperature of the adsorbent, and therefore slows down the “adsorption kinetics” [194,195].

In the current study, the “isosteric heat of adsorptions” of the “CO$_2$” and “N$_2$” on the sample were predicted by applying “Clausius-Clapeyron” equation to the “single component adsorption” data gotten by experiments and by “Sips model”. As seen from
Figure 4.10 (a), (b), “isosteric heat of adsorption” of CO₂ predicted from “Sips model” adsorption data were in the range of 35.64–25.42 kJ mol⁻¹; while, the “isosteric heat of adsorption” value of the N₂ for the sample was obtained as 16.77 kJ/mole. The higher isosteric heat value of CO₂ implies the stronger interaction of CO₂ with HS-AC than that of N₂, in agreement with the pure component adsorption isotherms.

Table 4.6. Toth and Sips parameters for the adsorption of CO₂ and N₂ on HS-AC at 30°C, 50°C, 70°C

<table>
<thead>
<tr>
<th>Model</th>
<th>Adsorbate</th>
<th>Temperature (°C)</th>
<th>b*(Toth) (m mole g⁻¹)</th>
<th>b (Sips)</th>
<th>t (Toth) n (Sips)</th>
<th>Q (Joule mole⁻¹)</th>
<th>SSE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toth</td>
<td>CO₂</td>
<td>70</td>
<td>0.0032</td>
<td>0.3705</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>0.0068</td>
<td>0.3467</td>
<td>35767.56</td>
<td>0.042034</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>0.0165</td>
<td>0.3199</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>70</td>
<td>0.0004</td>
<td>0.6801</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>0.0006</td>
<td>0.6611</td>
<td>13998.26</td>
<td>0.00007</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>0.0008</td>
<td>0.6396</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sips</td>
<td>CO₂</td>
<td>70</td>
<td>0.0019</td>
<td>1.2747</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>0.0030</td>
<td>1.3321</td>
<td>21796.77</td>
<td>0.06926</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>0.0051</td>
<td>1.4035</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>N₂</td>
<td>70</td>
<td>0.0008</td>
<td>1.0278</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>50</td>
<td>0.0010</td>
<td>1.0376</td>
<td>10781.90</td>
<td>0.00005</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
<td>0.0013</td>
<td>1.0479</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Qₘₐ value for N₂ remained almost constant (≈17 kJ mol⁻¹, see Figure 4.10 (b)) during the adsorption process, Qₘₐ value for CO₂ had an initial decreasing trend and approaches to a constant value with increasing loading of CO₂ (see Figure 4.10 (a)). The high isosteric heat value of CO₂ at the beginning of the adsorption can be attributed to the filling of narrow micropores first; and the decreasing isosteric heat in the later stages of the adsorption indicates the weaker interaction of CO₂ molecules in the larger micropore sizes [14].
Multi-Component Adsorption Isotherms

Binary adsorption equilibrium of “CO₂” and “N₂” mixtures was predicted by utilizing the MATLAB script IAS, which is based on the “Ideal Adsorption Solution Theory (IAS)” and written by D.D.Do [170], and by using the Toth model parameters. In Figures 4.11 – 4.13, the adsorbed amount of CO₂ and N₂ versus partial pressure of the adsorbate are presented for the volume concentration ratios of (a) CO₂/N₂:14/86 (b) CO₂/N₂:30/70 at “30°C”, “50°C”, and “70°C”, where conditions which may exist in a post-combustion capture unit, respectively [190]. In the figures, the IAS binary adsorption isotherms were presented by dashed lines and the experimental pure adsorption data of CO₂ and N₂ were included by solid line for the comparison purpose.

Figure 4.10. Isosteric heats of adsorption of CO₂ (a) and N₂ (b) on HS-AC as estimated by the Clausius–Clapeyron equation (The solid points represent the experimental isotherm data; the solid line represents the value from the Sips model).
Figure 4.11. Uptake versus partial pressure of multicomponent gas adsorption equilibria at 30°C (solid lines: pure adsorption data, dashed lines: binary isotherms predicted by IAS–Toth).

(a) CO₂/N₂: 14/86 (vol.%)
(b) CO₂/N₂: 30/70 (vol.%)

Figure 4.12. Uptake versus partial pressure of multicomponent gas adsorption equilibria at 50°C (solid lines: pure adsorption data, dashed lines: binary isotherms predicted by IAS–Toth).

(a) CO₂/N₂: 14/86 (vol.%)
(b) CO₂/N₂: 30/70 (vol.%)
Valenzuela and Myers stated that “the IAST predictions are independent of the particular equation and the only requirement for an accurate estimation is a high fit quality between the single gas experimental data and the particular model selected” [191]. In this dissertation, the single gas data fit Toth model very well so the IAST predictions are expected to be consistent with the real case. As seen from Figures 4.11 – 4.13, the binary “adsorption isotherms” of “CO$_2$” and “N$_2$” mixture is below the pure component isotherms. Considering the data given in Figures 4.11 – 4.13, the percentage difference between the pure and binary adsorption curves of CO$_2$ is less than the one obtained for N$_2$. For instance, CO$_2$ adsorption achieved for the binary mixture consisting of 30/70 %vol. CO$_2$/N$_2$ at 120 kPa and 30$^\circ$C (see Figure 4.11(b)) was more than 96% of the pure CO$_2$ adsorption capacity; whereas, adsorbed amount of N$_2$ in the same binary mixture was only 45% of the pure N$_2$ adsorption capacity. In addition, multiple range tests were applied by StatGraphics software to check if there is a statistically difference between the “pure” and “binary” adsorption capacities of the gases “CO$_2$” and “N$_2$”. The results overlapped the observations and for CO$_2$ gas, one homogenous group was identified which means the pure and binary capacities of it statistically indifferent. Nevertheless, for N$_2$, two homogenous groups were identified indicating the pure and binary adsorption capacities of N$_2$ are statistically different. This is because CO$_2$ is a strong adsorbate and...
its adsorption is not affected significantly by N\textsubscript{2} in the mixture. Nevertheless, CO\textsubscript{2} causes a substantial reduction in the adsorption of N\textsubscript{2}.

As stated, the difference between the CO\textsubscript{2} adsorption in the binary mixture with the one of pure CO\textsubscript{2} is small when CO\textsubscript{2} concentration in the mixture is high and the temperature is low. Apart from the adsorbate nature, the adsorption also depends on the volume ratio of the gases in the gas mixture, the adsorption “pressure” and “temperature”. As volume ratio of “CO\textsubscript{2}” in the binary mixture decreases and temperature increases, CO\textsubscript{2} adsorption decreases. At this point, it should be noted that the characteristics of temperature dependence of CO\textsubscript{2} adsorption in pure component and binary mixture are very similar.

Furthermore, the adsorption isotherms are plotted for partial pressures from 0 to 120 kPa in Figures 4.11 – 4.13 in order to investigate the deviation of binary mixture isotherms from the pure component adsorption in a wide range of partial pressures. However, since the CO\textsubscript{2} adsorption from the flue gases is of main interest in this dissertation, the adsorption amounts at a partial pressure corresponding to a total pressure of 120 kPa, which is the case for flue gases, should be further discussed. A total pressure of 120 kPa corresponds to 16.8 and 36 kPa partial pressures of CO\textsubscript{2} for 14/86 and 30/70 %vol. CO\textsubscript{2}/N\textsubscript{2} mixtures, respectively. In Figure 4.13 (a), at 16.8 kPa partial pressure, there is almost no difference between the pure CO\textsubscript{2} and binary mixture adsorptions. In addition, at this low partial pressure, the adsorption of both pure component and binary mixture are relatively low. Increasing the temperature is another factor that reduces the adsorption. The combination of these two adsorption-reducing effects in the case presented in Figure 4.13 (a) resulted in a very low adsorption; therefore, the very small difference between the adsorptions of pure component and binary mixture may be misleading for this case.

The “equilibrium separation factor” for a “binary mixture of CO\textsubscript{2} and N\textsubscript{2}”, \( S_{CO_2/N_2} \), which is another important parameter in the evaluation of adsorption characteristics, is calculated by Eq. (4. 1) [192].

\[
S_{CO_2/N_2} = \frac{x_{CO_2}/x_{N_2}}{y_{CO_2}/y_{N_2}} \quad \text{Eq. (4.1)}
\]
Where; “$x$ refers to the molar fraction in the adsorbed phase and $y$ to the molar fraction in the gas phase”.

![Graph showing CO$_2$/N$_2$ separation factor](image)

**Figure 4.14.** Separation factor of CO$_2$ over N$_2$ at 30°C (blue), 50°C (green), and 70°C (red).

Figure 4.14 shows “CO$_2$/N$_2$ separation factor” for HS-AC at a “total pressure of 130 kPa” for the temperatures at 30, 50, 70°C. This figure indicates that the sample is “highly selective for CO$_2$ over N$_2$”, in particular at “low partial pressures” making it a good candidate for “CO$_2$ separation” from the “post-combustion flue gases” that have low CO$_2$ partial pressure [190].

### 4.5. Specific Heat Capacity (Cp) of HS-AC

Cp values of the HS-AC showed a peaked in the range of study temperatures (30 to 140°C). It varied 0.8 and 1.34 J/g-K (see Figure 4.15). Although, some activated carbons like phenolic resin-derived ACs shows a linear upward trend with temperature, some of them like biomass based ACs, as in this case, shows a peak value in a temperature range. This peak has been ascribed to oxidation reactions of biomass based carbons during the experiment. It is noteworthy that surface characteristics of the adsorbent effects the specific heat capacity of it. For instance, AC adsorbents with an acidic character shows higher specific heat capacities which is undesirable for the temperature driven cyclic
adsorption processes because it effects the energy required during the regeneration step [193].

![Graph showing the specific heat of the HS-AC evaluated against temperature.]

Figure 4.15. Specific heat of the HS-AC evaluated against temperature.

4.6. Calculation of Thermal Energy Requirement

The “thermal energy input (Q)” required to regenerate the adsorbent is the sum of “heat of desorption (\(Q_{st}\))” and the “sensible heat” which is necessary to increase the adsorbent temperature from the “adsorption temperature” to “desorption temperature”.

\[
Q = Q_{st} + \text{sensible heat} \quad (Eq. 4.2)
\]

“Sensible heat” is a function of “adsorbent’s heat capacity, \(C_p\), “difference between adsorption and desorption temperatures, \(\Delta T\), “the adsorption capacity of the adsorbent material”. The equation which was used for the calculation of “sensible heat” is given in Eq. (4.3) [194,195]:

\[
\text{Sensible Heat} = \frac{C_p \Delta T}{\text{adsorption capacity}} \quad (Eq. 4.3)
\]
$C_p$ was measured in the laboratory. “Isosteric heat of desorption” was calculated by using Clausius–Clapeyron. Adsorption capacity was taken from the IAST calculation results.

The measured specific heat values, $C_p$, for each temperature and the calculated thermal energy requirement for the 14% and 30% CO$_2$ feed gas concentrations and for adsorption temperatures of 30°C, 50°C, 70°C and “desorption” temperatures of 120°C, 130°C were presented in Table 4.7. In the calculation of the thermal energy requirement, 75% of the sensible heat is assumed to be provided by the recovered energy [195].

As presented in Table 4.7, between 46 – 71 kJ energy is required for desorption of 1 mole CO$_2$. To understand the effect of the three factors, namely “adsorption temperature”, “CO$_2$ concentration in the feed gas”, and “desorption temperature”, a statistical analysis was conducted using StatGraph, and it is found that all the three factors have a statistically significant effect on Thermal Energy Requirement at the 95.0% confidence level. The effect of temperature of desorption on the thermal energy requirement is less when compared with the ones of other two factors.

4.7. Calculation of “net” CO$_2$ Capture Amount

The thermal energy required for the CO$_2$ capture process was assumed be produced by utilizing a hard coal combustion. The CO$_2$ emission factor of the hard coal was taken as 94.5 ton CO$_2$/TJ (and/or 2.55 kg CO$_2$/kg coal), which is the value reported by NIR document for hard coal in Turkey. The net CO$_2$ capture amount of an adsorbent can be calculated by subtracting the CO$_2$ generated during the production of energy required for the desorption from the total “CO$_2$ adsorption capacity of the adsorbent”. Using this approach, the net CO$_2$ uptake achieved by using HS-AC sample is calculated based on 1 kg of adsorbent and the results given in Table 4.8. The net CO$_2$ uptake of HS-AC was calculated between 0.016 – 0.064 kg CO$_2$/kg adsorbent; in other words, up to the emissions from 0.025 kg coal could be eliminated with using 1 kg HS-AC adsorbent.
### Table 4.7. Thermal energy requirement for different adsorption cases.

<table>
<thead>
<tr>
<th>Adsorption Temperature (°C)</th>
<th>Feed gas CO₂ Concentration (vol.%)</th>
<th>Desorption Temperature (°C)</th>
<th>Cp (J g⁻¹ K⁻¹)</th>
<th>Sensible Heat (kJ mole⁻¹)</th>
<th>Net Sensible Heat Requirement (kJ mole⁻¹)</th>
<th>Thermal Energy Requirement (kJ mole⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>14</td>
<td>120</td>
<td>1.33</td>
<td>117.66</td>
<td>29.42</td>
<td>57.73</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>130</td>
<td>1.25</td>
<td>122.87</td>
<td>30.72</td>
<td>59.03</td>
</tr>
<tr>
<td>50</td>
<td>14</td>
<td>120</td>
<td>1.33</td>
<td>139.41</td>
<td>34.85</td>
<td>63.16</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>130</td>
<td>1.25</td>
<td>149.75</td>
<td>37.44</td>
<td>65.75</td>
</tr>
<tr>
<td>70</td>
<td>14</td>
<td>120</td>
<td>1.33</td>
<td>152.63</td>
<td>38.16</td>
<td>66.47</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>130</td>
<td>1.25</td>
<td>172.14</td>
<td>43.03</td>
<td>71.34</td>
</tr>
</tbody>
</table>

### Table 4.8. “Net” CO₂ uptake value of each adsorption process cases.

<table>
<thead>
<tr>
<th>Adsorption Temperature (°C)</th>
<th>Feed gas CO₂ concentration (vol.%)</th>
<th>Desorption Temperature (°C)</th>
<th>CO₂ adsorption capacity (kg CO₂/kg adsorbent)</th>
<th>Net CO₂ uptake (kg CO₂/kg adsorbent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>14</td>
<td>120</td>
<td>0.0448</td>
<td>0.0392</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>130</td>
<td>0.0711</td>
<td>0.0639</td>
</tr>
<tr>
<td>50</td>
<td>14</td>
<td>120</td>
<td>0.0448</td>
<td>0.0391</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>130</td>
<td>0.0711</td>
<td>0.0638</td>
</tr>
<tr>
<td>70</td>
<td>14</td>
<td>120</td>
<td>0.0294</td>
<td>0.0234</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>130</td>
<td>0.0496</td>
<td>0.0444</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>130</td>
<td>0.0294</td>
<td>0.0232</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td></td>
<td>0.0496</td>
<td>0.0442</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>120</td>
<td>0.0192</td>
<td>0.0164</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td></td>
<td>0.0339</td>
<td>0.0303</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>130</td>
<td>0.0192</td>
<td>0.0162</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td></td>
<td>0.0339</td>
<td>0.0301</td>
</tr>
</tbody>
</table>
4.8. Dynamic Adsorption Experiments

After being characterized, HS-AC was evaluated in terms of its dynamic performance for the CO₂ separation from post-combustion gas streams. For this purpose, fixed bed experiments were conducted. The characteristics of the fixed bed together with the physical properties of HS-AC, which were estimated following the methodology detailed in Chapter 3, are summarized in Table 4.9.

Table 4.9. Physical properties of HS-AC and characteristics of the fixed-bed reactor.

<table>
<thead>
<tr>
<th>HS-AC properties</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET surface area (m² g⁻¹)</td>
<td>708.53</td>
</tr>
<tr>
<td>Helium (real) density (g cm⁻³)</td>
<td>2.219</td>
</tr>
<tr>
<td>Apparent density (g cm⁻³)</td>
<td>0.727</td>
</tr>
<tr>
<td>Particle porosity, εₚ</td>
<td>0.672</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fixed Bed Reactor</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Height of adsorbent layer (cm)</td>
<td>11.6</td>
</tr>
<tr>
<td>Internal bed diameter (cm)</td>
<td>1.3</td>
</tr>
<tr>
<td>Mass of adsorbent (g)</td>
<td>5.521</td>
</tr>
<tr>
<td>Particle size (mm)</td>
<td>1-3</td>
</tr>
<tr>
<td>Bed density (gr cm⁻²)</td>
<td>0.359</td>
</tr>
<tr>
<td>Packed bed porosity, ε₀</td>
<td>0.506</td>
</tr>
<tr>
<td>Total porosity, ε₉</td>
<td>0.838</td>
</tr>
</tbody>
</table>

4.8.1 Binary CO₂/N₂ Breakthrough Experiments

To determine the effectiveness of HS-AC in separating CO₂ from CO₂/N₂ streams and test reproducibility of the system, HS-AC was subjected to “six consecutive adsorption–desorption cycles” at two temperatures, 30 and 50°C, and two CO₂ concentrations, 14 and 30 vol.% (balance N₂). Under these conditions, the maximum CO₂ “adsorption capacity of the adsorbent” as well as breakthrough times were evaluated.
For the mixture of 30:70 vol.% CO₂:N₂, the temperature and gas concentration profiles at the column outlet for the “six-consecutive adsorption-desorption cycles” at “30°C” and atmospheric pressure are presented in Figure 4.16 as an example. As seen from the CO₂ concentration profiles, “CO₂” was not detected initially, which is attributed to its adsorption on the adsorbent bed. The thermal wave observed during this step is another indicator of the existence of adsorption, which is inherently exothermic. As time progressed, outlet CO₂ concentration increased to its feed level implying that the bed was saturated in CO₂. During the subsequent desorption step, the bed was heated to 120°C. The CO₂ concentration first reached a maximum value and then reduced until complete regeneration was reached. After that point, the bed was cooled. The adsorbent, HS-AC, showed stable performance throughout the six consecutive cycles during the breakthrough experiments for each adsorption case.

![Graph showing temperature and gas concentration profiles](image)

**Figure 4.16.** Example of a complete breakthrough experiment consisting of six consecutive adsorption–desorption cycles at 30°C for a mixture of 30/70 vol.% CO₂/N₂: 1- adsorption step, 2- desorption step, and 3- cooling step.

**Figure 4.17** represents the breakthrough curves; where, “C/C₀ represents the ratio between the concentration leaving the bed at a given time (C) and that in the feed (C₀).”
Figure 4.17 (a) and (c) show breakthrough curves of CO$_2$ and N$_2$, for a feed stream with 14 vol.% CO$_2$ (N$_2$ balance), at 130 kPa, at 30 and 50°C, respectively; while, Figure 4.2 (b) and (d) show breakthrough curves of CO$_2$ and N$_2$, for a feed stream with 30% vol. CO$_2$ (N$_2$ balance), at 130 kPa, at 30°C and 50°C, correspondingly. As seen in Figure 4.17, the concentration ratios (C/C$_0$) of CO$_2$ (represented by circles) and N$_2$ (represented by diamonds) overlapped in the consecutive cycles, indicating good reproducibility of the adsorption-desorption process.

The N$_2$ concentration at the outlet of the column exceeded its concentration in the feed during the adsorption step (C/C$_0$>1) because the bed is full of N$_2$ due to the initial conditioning. The ratio of C$_{N_2\text{-outlet}}$/C$_{N_2\text{-feed}}$ was around 1.2 for the feed stream with 14% CO$_2$ and around 1.4 for the feed stream of 30% “CO$_2$”, since N$_2$ in the bed was displaced by the CO$_2$, phenomenon known as roll-up effect. Higher CO$_2$ concentrations resulted in greater roll-up effect that pushed more N$_2$ out of the bed.

The data obtained from the breakthrough curves were transformed into dynamic uptake capacity of the adsorbent bed by integration. These results as well as the breakthrough times for the specified operating conditions are collected in Table 4.10.
Figure 4.17. CO$_2$ (circles) and N$_2$ (diamonds) breakthrough curves of the experiments with the following CO$_2$/N$_2$ feed gas compositions: 14/86 vol.% at 30°C (a), 30/70 vol.% at 30°C (b), 14/86 vol.% at 50°C (c), 30/70 vol.% at 50°C (d).
As seen from Table 4.10., the amount of CO\textsubscript{2} adsorbed depends on the “CO\textsubscript{2} partial pressure” in feed gas stream and the “adsorption temperature”. The breakthrough times were in the range of 4 to 8 min depending on the feed condition. As expected during physical adsorption, the higher “temperature” the lower is the “amount adsorbed” and the shorter is the “breakthrough time”. Besides, uptake capacity increased by increasing the “CO\textsubscript{2} concentration” in the “feed gas mixture”. Therefore, at a similar adsorption temperature the uptake capacity was higher for the 30% CO\textsubscript{2} experiment.

In addition, the points showing the CO\textsubscript{2} uptakes at 130 kPa for the 14 and 30% CO\textsubscript{2} “breakthrough experiments” are plotted in “Figure 4.18” with graph showing the pure CO\textsubscript{2} adsorption isotherms at the two different temperatures. As might be expected and observed in the IAST model results, the capacities are a slightly below those of the pure CO\textsubscript{2} isotherms at the same CO\textsubscript{2} partial pressures; however, a good consensus exists between the adsorbed amounts CO\textsubscript{2} in breakthrough experiments and those obtained from the corresponding pure isotherm.
4.8.2. Cyclic Adsorption Experiments

The main element of the design of a cyclic adsorption process is determining the sequence of steps and the number of beds. However, it is a quite complex task because the feed gas composition and its condition, the adsorbent used, and the target of relevant performance indicators ("CO₂ purity", "recovery", "productivity" and "energy requirement") affect the decision. Besides, to guarantee continuity in the processing of the feed stream, at least one bed should have completed regeneration and be ready to process the feed gas when the adsorption step finishes in another column. This adds extra complexity to the system.

In this part of the dissertation, different TSA and VSA cycles in the fixed bed were designed considering the results of the breakthrough experiments from the previous section and using the characteristics of the fixed bed. They were conducted in the same "fixed-bed adsorption unit" feeding "binary gas mixtures" of two different compositions at two adsorption temperatures: 14 and 30% CO₂ (balance N₂) and 30 and 50°C.
The performances of the short cyclic adsorption experiments were evaluated in terms of the achievable “purity and recovery of the CO$_2$”, the “productivity”, and “energy” requirements of the process. Unlike the dynamic breakthrough experiments, the cyclic adsorption-desorption experiments were designed for short steps to recreate the conditions in real adsorption processes at an industrial scale. Faster cycling implies increase adsorbent bed usage and contributes to CO$_2$ productivity; thereby, the reduction of the plant size. Therefore, the cyclic experiments provide neither the maximum saturation capacity of the bed during “adsorption step” nor complete regeneration of bed during the “desorption step”.

Another fundamental feature of the application of a solid sorbent in a cyclic process is reproducibility. It is important to know the stability behavior of adsorbent in prolonged cyclic use. Therefore, at least 30 cycles were carried out of each configuration and the HS-AC exhibited no signs of deactivation during the prolonged process in both TSA and VSA cycling. Besides, all the Figures in this section show the effluent gas composition and the values of the characteristic parameters of each configuration from the 4th cycle onwards for both the TSA and VSA cases. This is when the cyclic steady state was achieved.

4.8.2.1. Temperature Swing Adsorption (TSA) Cycles

Several TSA cycle configurations were designed to assess the HS-AC performance in temperature-driven cyclic processes. Besides, the effects of these cyclic adsorption-desorption processes on the process parameters was assessed.

The TSA configurations included a different number of steps required to ensure 4 beds working synchronously. The main steps in any configuration were adsorption, rinse with CO$_2$, regeneration by indirect heating, and cooling. The feed and cooling steps were arranged to equal duration, while timing of rinse and heating steps varied to keep the sum of them equal to the total duration of feed and cooling steps. Furthermore, the total duration of each TSA cycle configuration for each feed condition was kept constant to
benchmark the performance of the configurations on a fair basis and ensure the 4-bed cycle simulation.

The durations of the adsorption steps were set close to the breakthrough time at the corresponding feed conditions to enhance the CO₂ purity. Longer adsorption step times could indeed favour the CO₂ product purity because of the increase in the CO₂ loading within the bed. However, if the front eventually broke through the recovery would decrease rapidly. Thus, selecting an adsorption time slightly shorter than the breakthrough time is reasonable to balance the CO₂ purity and recovery. Beside, setting the adsorption step duration long enough contributes to higher cyclic capacity and lesser specific energy consumption alongside a higher CO₂ purity. The greater share of heat is consumed for the actual CO₂ desorption and thereby it is used in a more effective manner [58].

In all the configurations, the fixed bed was rinsed with pure CO₂ at R:F = 0.5 and/or 0.7 “volumetric flow rate of CO₂ in the rinse step/ volumetric flow rate of CO₂ in the adsorption step” to increase adsorbed concentration of CO₂ and flush out the light product (N₂). Since the single fixed bed unit does not allow the recirculation of the product, pure CO₂ gas was used during rinse step.

The “desorption temperature” was at 120°C for all the TSA configurations, but in some particular cases the desorption temperature increased to 130°C in order to evaluate the temperature effect on the process performance and energy requirements.

In cooling steps, while the bed was cooled down with indirect air circulation, a purge of N₂ of 10 mL/min was fed to the bed as “sweep gas” to improve the recovery of the desorbed components and clean the bed before the adsorption step. N₂ was fed to the column co-currently to the feed since the design of the single fixed bed unit restrains counter flow of feed gases.

One of the TSA scenarios for a 30% CO₂ feed concentration at 30°C is plotted in Figure 4.19 as an example. As can be seen, 42 consecutive temperature-driven “adsorption-
desorption cycles” were conducted and variation of the molar fractions of CO$_2$ and N$_2$ kept stable upon cycling.

![Graph](image)

**Figure 4.19.** TSA run at 30°C with 30% CO$_2$ feed concentration.

The configurations and their effects on the process performances for each feed condition are discussed in the following paragraphs.

**TSA configurations for the adsorption of 14% CO$_2$ at 30°C**

The adsorption temperature and the CO$_2$ feed concentration were set at 30°C and 14 vol.% (balance N$_2$), respectively. The “total cycle time” was established in 28 min and the “duration of the adsorption step” was set to a value close to the “breakthrough time” (7 min) for each configuration.

The operating conditions of each cycle configuration are presented in Table 4.11.
Table 4.11. Operating conditions of the TSA configurations for the adsorption of 14% CO₂ at 30°C.

<table>
<thead>
<tr>
<th></th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>N₂ flow (mL/min)</th>
<th>CO₂ flow (mL/min)</th>
<th>t (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Configuration A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1.3</td>
<td>86</td>
<td>14</td>
<td>7</td>
</tr>
<tr>
<td>Rinse</td>
<td>30</td>
<td>1.3</td>
<td>-</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Heating-1</td>
<td>120</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>Heating-2</td>
<td>120</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>Cooling</td>
<td>30</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td><strong>Configuration B</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1.3</td>
<td>86</td>
<td>14</td>
<td>7</td>
</tr>
<tr>
<td>Rinse</td>
<td>30</td>
<td>1.3</td>
<td>-</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>Heating-1</td>
<td>120</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Heating-2</td>
<td>120</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Cooling</td>
<td>30</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td><strong>Configuration B-I</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1.3</td>
<td>86</td>
<td>14</td>
<td>7</td>
</tr>
<tr>
<td>Rinse</td>
<td>30</td>
<td>1.3</td>
<td>-</td>
<td>9.8</td>
<td>4</td>
</tr>
<tr>
<td>Heating-1</td>
<td>120</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>Heating-2</td>
<td>120</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>Cooling</td>
<td>30</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td><strong>Configuration C-I</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1.3</td>
<td>86</td>
<td>14</td>
<td>7</td>
</tr>
<tr>
<td>Rinse-1</td>
<td>30</td>
<td>1.3</td>
<td>-</td>
<td>9.8</td>
<td>2</td>
</tr>
<tr>
<td>Rinse-2</td>
<td>80</td>
<td>1.3</td>
<td>-</td>
<td>9.8</td>
<td>2</td>
</tr>
<tr>
<td>Heating-1</td>
<td>120</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Heating-2</td>
<td>120</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Cooling</td>
<td>30</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>7</td>
</tr>
</tbody>
</table>

The molar flow rate and outlet gas composition for each configuration are plotted in Figure 4.20. The characteristic performance parameters of the different TSA configurations are shown in Figure 4.21.
Figure 4.20 Experimental profiles at bed exit during the TSA cycles for a feed with 14% CO₂ feed at 30°C. (a), (b), (c), (d) concentration; (e), (f), (g), (h) molar flow rates. N₂ (green), CO₂ (blue) and bed temperature (red).
Configuration A was implemented in four steps (adsorption, rinse, heating and cooling) selecting the same duration for each step (7 min), thereby 4 beds could be reproduced. After the adsorption step, a rinse step with R:F ratio of 0.5 was carried out to enrich the CO₂ product purity by increasing the amount of CO₂ adsorbed on the bed. During the desorption step, the temperature increased to 120°C by indirect heating and a small flow of N₂ gas was applied as sweep gas to collect the desorbed CO₂.

Tili et al. in their research showed that desorption by heating solely led to almost pure CO₂ but at the expense of a low recovery [147]. Thus, in our experiment configuration, 10 mL/min of N₂ flow swept the bed upon heating to reach reasonable levels of CO₂ recovery. During the cooling step, the bed was indirectly cooled down by air and 10 mL/min of N₂ purged the bed to recover the desorbed CO₂ and leave less CO₂ retained in the bed for the subsequent adsorption step, thereby achieving greater recovery. Configuration A reached a “CO₂ purity” of 56%, a “CO₂ recovery” of 76%, and a “productivity” of 1.95 mol CO₂/kg-h.
In Configurations B and B-I some improvements in the heating step were introduced to tune the performance of the TSA cycles. In configuration B, the rinse step duration was decreased to 4 min keeping the R:F ratio (vol. basis) at 0.5. The time subtracted from the rinse step (3 min) was added to the heating step so its duration increased to 10 min. Thereby, the total duration of the rinse plus heating steps was kept constant and the 4-bed configuration was still simulated. Besides, the heating step was split in two separate steps. During the first heating stage (5 min), the exit valve downstream of the reactor was closed and the pressure inside the reactor increased. Then, during the second heating stage (5 min), a purge of N₂ (10 mL/min) fed the column and the exit valve was opened to let the CO₂ out and recover the product. The main idea behind this approach was to reduce the N₂ sweep gas during the regeneration step and boost the CO₂ desorption by adding a pressure gradient to the thermal expansion. With this configuration, the purity increased to 65% but the recovery slightly decreased. Then, Configuration B-I was established by setting the R:F ratio to 0.7 and keeping all the steps as in Configuration B so as to evaluate the effect of the CO₂ flow rate during the rinse step. The fundamental difference between these two configurations is the increase of the CO₂ flow rate during the rinse step from 7 to 9.8 mL/min. Besides, the timing of the first and second heating steps were finally changed to 4 and 6 min (10 min total), respectively, because the pressure inside the reactor during the first heating stage exceeded the limit value of the BPR (back pressure regulator).

As seen from Figure 4.20 (c), the CO₂ concentration during the desorption step reached a higher peak value (nearly 80%) when compared to that of Configuration B which was around 70% (See Figure 4.20(b)). As observed in Figure 4.21, extending duration of the second heating stage increased the recovery value from 65% to 86%. Besides, introducing a higher R:F ratio led to a higher CO₂ purity (69%). In addition, the productivity increased to 2.03 mol CO₂/kg-h. It is worth noting that the first heating step without exiting flow was of significant importance as the absence of N₂ purge allowed a higher purity of CO₂.

In the last configuration, the rinse step was divided into two steps and heat was introduced to the bed at the half time of this step, and a new configuration which was labelled as C-I is established. In this configuration, during the first part of heating, the pressure inside
the bed did not reach the limit value as quick as configuration B-I. Thus, the first heating part in this configuration was able to be extended again to 5 min. This might be the reason of N\textsubscript{2} leaving the bed during the heat induced rinse step. As seen in “Figure 4.5 (h)”, there was a small N\textsubscript{2} peak showing this. The purity was increased to 77%; however, the recovery and productivity decreased to 77% and 1.83 mol CO\textsubscript{2}/kg-h, respectively.

\textit{TSA configurations for the adsorption of 30\% CO\textsubscript{2} at 30\textdegree C}

The adsorption temperature was maintained at 30\textdegree C but the “concentration of CO\textsubscript{2}” in the feed increased to “30 vol.\%” (N\textsubscript{2} balance). The total cycle time was set at 20 min and the duration of “adsorption step” was set at 5 min, a value close to “breakthrough time” at this feed condition.

Table 4.12 gives the operating conditions including temperature, the step times and flow rates for each cycle configuration. The experimental profiles at bed exit and the calculated characteristic performances of the different TSA configurations are shown in “Figure 4.22” and “Figure 4.23”, respectively.

The basic Configuration A with a R:F = 0.5 run with four steps of equivalent duration (5 min). In this experiment, the CO\textsubscript{2} concentration reached values above 90\% during the desorption stage (see Figure 4.22 (a)), compared to the 80\% obtained in the similar configuration feeding 14\% CO\textsubscript{2} (see Figure 4.20 (a)). This is because the “higher partial pressure of CO\textsubscript{2}” in the feed serves a higher CO\textsubscript{2} adsorption capacity of the bed. The resultant product “purity” and “recovery” were 78\% and 72\%, respectively (see Figure 4.23). Besides, a higher “productivity” of 3.96 mol CO\textsubscript{2}/kg-h, was achieved (1.95 mol CO\textsubscript{2}/kg-h was obtained with a 14\% CO\textsubscript{2} feed concentration). However, in this Configuration A, the CO\textsubscript{2} outlet concentration (see Figure 4.22 (a)) gradually increased during the rinse step indicating a substantial amount CO\textsubscript{2} leaving the bed, which is undesirable for the adsorption process.

In Configuration B, the problem was solved by setting a longer heating time to enhance the regeneration. This resulted in an actual higher maximum temperature during the
desorption stage, as can be seen in Figure 4.22 (g). For instance, while the maximum temperature in the desorption step was around 120°C in Configuration A (see Figure 4.22 (f)), the temperature actually increased above 130°C in Configuration B and B-I. The higher desorption temperature led CO₂ to desorb to a larger extent and, as seen in Figure 4.22 (b), CO₂ outlet concentration remained below 10% during the rinse step due to a more effective regeneration. All of these implied a larger “cyclic capacity” and resulted in higher “CO₂ purity” and recovery (89% and 87%, respectively). In addition, the productivity increased to 4.33 mol CO₂/kg-h. To evaluate the effect of a higher R:F ratio, Configuration B-I run with a R:F = 0.7. However, the higher CO₂ concentration during the rinse step caused an increase in the pressure inside the bed during the first heating step when the exit valve was closed. Thus, the first heating step ended after 2.5 min, 30 seconds less than in Configuration B, because the actual pressure exceeded the maximum of the BPR (i.e., 2.5 bar) installed in the experimental unit. The purity and recovery of CO₂ obtained were 86% and 82% (see Figure 4.23), respectively. There were no further improvements by rising the R:F ratio. Yet, if the pressure limit was higher in the system, the first heating stage could have proceeded for a longer time at the expense of a shorter second heating stage which, in turn, could have improved the process performances.

In configuration C-I, while the purity increased to 93%, the recovery decreased to 71%, similar to the previous feed case conducted with 14% CO₂. This can be attributed to the temperature increase in the second part of the rinse step which may cause escape of some part of CO₂ adsorbed in the bed as seen in the Figure 4.22 (d), where the CO₂ concentration increased at the bed exit in rinse step.

Lastly, to evaluate the effect of the “desorption temperature” on the process performance, desorption temperature set point increased to 130°C keeping the other parameters in the cycle B unchanged and a new cycle labelled as Configuration D was established. As seen from Figure 4.23, there were no important differences regarding to “CO₂ product purity” and “recovery” between Configuration B and D. The reason was that the temperature increase was not enough to drastically change the temperature profile of the cycle (real ΔT was maintained) (see Figure 4.22 (j)) due to the limited heating step time; consequently, the cyclic capacity neither changed.
Table 4.12. Operating conditions of the TSA configurations for the adsorption of 30% CO$_2$ at 30$^\circ$C.

<table>
<thead>
<tr>
<th></th>
<th>T ($^\circ$C)</th>
<th>P (bar)</th>
<th>$N_2$ flow (mL/min)</th>
<th>CO$_2$ flow (mL/min)</th>
<th>t (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Configuration A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1.3</td>
<td>70</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>Rinse</td>
<td>30</td>
<td>1.3</td>
<td>-</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>Heating</td>
<td>120</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Cooling</td>
<td>30</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td><strong>Configuration B</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1.3</td>
<td>70</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>Rinse</td>
<td>30</td>
<td>1.3</td>
<td>-</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>Heating-1</td>
<td>120</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Heating-2</td>
<td>120</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Cooling</td>
<td>30</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td><strong>Configuration B-I</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1.3</td>
<td>70</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>Rinse</td>
<td>30</td>
<td>1.3</td>
<td>-</td>
<td>21</td>
<td>4</td>
</tr>
<tr>
<td>Heating-1</td>
<td>120</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>2.5</td>
</tr>
<tr>
<td>Heating-2</td>
<td>120</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>3.5</td>
</tr>
<tr>
<td>Cooling</td>
<td>30</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td><strong>Configuration C-I</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1.3</td>
<td>70</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>Rinse-1</td>
<td>30</td>
<td>1.3</td>
<td>-</td>
<td>21</td>
<td>2</td>
</tr>
<tr>
<td>Rinse-2</td>
<td>80</td>
<td>1.3</td>
<td>-</td>
<td>21</td>
<td>2</td>
</tr>
<tr>
<td>Heating-1</td>
<td>120</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Heating-2</td>
<td>120</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Cooling</td>
<td>30</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td><strong>Configuration D</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1.3</td>
<td>70</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>Rinse</td>
<td>30</td>
<td>1.3</td>
<td>-</td>
<td>15</td>
<td>4</td>
</tr>
<tr>
<td>Heating-1</td>
<td>130</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Heating-2</td>
<td>130</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Cooling</td>
<td>30</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>5</td>
</tr>
</tbody>
</table>
In this case study the adsorption temperature increased to 50°C to evaluate the effect on cycle performances. The configurations were assessed for a feed gas with “14% CO2”.

The total cycle time was set at 18 min and the duration of “adsorption step” to a value close to “breakthrough time” (4.5 min).

**Figure 4.22.** Experimental profiles at bed exit during the TSA cycles for a feed with 30% CO2 at 30°C. (a), (b), (c), (d), (e) concentration; (f), (g), (h), (i) molar flow rates. N2 (green), CO2 (blue) and bed temperature (red).

**Figure 4.23.** Characteristic performances of different TSA configurations (30% CO2 at 30°C).

**TSA configurations for the adsorption of 14% CO2 at 50°C**

In this case study the adsorption temperature increased to 50°C to evaluate the effect on the cycle performances. The configurations were assessed for a feed gas with “14% CO2”. The total cycle time was set at 18 min and the duration of “adsorption step” to a value close to “breakthrough time” (4.5 min).
The operating conditions including temperature, the step times and flow rates of each cycle configuration are given in Table 4.13. The experimental profiles at bed exit and the calculated characteristic performances of the different TSA configurations are represented in “Figure 4.24” and “Figure 4.25”, respectively.

Table 4.13. Operating conditions of the TSA configurations for the adsorption of 14% CO₂ at 50°C.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>Adsorption</th>
<th>Rinse</th>
<th>Heating</th>
<th>Cooling</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (°C)</td>
<td>P (bar)</td>
<td>N₂ flow (mL/min)</td>
<td>CO₂ flow (mL/min)</td>
<td>t (min)</td>
</tr>
<tr>
<td>Configuration A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1.3</td>
<td>86</td>
<td>14</td>
</tr>
<tr>
<td>Rinse</td>
<td>50</td>
<td>1.3</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>Heating</td>
<td>120</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Cooling</td>
<td>50</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Configuration B</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1.3</td>
<td>86</td>
<td>14</td>
</tr>
<tr>
<td>Rinse</td>
<td>50</td>
<td>1.3</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>Heating-1</td>
<td>120</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Heating-2</td>
<td>120</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Cooling</td>
<td>50</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Configuration B-I</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1.3</td>
<td>86</td>
<td>14</td>
</tr>
<tr>
<td>Rinse</td>
<td>50</td>
<td>1.3</td>
<td>-</td>
<td>9.8</td>
</tr>
<tr>
<td>Heating-1</td>
<td>120</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Heating-2</td>
<td>120</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Cooling</td>
<td>50</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Configuration C-I</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1.3</td>
<td>86</td>
<td>14</td>
</tr>
<tr>
<td>Rinse-1</td>
<td>50</td>
<td>1.3</td>
<td>-</td>
<td>9.8</td>
</tr>
<tr>
<td>Rinse-2</td>
<td>80</td>
<td>1.3</td>
<td>-</td>
<td>9.8</td>
</tr>
<tr>
<td>Heating-1</td>
<td>120</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Heating-2</td>
<td>120</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Cooling</td>
<td>50</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Configuration D</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1.3</td>
<td>86</td>
<td>14</td>
</tr>
<tr>
<td>Rinse-1</td>
<td>50</td>
<td>1.3</td>
<td>-</td>
<td>9.8</td>
</tr>
<tr>
<td>Rinse-2</td>
<td>80</td>
<td>1.3</td>
<td>-</td>
<td>9.8</td>
</tr>
<tr>
<td>Heating-1</td>
<td>130</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Heating-2</td>
<td>130</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Cooling</td>
<td>50</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
</tr>
</tbody>
</table>
Figure 4.24. Experimental profiles at the bed exit during the TSA cycles for a feed with 14% CO₂ at 50°C. (a), (b), (c), (d) concentration; (e), (f), (g), (h) molar flowrates. N₂ (green), CO₂ (blue) and bed temperature (red).
The purity and recovery of CO\textsubscript{2} were found as 38\% and 43\%, respectively, in Configuration A with even step times (4.5 min). Again, the process performances were enhanced and 51\% of purity and 47\% of CO\textsubscript{2} recovery was achieved by Configuration B where the regeneration step was extended. Increasing the R:F ratio to 0.7 (Configuration B-I) barely changed the experimental profile. As can be seen in Figure 4.24 (f), the increase in the “molar flow of CO\textsubscript{2}” during the regeneration reached a higher value and this improved the recovery to 49\%. The productivity also increased to 1.11 mol CO\textsubscript{2}/kg-h from 0.97 mol CO\textsubscript{2}/kg-h.

In Configuration C-I, light heating was applied at the middle of the rinse step dividing the rinse step was divided into two stages. As seen in Figure 4.24 (g), bed temperature in this configuration started to raise 1 min earlier than in Configurations B and the N\textsubscript{2} peak was also observed during the rinse step. This peak indicates that N\textsubscript{2} kept in the bed is leaving the adsorber. However, no CO\textsubscript{2} flow was observed at the outlet of the column in this rinse step. As a result, in this configuration, the purity increased to 58\% and the recovery to 63\%. The productivity also increased to 1.38 mol CO\textsubscript{2}/kg-h.

![Figure 4.25. Characteristic performances of different configurations of TSA cycles (14\% CO\textsubscript{2} at 50\°C).](image)
In Configuration D, Configuration C-I was rerun out at a higher desorption temperature (130°C). The higher temperature increased ΔT (see Figure 4.24. (h)) and, accordingly, a larger cyclic capacity rose the productivity to 1.64 mol CO\(_2\)/kg-h. It is widely known that larger “ΔT” would lead larger cyclic capacity at expense of longer cycle step times. Herein, the duration of the cycles kept constant. Besides, the recovery increased to 77%, while the purity remained almost constant at about 60% CO\(_2\).

In all the configurations, the CO\(_2\) concentration at the outlet gas stream only reached about 60 vol.% during the desorption step, the lowest value among the experiments conducted in the current study. This is because of the low CO\(_2\) concentration in feed and the increased adsorption temperature (50 °C), unfavourable conditions for adsorption.

**TSA configurations for the adsorption of 30% CO\(_2\) at 50°C**

The configurations were conducted with 30% CO\(_2\) (balance with N\(_2\)) concentration at the high feed temperature (50 °C). The “total cycle time” was established as 12 min and the duration of the “adsorption step” close to the breakthrough time (3 min).

Table 4.14 gives the operating conditions including temperature, step times and flow rates for each configuration. The “molar flow rate” and “concentration” profiles at the bed exit for each configuration are shown in Figure 4.26. Besides, the characteristic performances of the different TSA configurations are presented in Figure 4.27.

In this feed condition, 60% purity and 42% recovery with 2.31 mol CO\(_2\)/kg-h productivity was achieved with the basic configuration (configuration A) in which durations of each step were set as 3 min. In Configuration B-I, the regeneration step took 4 min allowing a desorption peak temperature slightly above 120°C (see Figure 4.26 (e)). This, alongside a R:F ratio of 0.7, resulted in the target component CO\(_2\) desorption to a greater extent. The “purity” and “recovery” of CO\(_2\) obtained were 64 and 51%, respectively. The productivity reached 2.74 mol CO\(_2\)/kg·h. For Configuration C-I, where light heating was applied at the middle of the “rinse step”, the “CO\(_2\) concentration” during desorption went beyond 90% (see Figure 4.26 (c)). A small N\(_2\) peak was again observed during the rinse
step but there was not molar flow of CO$_2$ (see Figure 4.26 (f)), confirming that the CO$_2$ entering the bed was retained. Herewith, the CO$_2$ purity achieved about 85% and the CO$_2$ recovery increased to 66%. Besides, the productivity reached 3.46 mol CO$_2$/kg·h.

Table 4.14. Operating conditions of the TSA configuration for the adsorption of 30% CO$_2$ at 50 °C.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>N$_2$ flow (mL/min)</th>
<th>CO$_2$ flow (mL/min)</th>
<th>t (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Configuration A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1.3</td>
<td>70</td>
<td>30</td>
<td>3</td>
</tr>
<tr>
<td>Rinse</td>
<td>50</td>
<td>1.3</td>
<td>-</td>
<td>15</td>
<td>3</td>
</tr>
<tr>
<td>Heating</td>
<td>120</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Cooling</td>
<td>50</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td><strong>Configuration B-I</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1.3</td>
<td>70</td>
<td>30</td>
<td>3</td>
</tr>
<tr>
<td>Rinse</td>
<td>50</td>
<td>1.3</td>
<td>-</td>
<td>21</td>
<td>2</td>
</tr>
<tr>
<td>Heating-1</td>
<td>120</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Heating-2</td>
<td>120</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Cooling</td>
<td>50</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td><strong>Configuration C-I</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1.3</td>
<td>70</td>
<td>30</td>
<td>3</td>
</tr>
<tr>
<td>Rinse-1</td>
<td>50</td>
<td>1.3</td>
<td>-</td>
<td>21</td>
<td>1</td>
</tr>
<tr>
<td>Rinse-2</td>
<td>80</td>
<td>1.3</td>
<td>-</td>
<td>21</td>
<td>1</td>
</tr>
<tr>
<td>Heating-1</td>
<td>120</td>
<td>1.3</td>
<td>-</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Heating-2</td>
<td>120</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>Cooling</td>
<td>50</td>
<td>1.3</td>
<td>10</td>
<td>-</td>
<td>3</td>
</tr>
</tbody>
</table>

As seen in Figure 4.27, N$_2$ purity reached in the TSA configurations at this feed condition was lower than in the previous cycles run at an “adsorption temperature” of “30°C”. It is because CO$_2$ left the bed at the first stages of adsorption, as evidenced in the gas concentration profiles which were illustrated in Figure 4.26. The capacity of HS-AC to adsorb CO$_2$ drastically decreased at this higher temperature (50°C), and CO$_2$ was not adsorbed effectively. This resulted in an increase of the outlet molar flow of CO$_2$ during the “adsorption step”, and a consequent decrease in N$_2$ purity of the decarbonized stream.
Figure 4.26. Experimental profiles at the bed exit during the TSA cycles for a feed with 30% CO$_2$ at 50°C. (a), (b), (c) concentration; (d), (e), (f) molar flowrates. N$_2$ (green), CO$_2$ (blue) and bed temperature (red).
4.8.2.2. Energy Requirements of the TSA Configurations and Comparative Assessment of Cycle Performances

The energy needed to regenerate the adsorbent has a substantial effect on the cost related with the process of adsorption. The energy requirement for “CO₂ capture” of the TSA configurations were investigated by considering the thermodynamic properties of the adsorbed phase, such as “heat of adsorption” (“latent heat”) and “specific heat capacity” (“sensible heat”). The working capacity of adsorbent, which is the difference between the amount adsorbed “CO₂ at the end of the adsorption step” and the end of desorption step, is one of the most important parameter used in the calculation of this “sensible heat” of the process. Thus, the working capacities of adsorbent and the thermal energy requirements of each configuration were calculated and are demonstrated in Figure 4.28 and Figure 4.29, respectively.
As can be seen from the Figure 4.28, operating concentration and temperature affected the working capacity of the adsorbent. The “working capacity of the adsorbent” were highest at the feed condition at 30°C and with 30% CO₂ concentration; whereas, the lowest at the feed condition at 50°C and with 14% CO₂ concentration. Thus, the lower “adsorption temperature” and the higher “CO₂ concentration” in the feed resulted in higher working
capacity of adsorbent HS-AC. The working capacities were measured in the range of 1.62 and 0.31 mol CO$_2$/kg$_{adsorbent}$ that were a little lower than the values calculated in the breakthrough experiments at the same feed conditions. One of the reasons is that the adsorbent stayed partially saturated in the cyclic experiments because of the terminating of regeneration step before complete cleaning. In addition to this, the “temperature” at the beginning of the “adsorption step” in the cyclic ones were higher than the set value, also restricted the “working capacity” of the adsorbent.

As seen from “Figure 4.29”, the thermal energy requirements of the cycles were inversely proportional to working capacities. In other words, lower specific regeneration energy required when the “CO$_2$ working capacity of the adsorbent” was higher. The thermal energy requirements for regeneration were calculated between 1.06 and 2.35 MJ/ kg CO$_2$ (295.4-653.2 kWh/ kg CO$_2$) depending on the feed conditions and the configuration design.

As might be expected, the larger working capacities were achieved in the configurations conducted at 30°C, and their specific energy consumptions were smaller than the configurations conducted at 50°C. The cyclic capacity of the adsorbent and the energy requirement values showed a substantial enhancement in each configuration. With the configurations BI, a greater CO$_2$ recovery was achieved and the cyclic capacity of the adsorbent increased and therefore the specific energy consumption decreased. The cyclic capacities of the adsorbent were improved, thereby; the specific energy consumptions were decreased by the configurations C, which were conducted at the 50°C. Lastly, increasing the desorption temperature to 130°C at the feed conditions 14% CO$_2$ at 50°C (configuration D) did not lead to higher energy requirements thanks to the higher working capacities and lower specific heat value (Cp) of the biomass based adsorbent at higher temperature. As explained before, because of the unchanging temperature profile, the higher temperature for desorption did not affect the process performance and so the energy requirement of the cycle conducted with 30% CO$_2$ at 30°C.

Parallel to the enhancement of cyclic capacity of the TSA cycles, the configurations carried out at different feed conditions also showed improvement both on “CO$_2$ recovery”
and “purity” values: the “CO₂ purity” and “CO₂ recovery” for the feed condition of 14% CO₂ at 30°C were improved from 56 to 69% and 76% to 86%, respectively (from Configuration A to Configuration B-I). The “CO₂ purity” and “CO₂ recovery” for the feed condition of 30% CO₂ at 30°C were improved from 78 to 89% and 72% to 87%, respectively (from Configuration A to Configuration B). The CO₂ purity and recovery for the feed condition of 14% CO₂ at 50°C were improved from 38 to 58% and 43% to 63%, respectively (from Configuration A to Configuration C). Increasing the desorption temperature to 130°C (Configurations D) at this feed condition improved the purity and recovery further to 60% and 77%, respectively. The “CO₂ purity” and “CO₂ recovery” for the feed condition of 30% CO₂ at 50°C were improved from 60 to 85% and 42% to 66%, respectively (from Configuration A to Configuration C).

The performances of Configurations B-I in all the feed condition gave better results than that of Configurations A thanks to the extension of heating step with using less N₂ purge gas. In this study, the pressure limit in the fixed bed was 2.3 bar. In real life applications, the first heating step duration in the Configurations B can be extended and especially the purity values can be improved further.

The situation for the Configurations C was more complex. As explained before, Configurations C was designed by introducing a low amount of heat during the second half of the rinse step as a preliminary heating to increase the temperature up to an intermediate level and to get rid of the N₂ remained in the bed after the adsorbent step; thereby, to achieve purer CO₂ product at the end of the process [58]. Obtaining a high-purity product is crucial in the application of carbon capture and storage (CCS) because this eliminates the downstream processing requirements prior to pipeline transport. Typically, a purity of at least 95% CO₂ is specified [157]. However, there are no experimental work which succeeded to achieve such a high value with a TSA cycle using standard adsorbents in the literature.

In our case, Configuration C had adverse effect on the recovery results in the experiments conducted at 30°C; while, it improved the product purity (93% of CO₂ purity was achieved with the Configuration C at 30°C and 30% CO₂ feed condition). The recoveries
decreased because CO$_2$ also left the column during the heat induced rinse step with N$_2$. As seen from Figure 4.28, the cyclic working capacity of adsorbent with this configuration at 30°C decreased because of the decrease in the temperature differences between the adsorption and regeneration steps. However, the cyclic experiments conducted at temperatures 50°C showed improvement with Configuration C on both the “recovery and purity of CO$_2$ product”. As seen from Figure 4.24 and Figure 4.26, there were a small N$_2$ peak during the second part of the rinse step. This N$_2$, which is actually contained in the bed after the adsorption step, left the reactor before the heating step and the purity increases accordingly. In addition, the duration of rinse step, during which the heat was introduced, was very short and almost no “CO$_2$ flow” was observed at the exit gas during the step while the N$_2$ was leaving the bed; therefore, recovery did not decrease as in the previous feed condition. Moreover, the working capacity of the adsorbent increased and energy requirements were decreased. In the real systems, the purity can be improved further by recycling the small amount of CO$_2$, which leaves the reactor during this rinse step, into the feed stream.

The effects of the feed condition on the “purity and recovery of CO$_2$”, and productivity of the cycle is the another aspect to be discussed. The purity values in configurations conducted at the low adsorption temperature (30°C) were higher with the same CO$_2$ molar fraction in the feed. Because CO$_2$ concentration in the bed at the beginning of the heating step was higher for the lower adsorption temperature. This provided a larger amount of the target component (CO$_2$) which can be desorbed at the specified desorption temperature. On the other hand, the recovery increased when there is a higher the temperature difference, $\Delta T$, between adsorption and desorption steps; namely recovery values were higher at 30°C for both CO$_2$ concentrations (14% and 30%). In fact, higher temperature difference ensured lower “the pressure” at the end of the “cooling step” and lower CO$_2$ fraction at the beginning of the adsorption stage in the gas phase. Thereby, more CO$_2$ was recovered at the end of the process. In addition, from Figures 4.21, 4.23, 4.25 and 4.27, it can also be deduced that the productivity values were higher for the configurations which have higher amount of “CO$_2$ recovered” per cycle and shorter cycle time. At the same temperature, the productivity improved with the increase in CO$_2$ concentration in the feed gas stream. This was also attributed to the shorter cycle time with
the higher CO\textsubscript{2} concentration experiments. The higher adsorption temperature also restricted the productivity of the cycle.

It was noticed that a significant amount of CO\textsubscript{2} was purged out of the bed initially during the cooling step. In real applications, because of the high “CO\textsubscript{2} concentration” of the effluent during the first few seconds of cooling step, the effluent could potentially be collected in the product tank. Then, it could be recycled into the feed stream to reduce CO\textsubscript{2} loss and increase the “recovery”. To demonstrate this, the recovery and purity values of each configuration were calculated again by taking into account the initial “N\textsubscript{2} purge” effluent up to a “CO\textsubscript{2} concentration” of 50% directly to the product stream. The results are shown in Table 4.1 for each feed condition. As seen in the table, while the CO\textsubscript{2} recoveries increased in most of the configurations, CO\textsubscript{2} purities decreased a little by means of dilution with N\textsubscript{2} gas used during the cooling step. In addition, the working capacities of the adsorbent were increased as a result of the increase in the amount of product recovery. The new working capacity were found between 0.35 – 1.82 mol CO\textsubscript{2}/kg adsorbent. Accordingly, the thermal energy requirements were found between 1.02 and 2.16 MJ/ kg which were a little lower than the previous calculations where the product stream did not be included in the cooling step stream. However, there is always a trade off between the “purity” and “recovery”, and this should be considered while deciding on the utilization of the purge effluent as a product stream.

As a conclusion, the optimal operation condition, which maximizes the “productivity” and minimizes the “specific energy requirement”, for the single-bed five-step TSA process was observed at “adsorption temperature” of 30°C with 30% CO\textsubscript{2}, “desorption temperature” of 120°C with configuration B. CO\textsubscript{2} purity of 89% and 87% recovery were obtained for the optimal operation condition.

The TSA configurations provided a substantial improvement in operation performance parameters while using a biomass based activated carbon adsorbent with regeneration temperatures up to 130°C and without making use of compression or vacuum. Thus, they have a very high potential to be used in a post-combustion capture process for subsequent
CO₂ storage. Of course, the process configuration (number of beds, step duration, etc.) has not been optimized yet to maximize the efficiency.

4.8.2.3. Vacuum Swing Adsorption (VSA) Cycles

In this section, the analysis of several “Vacuum Swing Adsorption (VSA)” configurations with potential to be applied to the separation of CO₂ from industrial flue gas is presented. The characteristic parameters have been estimated with Equations 3.18 – 3.22. The configurations were experimentally tested in the single fixed-bed unit for the same feed conditions evaluated in the TSA experiments: 14 and 30% CO₂, balance N₂, in the feed gas and adsorption temperatures of 30 and 50°C.

The VSA configurations represented a real system with 3 columns working synchronously to guarantee the continuous processing of the feed. The main steps in the configurations were: adsorption, rinse with CO₂, blowdown (vacuum), purge with N₂ and pressurization. The timing for these steps and their configurations were explained in detail in “Section 3.5.3.3”. It is worth noting that the feed steps were scheduled equal to half of the sum of the duration of rinse with CO₂, evacuation, and purge with N₂ steps to provide continuous feed processing in a system with three columns.

In this section, the effect of the step duration on the process performance of the VSA configurations will be discussed. It should be noted that the total duration of the cycles for each feed condition kept constant while the duration of the individual steps, with the exception of the adsorption stage, changed. The duration of the adsorption step was set close to the breakthrough time, but half a minute longer than in the TSA cases for a similar feed condition, because regeneration with vacuum produces more CO₂.
Table 4.15. CO₂ recovery and purity recalculation including the cooling step.

<table>
<thead>
<tr>
<th>Feed conditions</th>
<th>Configuration</th>
<th>CO₂ Recovery (%)</th>
<th>CO₂ Purity (%)</th>
<th>Working Capacity (mmols/g)</th>
<th>Energy Requirement (MJ/kg CO₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Heating</td>
<td>Cooling</td>
<td>Total</td>
<td>Heating</td>
</tr>
<tr>
<td>14% CO₂, 30°C</td>
<td>A</td>
<td>76</td>
<td>5</td>
<td>81</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>65</td>
<td>0</td>
<td>65</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td>B-I</td>
<td>86</td>
<td>0</td>
<td>86</td>
<td>69</td>
</tr>
<tr>
<td></td>
<td>C-I</td>
<td>77</td>
<td>0</td>
<td>77</td>
<td>77</td>
</tr>
<tr>
<td>30% CO₂, 30°C</td>
<td>A</td>
<td>72</td>
<td>9</td>
<td>81</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>87</td>
<td>8</td>
<td>95</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>B-I</td>
<td>82</td>
<td>10</td>
<td>92</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>71</td>
<td>4</td>
<td>75</td>
<td>93</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>87</td>
<td>10</td>
<td>97</td>
<td>87</td>
</tr>
<tr>
<td>14% CO₂, 50°C</td>
<td>A</td>
<td>43</td>
<td>19</td>
<td>62</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>47</td>
<td>6</td>
<td>53</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>B-I</td>
<td>49</td>
<td>8</td>
<td>57</td>
<td>51</td>
</tr>
<tr>
<td></td>
<td>C-I</td>
<td>63</td>
<td>5</td>
<td>68</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>77</td>
<td>14</td>
<td>91</td>
<td>60</td>
</tr>
<tr>
<td>30% CO₂, 50°C</td>
<td>A</td>
<td>42</td>
<td>17</td>
<td>59</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>B-I</td>
<td>51</td>
<td>15</td>
<td>66</td>
<td>64</td>
</tr>
<tr>
<td></td>
<td>C-I</td>
<td>66</td>
<td>16</td>
<td>82</td>
<td>85</td>
</tr>
</tbody>
</table>
**VSA configurations for the adsorption of 14% CO₂ at 30°C**

The total cycle time of the configurations for this feed condition was set at 22.5 min, with a R/F ratio of 0.5 (mol basis) and maximum evacuation pressure of 0.005 bar. The adsorption time was set to 7.5 minutes for all the configurations. The operating conditions of each configuration are summarized in Table 4.16.

### Table 4.16. Operating conditions of the VSA configurations for the adsorption of 14% CO₂ at 30°C.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>N₂ flow (mL/min)</th>
<th>CO₂ flow (mL/min)</th>
<th>t (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Configuration A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1</td>
<td>86</td>
<td>14</td>
<td>7.5</td>
</tr>
<tr>
<td>Rinse</td>
<td>30</td>
<td>1</td>
<td>-</td>
<td>7</td>
<td>7.5</td>
</tr>
<tr>
<td>Blowdown</td>
<td>30</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>7.5</td>
</tr>
<tr>
<td><strong>Configuration B</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1</td>
<td>86</td>
<td>14</td>
<td>7.5</td>
</tr>
<tr>
<td>Rinse</td>
<td>30</td>
<td>1</td>
<td>-</td>
<td>15</td>
<td>3.5</td>
</tr>
<tr>
<td>Blowdown</td>
<td>30</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>11.5</td>
</tr>
<tr>
<td><strong>Configuration C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1</td>
<td>86</td>
<td>14</td>
<td>7.5</td>
</tr>
<tr>
<td>Rinse</td>
<td>30</td>
<td>1</td>
<td>-</td>
<td>15</td>
<td>3.5</td>
</tr>
<tr>
<td>Blowdown</td>
<td>30</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>Purge</td>
<td>30</td>
<td>0.005</td>
<td>10</td>
<td>-</td>
<td>3.5</td>
</tr>
<tr>
<td><strong>Configuration D</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressurization</td>
<td>30</td>
<td>1</td>
<td>86</td>
<td>14</td>
<td>1</td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1</td>
<td>86</td>
<td>14</td>
<td>6.5</td>
</tr>
<tr>
<td>Rinse</td>
<td>30</td>
<td>1</td>
<td>-</td>
<td>15</td>
<td>3.5</td>
</tr>
<tr>
<td>Blowdown</td>
<td>30</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td>Purge</td>
<td>30</td>
<td>0.005</td>
<td>10</td>
<td>-</td>
<td>3.5</td>
</tr>
<tr>
<td><strong>Configuration E</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressurization</td>
<td>30</td>
<td>1</td>
<td>86</td>
<td>14</td>
<td>1</td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1</td>
<td>86</td>
<td>14</td>
<td>6.5</td>
</tr>
<tr>
<td>Rinse</td>
<td>30</td>
<td>1</td>
<td>-</td>
<td>15</td>
<td>3.5</td>
</tr>
<tr>
<td>Blowdown</td>
<td>30</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>9</td>
</tr>
<tr>
<td>Purge</td>
<td>30</td>
<td>0.005</td>
<td>10</td>
<td>-</td>
<td>2.5</td>
</tr>
</tbody>
</table>

The CO₂ concentration profiles and molar flow rates obtained at the cyclic steady state (CSS) for the different cycle configurations are presented in Figure 4.30. The characteristic performances of the different VSA configurations are presented in Figure 4.31.
(c) Configuration C

Time (min)
Concentration (%)
Pressure (kPa)

(d) Configuration D

Time (min)
Concentration (%)
Pressure (kPa)

(b) Configuration C

Time (min)
FCO$_2$ out (mmole/min)
FN$_2$ out (mmole/min)

(i) Configuration D

Time (min)
FCO$_2$ out (mmole/min)
FN$_2$ out (mmole/min)
Figure 4.30. Experimental profiles at the bed exit during the VSA cycles for a feed with 14% CO₂ at 30°C. (a), (b), (c), (d), (e) concentration and total pressure, (f), (g), (h), (i), (j) molar flow rates. N₂ (green), CO₂ (blue) and bed pressure (light brown).
During the adsorption step, CO$_2$ was preferentially adsorbed over N$_2$ and this step finalized before the HS-AC bed reached complete saturation. During this step, the gas leaving the adsorber enriched in N$_2$ and the concentration of CO$_2$ at the outlet of the bed was almost negligible (see “Figure 4.30 (a), (b), (c), (d), (e)”). The cycles started with the re-pressurization of the bed to atmospheric conditions that took about 1 min. Then, the pressure during the adsorption was maintained at 120 kPa to sustain adsorption and overcome the pressure drop in the set up.

Adding a CO$_2$ rinse step by recirculating a fraction of the product in the same direction with the feed before the blowdown step is a widely used method when the product of interest is the strong adsorbate, as in our case. The main idea of adding this rinse step is to displace the raffinate (N$_2$) retained in the bed porosity after the adsorption step and enrich the adsorbed phase in CO$_2$ in order to achieve higher CO$_2$ product purity. For the current case, since the experiments were conducted with a single fixed bed unit, it was impossible to recirculate the product. Therefore, pure CO$_2$ was fed in the same direction with the feed after the adsorption step to investigate the effect of recirculation. In Configuration A, the rinse step was conducted with 7 mL/min of CO$_2$ for 7.5 min which represents 50% of the CO$_2$ in the feed stream. In the subsequent Configurations of B, C,
D and E, the duration of the CO\textsubscript{2} rinse step was reduced to 3.5 min by keeping the total mole of CO\textsubscript{2} fed to the system constant. That much amount of time was added to the evacuation step in order to maintain the configuration with three columns. As seen from pressure graphs in Figure 4.30, at the beginning of the rinse step, the total pressure of the bed dropped slightly because of the reduction of the flow rate fed to the system.

Then, the product (CO\textsubscript{2}) was recovered by reducing the pressure in the blowdown (evacuation) step. The duration of the regeneration step under vacuum in Configuration A was set equal to that of the adsorption step (7.5 min); then, as stated before, the evacuation step extended to 11.5 min in subsequent configurations. At the beginning of the evacuation steps of these configurations, the bed pressure rapidly fell from approximately 120 kPa to 20 kPa and a peak in the molar flow rates of both N\textsubscript{2} and CO\textsubscript{2} was observed. The sharp N\textsubscript{2} peak was due to the Nitrogen retained in the void spaces of the unit and the inter-particular volume of the bed. The CO\textsubscript{2} peak was attributed to the CO\textsubscript{2} desorbed from the HS-AC as a result of the pressure reduction. After this point, the pressure kept decreasing but at a slower pace until it reached the final set point of 0.5 kPa.; meanwhile, the CO\textsubscript{2} concentration increased up to 100% (see Figure 4.30 (a), (b), (c), (d) and (e)).

In Configuration B, the extension of the evacuation resulted in the increase of CO\textsubscript{2} concentration near 100 % and the decrease of N\textsubscript{2} concentration to approximately 5% (see Figure 4.30 (b)). The extension of the blowdown step in Configuration B allowed both the purity and recovery to increase slightly from 68% to 71 % and from 75% to %78 CO\textsubscript{2}, respectively.

The blowdown steps of Configurations C and D were also scheduled to 11.5 min but, during the last 3.5 min of it—called as purge step—a low N\textsubscript{2} purge flow (10 mL/min) was introduced to the bed at the reduced pressure. The aim was to sweep the CO\textsubscript{2} retained in the bed, which had not been desorbed during blowdown step; thereby, prevent the CO\textsubscript{2} from leaving the column with the raffinate (N\textsubscript{2}) during the next adsorption step. In the last configuration (Configuration E), the N\textsubscript{2} purge flow introduced to the bed at the last
2.5 min (1 min shorter) in order to evaluate the effect of the purge step duration on the process parameters.

During the N₂ purge step, the low pressure of the system was maintained as in the blowdown step. As seen from Figure 4.30 (h), (i) and (j), at the beginning of the purge step (approximately at t=19 min for the configurations of C and D and t=20 min for the Configuration E), CO₂ molar flow rate in the effluent increased instantaneously due to the sweeping effect of N₂ purge that pushes the CO₂ retained in the void volume of the system. Simultaneously, the CO₂ concentration showed a decay during the N₂ purge step.

As can be seen in Figure 4.30 (a) and (b), CO₂ concentration at the exit during the adsorption and rinse steps in Configurations A and B were about 5%, while it is less than 1% in Configurations C, D and E in which purge step was present. Hence, adding the purge step resulted in a higher purity of N₂ (%99) and a lower loss of CO₂ during the adsorption and rinse steps. In addition, as can be seen in Figure 4.30 (h), (i), (j), the molar flow peak of CO₂ in configuration C, D and E in evacuation step reached a higher value than that in configuration A and B. Thus, introducing a stream of N₂ further reduced the partial pressure of CO₂ in the bed and favoured its desorption; thereby, improved the recovery of CO₂—the recovery values of CO₂ in the Configuration C, D and E were calculated as 100%.

Lastly, in the Configurations D and E, the pressurization of the bed was carried out for 1 minute in order to increase the bed pressure to adsorption pressure. During the pressurization step, the feed gas was at the same flow rate with the feed step and the bed outlet was closed, and neither N₂ nor CO₂ leave the bed. Therefore, CO₂ and N₂ concentrations detected could only be residuals in the outlet line. Pressurization of the bed which is provided by the flow introduced in the same direction with the feed prevented the loss of CO₂ at the beginning of the adsorption step and CO₂ purity was improved to 83%. In Configuration E, the decrease of the length of the purge step did not changed the CO₂ and N₂ concentration profiles at the column outlet; so the process performances at this feed condition.
VSA configurations for the adsorption of 30% CO₂ at 30°C

To simulate industrial off gases of higher CO₂ concentration, a feed gas with 30% CO₂ was also tested for the 3, 4 and 5-step VSA configurations simulating the operation with 3 columns. The total cycle time was set at 16.5 min, a R/F ratio of 0.5 (mol basis) was selected and an evacuation pressure of 0.005 bar (0.5 kPa). The flow rates and step times are summarized in Table 4.17.

Table 4.17. Operating conditions of the VSA configurations for the adsorption of 30% CO₂ at 30°C.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>N₂ flow (mL/min)</th>
<th>CO₂ flow (mL/min)</th>
<th>t (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Configuration A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1</td>
<td>70</td>
<td>30</td>
<td>5.5</td>
</tr>
<tr>
<td>Rinse</td>
<td>30</td>
<td>1</td>
<td>-</td>
<td>15</td>
<td>5.5</td>
</tr>
<tr>
<td>Blowdown</td>
<td>30</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>5.5</td>
</tr>
<tr>
<td><strong>Configuration B</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1</td>
<td>70</td>
<td>30</td>
<td>5.5</td>
</tr>
<tr>
<td>Rinse</td>
<td>30</td>
<td>1</td>
<td>-</td>
<td>33</td>
<td>2.5</td>
</tr>
<tr>
<td>Blowdown</td>
<td>30</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>8.5</td>
</tr>
<tr>
<td><strong>Configuration C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1</td>
<td>70</td>
<td>30</td>
<td>5.5</td>
</tr>
<tr>
<td>Rinse</td>
<td>30</td>
<td>1</td>
<td>-</td>
<td>33</td>
<td>2.5</td>
</tr>
<tr>
<td>Blowdown</td>
<td>30</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>Purge</td>
<td>30</td>
<td>0.005</td>
<td>10</td>
<td>-</td>
<td>2.5</td>
</tr>
<tr>
<td><strong>Configuration D</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressurization</td>
<td>30</td>
<td>1</td>
<td>70</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1</td>
<td>70</td>
<td>30</td>
<td>4.5</td>
</tr>
<tr>
<td>Rinse</td>
<td>30</td>
<td>1</td>
<td>-</td>
<td>33</td>
<td>2.5</td>
</tr>
<tr>
<td>Blowdown</td>
<td>30</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>Purge</td>
<td>30</td>
<td>0.005</td>
<td>70</td>
<td>-</td>
<td>2.5</td>
</tr>
<tr>
<td><strong>Configuration E</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressurization</td>
<td>30</td>
<td>1</td>
<td>70</td>
<td>30</td>
<td>1</td>
</tr>
<tr>
<td>Adsorption</td>
<td>30</td>
<td>1</td>
<td>70</td>
<td>30</td>
<td>4.5</td>
</tr>
<tr>
<td>Rinse</td>
<td>30</td>
<td>1</td>
<td>-</td>
<td>33</td>
<td>2.5</td>
</tr>
<tr>
<td>Blowdown</td>
<td>30</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>Purge</td>
<td>30</td>
<td>0.005</td>
<td>10</td>
<td>-</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The CO₂ concentration profiles and molar flowrates measured at the exit of the bed for the different cycle configurations of this adsorption condition are plotted in Figure 4.32.
Pressure (kPa) vs. Concentration (%) vs. Time (min)

(a) Configuration A

(b) Configuration B

Pressure (kPa) vs. FCO₂, out (mmole/min) vs. Time (min)

(f) Configuration A

(g) Configuration B
Figure 4.32. Experimental profiles at the bed exit during the VSA cycles for a feed with 30% CO$_2$ at 30°C. (a), (b), (c), (d), (e) concentration and total pressure, (f), (g), (h), (i), (j) molar flow rates. N$_2$ (green), CO$_2$ (blue) and bed pressure (light brown).
The results of the process performances of the VSA cycles conducted with 30% CO\textsubscript{2} balance with 70% N\textsubscript{2} feed at 30°C for the “Configurations A, B, C, D and E” are plotted in Figure 4.33.

![Figure 4.33. Characteristic performances of the different VSA configurations (30% CO\textsubscript{2} at 30°C).](image)

As seen from Figure 4.32 (f), in Configuration A, the CO\textsubscript{2} molar flow with a concentration over 10% was observed during the adsorption step which implies an insufficient regeneration in the previous step and is very unfavourable for a cyclic adsorption process. The purity and recovery of CO\textsubscript{2} was calculated as 91% and 75%. Although, the extension of evacuation step in Configuration B improved the recovery to 83%, a small CO\textsubscript{2} molar flow was still being detected at the outlet of the bed during the adsorption step (see Figure 4.32 (g)).

In the Configurations C, D and E, the purge step increased the performance of regeneration so that the molar flow of CO\textsubscript{2} was almost zero during the adsorption and rinse steps (see Figure 4.32 (h), (i) and (j)). Furthermore, CO\textsubscript{2} concentration showed a simultaneous decay during the purge step because of introducing N\textsubscript{2} (see Figure 4.32 (c), (d) and (e)). The recovery increased to 91% in Configuration C and reached to 100% in
configurations D and E which utilize pressurization step. In Configurations D and E, CO$_2$ concentration at the exit decreased to less than 1% during the adsorption step (see Figure 4.32 (d) and (e)), indicating more effective recovery results. As can be seen from Figure 4.33, for all configurations at this feed condition the purity value of CO$_2$ was about 90% and did not change significantly. In Configuration E, which have shorter N$_2$ purge step, CO$_2$ concentration decreased to approximately 50% (see Figure 4.32 (e)) at the end of the purge step while it was about 35% (see Figure 4.32 (d)) in Configuration D. Thus, CO$_2$ purity in Configuration E was found a bit higher, 92%.

The VSA configurations for the adsorption condition of 14% CO$_2$ at 50°C

To evaluate the VSA cycle performances at the higher temperature, the cyclic experiments with vacuum were conducted at 50°C with the 14% and 30% CO$_2$ concentrations in the feed streams.

The total cycle times were established as 15 min for 14% CO$_2$, setting an R/F ratio of 0.5 and evacuation pressure of 0.005 bar (0.5 kPa). The flowrates and step times are presented in Table 4.18.

The variation of concentration and molar flowrates at the outlet during the cycle are presented in Figure 4.34. Additionally, the resulting CO$_2$ purity, recovery and productivity values are plotted in Figure 4.35.
Table 4.18. Operating conditions of the VSA configurations for the adsorption of 14% CO₂ at 50°C.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>N₂ flow (mL/min)</th>
<th>CO₂ flow (mL/min)</th>
<th>t (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Configuration A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1</td>
<td>86</td>
<td>14</td>
<td>5</td>
</tr>
<tr>
<td>Rinse</td>
<td>50</td>
<td>1</td>
<td>-</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>Blowdown</td>
<td>50</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td><strong>Configuration B</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1</td>
<td>86</td>
<td>14</td>
<td>5</td>
</tr>
<tr>
<td>Rinse</td>
<td>50</td>
<td>1</td>
<td>-</td>
<td>17.5</td>
<td>2</td>
</tr>
<tr>
<td>Blowdown</td>
<td>50</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>8</td>
</tr>
<tr>
<td><strong>Configuration C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1</td>
<td>86</td>
<td>14</td>
<td>5</td>
</tr>
<tr>
<td>Rinse</td>
<td>50</td>
<td>1</td>
<td>86</td>
<td>17.5</td>
<td>2</td>
</tr>
<tr>
<td>Blowdown</td>
<td>50</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>Purge</td>
<td>50</td>
<td>0.005</td>
<td>10</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td><strong>Configuration D</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressurization</td>
<td>50</td>
<td>1</td>
<td>86</td>
<td>14</td>
<td>1</td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1</td>
<td>86</td>
<td>14</td>
<td>4</td>
</tr>
<tr>
<td>Rinse</td>
<td>50</td>
<td>1</td>
<td>-</td>
<td>17.5</td>
<td>2</td>
</tr>
<tr>
<td>Blowdown</td>
<td>50</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>Purge</td>
<td>50</td>
<td>0.005</td>
<td>10</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td><strong>Configuration E</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressurization</td>
<td>50</td>
<td>1</td>
<td>86</td>
<td>14</td>
<td>1</td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1</td>
<td>86</td>
<td>14</td>
<td>4</td>
</tr>
<tr>
<td>Rinse</td>
<td>50</td>
<td>1</td>
<td>-</td>
<td>17.5</td>
<td>2</td>
</tr>
<tr>
<td>Blowdown</td>
<td>50</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>7</td>
</tr>
<tr>
<td>Purge</td>
<td>50</td>
<td>0.005</td>
<td>10</td>
<td>-</td>
<td>1</td>
</tr>
</tbody>
</table>
Figure 4.34. Experimental profiles at the bed exit during the VSA cycles for a feed with 14% CO$_2$ at 50°C. (a), (b), (c), (d), (e) concentration and total pressure, (f), (g), (h), (i), (j) molar flow rates. N$_2$ (green), CO$_2$ (blue) and bed pressure (light brown).
As seen from Figure 4.35, the purity values obtained for this adsorption condition (50°C) was lower than the previous VSA cycles conducted at 30°C with the same CO₂ concentration (14%). The high adsorption temperature affects the achieved purity value severely due to the lower adsorption capacity of the HS-AC adsorbent at higher temperatures. The purity and recovery were calculated as 60% and 75%, respectively in Configuration A. The extension in the evacuation step in Configuration B increased the recovery value slightly to 78%. Again, adding the purge step in Configuration C increased the recovery substantially from 78% to 89%. In this feed condition, adding the pressurization step (Configuration D), which prevented the loss of CO₂ during the feed step, increased both the process parameters of purity and recovery to 65% and 92%, respectively. Lastly, the decrease in the length of the N₂ purge step in Configuration E, diminished the CO₂ recovery to 86%; however, it increased the purity significantly from 65% to 78%.

The VSA configurations for the adsorption condition of 30% CO₂ at 50°C
For the last case, VSA process configurations with 30% CO₂ concentration in the feed at 50°C, were assessed in the same manner. The total cycle time was established as 10.5
min, setting an “R/F ratio of 0.5” and evacuation pressure of 0.005 bar (0.5 kPa) The flowrates and step times are presented in Table 4.19.

Table 4.19. Operating conditions of the VSA configurations for the adsorption of 30% CO₂ at 50°C.

<table>
<thead>
<tr>
<th></th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>N₂ flow (mL/min)</th>
<th>CO₂ flow (mL/min)</th>
<th>t (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Configuration A</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1</td>
<td>70</td>
<td>30</td>
<td>3.5</td>
</tr>
<tr>
<td>Rinse</td>
<td>50</td>
<td>1</td>
<td>-</td>
<td>15</td>
<td>3.5</td>
</tr>
<tr>
<td>Blowdown</td>
<td>50</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>3.5</td>
</tr>
<tr>
<td><strong>Configuration C</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1</td>
<td>70</td>
<td>30</td>
<td>3.5</td>
</tr>
<tr>
<td>Rinse</td>
<td>50</td>
<td>1</td>
<td>-</td>
<td>35</td>
<td>1.5</td>
</tr>
<tr>
<td>Blowdown</td>
<td>50</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>Purge</td>
<td>50</td>
<td>0.005</td>
<td>10</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>Configuration D</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressurization</td>
<td>50</td>
<td>1</td>
<td>70</td>
<td>30</td>
<td>0.8</td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1</td>
<td>70</td>
<td>30</td>
<td>2.7</td>
</tr>
<tr>
<td>Rinse</td>
<td>50</td>
<td>1</td>
<td>-</td>
<td>35</td>
<td>1.5</td>
</tr>
<tr>
<td>Blowdown</td>
<td>50</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>4</td>
</tr>
<tr>
<td>Purge</td>
<td>50</td>
<td>0.005</td>
<td>70</td>
<td>-</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>Configuration E</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressurization</td>
<td>50</td>
<td>1</td>
<td>70</td>
<td>30</td>
<td>0.8</td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1</td>
<td>70</td>
<td>30</td>
<td>2.7</td>
</tr>
<tr>
<td>Rinse</td>
<td>50</td>
<td>1</td>
<td>-</td>
<td>35</td>
<td>1.5</td>
</tr>
<tr>
<td>Blowdown</td>
<td>50</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Purge</td>
<td>50</td>
<td>0.005</td>
<td>10</td>
<td>-</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The comparison of the CO₂ concentration profiles and molar flowrates obtained for this adsorption condition are presented in Figure 4.36 for different cycle configurations. The characteristic parameters for this VSA configurations are also given in Figure 4.37.
Figure 4.36. Experimental profiles at the bed exit during the VSA cycles for a feed with 30% CO$_2$ at 50°C. (a), (b), (c), (d) concentration and total pressure, (e), (f), (g), (h) molar flow rates. N$_2$ (green), CO$_2$ (blue) and bed pressure (light brown).
In this feed condition, 84% CO\textsubscript{2} purity and 85% CO\textsubscript{2} recovery was obtained in the basic configuration (Configuration A). As can be seen in Figure 4.37, adding purge step (Configuration C) increased the recovery from 85% to 93%. Figure 4.36 (c) shows that CO\textsubscript{2} exit concentration reached to 100% during the evacuation step in configuration D where the pressurization step was introduced and purity of CO\textsubscript{2} increased to 88%. In this figure, it can also be noticed that although its pressurization step time decreased to 0.8 min, the pressure in the bed during the pressurization step reached to above 130 kPa for a second that is higher than the adsorption pressure. This high-pressure value might have enhanced the adsorption capacity of CO\textsubscript{2}; thus, might be the reason of the higher purity. In configuration E, similar to the previous tests, the reduction in the length of the purge step increased the purity to 93%, however, caused a decrease in the recovery of CO\textsubscript{2} from 93% to 84%.

4.8.2.4. VTSA Configuration for the Adsorption Condition of 30% CO\textsubscript{2} at 50°C

A final experiment was performed combining VSA and TSA. VTSA experiment was carried out in the feed condition of 30% CO\textsubscript{2} at 50°C with similar step times, R/F ratio and vacuum level to configuration E. In this case, the bed was heated during the vacuum
step to 80°C. The flowrates and step times of VTSA configuration can be seen in Table 4.20.

Table 4.20. Operating conditions of the VTSA configuration for the adsorption of 30% CO₂ at 50°C.

<table>
<thead>
<tr>
<th>Step</th>
<th>T (°C)</th>
<th>P (bar)</th>
<th>N₂ flow (mL/min)</th>
<th>CO₂ flow (mL/min)</th>
<th>t (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressurization</td>
<td>50</td>
<td>1</td>
<td>70</td>
<td>30</td>
<td>0.8</td>
</tr>
<tr>
<td>Adsorption</td>
<td>50</td>
<td>1</td>
<td>70</td>
<td>30</td>
<td>2.7</td>
</tr>
<tr>
<td>Rinse</td>
<td>50</td>
<td>1</td>
<td>-</td>
<td>35</td>
<td>1.5</td>
</tr>
<tr>
<td>Blowdown</td>
<td>80</td>
<td>0.005</td>
<td>-</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>Purge</td>
<td>50</td>
<td>0.005</td>
<td>10</td>
<td>-</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The corresponding CO₂ profiles are illustrated in Figure 4.38. Table 4.21 shows the purities of N₂ and CO₂, and recovery of CO₂ achieved for this configuration.

Figure 4.38. Experimental profiles at the bed exit during the VTSA cycle for a feed with 30% CO₂ at 50°C. (a) concentration and total pressure, (b) molar flow rates. N₂ (green), CO₂ (blue) and bed pressure (light brown).
As seen from Figure 4.38 (b), the maximum molar flow rate of CO\textsubscript{2} achieved was higher than it was in Configuration E where the blowdown temperature was kept at 50°C (See Figure 4.36 (h)). Also, the desorption was faster due to the increase in desorption kinetics with temperature during the evacuation step, which is evident the steeper molar flow rate profile compared to Configuration E. Comparing the results of Configuration E and VTSA showed that while a CO\textsubscript{2} recovery of 100% was achieved by VTSA, the purity decreased from 93% to 85%, i.e., combining the heating step with a vacuum step leaded to a total recovery but restrained the purity. In addition, the productivity was 6.32 mole CO\textsubscript{2}/kg-h in Configuration E and it increased to 7.76 mole CO\textsubscript{2}/kg-h in VTSA.

### Table 4.21. Characteristic performances of the VTSA configuration for a feed with 30% CO\textsubscript{2} at 50°C.

<table>
<thead>
<tr>
<th>Configuration</th>
<th>N\textsubscript{2} Purity (%)</th>
<th>CO\textsubscript{2} Purity (%)</th>
<th>CO\textsubscript{2} Recovery (%)</th>
<th>Productivity (mol CO\textsubscript{2}/kg.h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VTSA</td>
<td>98</td>
<td>85</td>
<td>100</td>
<td>7.76</td>
</tr>
</tbody>
</table>

As seen from Figure 4.38 (b), the maximum molar flow rate of CO\textsubscript{2} achieved was higher than it was in Configuration E where the blowdown temperature was kept at 50°C (See Figure 4.36 (h)). Also, the desorption was faster due to the increase in desorption kinetics with temperature during the evacuation step, which is evident the steeper molar flow rate profile compared to Configuration E. Comparing the results of Configuration E and VTSA showed that while a CO\textsubscript{2} recovery of 100% was achieved by VTSA, the purity decreased from 93% to 85%, i.e., combining the heating step with a vacuum step leaded to a total recovery but restrained the purity. In addition, the productivity was 6.32 mole CO\textsubscript{2}/kg-h in Configuration E and it increased to 7.76 mole CO\textsubscript{2}/kg-h in VTSA.

#### 4.8.2.5. Comparative Assessment of VSA Cycle Performances

The results obtained in VSA experiments shows that utilizing a purge step with N\textsubscript{2} enhanced CO\textsubscript{2} desorption prior to the following adsorption step; thus, a substantial rise in “CO\textsubscript{2} recovery” was achieved in “Configurations C” compared to “Configurations A” and “B”. The CO\textsubscript{2} recoveries reached practically 100% for the adsorption temperature 30°C and above 90% for the adsorption temperature 50°C. Introducing pressurization step increased the purity of CO\textsubscript{2} for all adsorption conditions (Configuration D). To increase the “product purity” further, the length of purge step was decreased in Configuration E. However, in this case, the product recovery decreased rapidly especially for the cycles with the adsorption temperature of 50°C. Thus, it is important to optimize the molar flow of the N\textsubscript{2} purge in order to enhance the CO\textsubscript{2} recovery avoiding a massive purity reduction.

Parallel to the improvement of the CO\textsubscript{2} recovery, the productivity of the cycles was also increased for all feed conditions in Configuration C. It should be noted that the
productivity values were higher for the configurations conducted with 30% CO₂, where the recovery values were higher and the cycle times were shorter.

The minimum N₂ purity achieved experimentally was 87% (Configuration A, with the adsorption conditions at 30% CO₂ at 30°C) because in this case there was a “CO₂ loss” during the “adsorption step”. However, it was observed that the refining purity values (N₂) were very similar in all the other cases studied, ranging between 93% and 99%, which reveals the preferential “selectivity of the adsorbent” HS-AC towards the adsorption of CO₂.

The highest “CO₂ purities” were obtained in Configurations E and the lowest ones were in Configurations A. Moreover, the feed CO₂ concentration also affects the CO₂ purity substantially. Utilizing a 30% CO₂ ratio in the feed, due to the higher “CO₂ adsorption capacity” of the HS-AC at the higher “partial pressure of CO₂”, the higher purity ratios were achieved. Meanwhile, the purities of CO₂ estimated in the experiments at 30°C were higher than those obtained in the corresponding experiments at 50°C, because the adsorbent material presents a higher selectivity towards CO₂ at lower adsorption temperatures.

The cyclic parameters were improved in these VSA configurations. The results revealed that the optimal temperature for CO₂ capture with HS-AC adsorbent under VSA operation was 30°C, and optimal “partial pressure of CO₂” in feed was 30%. The best cyclic result, which has 92% CO₂ purity with 100% recovery, obtained by Configurations E, at the adsorption conditions of 30% CO₂ and 30°C. It meets the storage requirement of CO₂.

At this point, it should be recalled that in order to maximize “product purity” and prevent contamination with “raffinate (N₂)”, the “blowdown” and “purge” steps can be conducted “counter-current” to the “feed”, as in the real VSA commercial application. Furthermore, in the experiments conducted in the current study, after pressurization step, when the bed outlet is opened, some part of the CO₂ fed left the bed in the raffinate. The “loss of CO₂” could be decreased again by conducting a counter-current repressurization with “raffinate
product”. Nevertheless, adding of pressure equalization steps with this 3 bed configurations could improve the cyclic parameters and with consequent energy savings [144,196].

Lastly, by increasing the column temperature during the vacuum stage from 50 to 80°C in configuration VTSA, both the percentage of CO₂ recovered and its productivity were improved. In “Figure 4.38 (b)”, it seen that VTSA configuration leads to the highest molar flow of CO₂ (~19.5 mmole/min) obtained in the outlet effluent for the feed condition of 30% CO₂ at 50°C. Therefore, a 30°C increase in temperature during the evacuation stage has a decisive impact on the cycle’s results, at the expense of the energy associated with heating the bed.

The comparison of the best performances among the two regeneration methods “TSA” and “VSA” showed that the “CO₂ recovery” and “CO₂ purity” of “VSA” were 100% and 92%, respectively, at P=0.5 kPa for 7 min of evacuation and 10 mL/min N₂ purging. “TSA” without “evacuation” could achieve 87% of “CO₂ recovery” and 89% of “CO₂ purity” for 120°C of “desorption” temperature (with the feed condition 30% CO₂ and at 30°C). Therefore, utilizing TSA deteriorates the adsorption performance by 13% in terms of “CO₂ recovery”; and 3.2% in terms of “CO₂ purity”. However, considering the potential use of residual heat sources in commercial applications, this performance loss is acceptable. Therefore, in the light of the findings of the current study, it can be deduced that the use of HS-AC with TSA cycles is a promising method for “CO₂ capture from post combustion”.
5. CONCLUSION

The following main conclusions can be drawn from the studies carried out in this dissertation.

I. Preparation and characterization of biomass based carbonaceous adsorbent and evaluation of its CO\textsubscript{2} capture capacity and theoretical energy requirement for regeneration.

The single step activation with CO\textsubscript{2} led to development of a highly microporous carbonaceous adsorbent from hazelnut-shells (HS-AC). Major contribution of HS-AC pores with sizes below 0.6 nm and 52\% of them below 0.36 nm was confirmed by NDDFT and QSDFT models. In agreement with the “pore size distribution” analysis, the calculated value of “isosteric heats of adsorption” of “CO\textsubscript{2}” and “N\textsubscript{2}” (28 kJ/mol and 17 kJ/mol) implies a highly microporous structure of the HS-AC and stronger interaction of CO\textsubscript{2} with HS-AC, which are desirable for “CO\textsubscript{2} capture” under typical “post-combustion conditions”.

IAST model showed that the CO\textsubscript{2} uptake performance of HS-AC is not influenced significantly by presence of “N\textsubscript{2}”. In addition, higher separation factor of CO\textsubscript{2} over N\textsubscript{2} at low CO\textsubscript{2} partial pressure makes the HS-AC a good candidate for CO\textsubscript{2} capture from post-combustion flue gases.

The theoretical thermal energy requirement of HS-AC, assuming in a “temperature swing adsorption process”, was calculated between 46.8 – 71.3 kJ/mol-CO\textsubscript{2} (1.1 – 1.6 MJ/kg-CO\textsubscript{2}) on the basis of the feed and regeneration conditions. Then, considering hard coal combustion for the production of the thermal energy required for regeneration, the net theoretical CO\textsubscript{2} uptake of HS-AC was calculated to be between 0.016 – 0.064 kg CO\textsubscript{2}/kg adsorbent.
II. Evaluation of dynamic performance of HS-AC in a fixed-bed experimental set-up.

Dynamic evaluation of CO$_2$ capture capacity of HS-AC with breakthrough experiments in a fixed-bed showed that HS-AC has a fast adsorption and desorption kinetics, which is very crucial in rapid swing adsorption processes. During the breakthrough experiments, the CO$_2$ uptake capacities were found between 0.66 – 1.63 mmole/g-ads. depending on the feed conditions –a good agreement with the IAST model results. In addition, the HS-AC adsorbent showed no sign of deactivation during the breakthrough experiments.

III. Design of cyclic adsorption processes.

New TSA configurations were devised providing use of less N$_2$ gas in regeneration step and providing preliminary heat in the rinse step before the “desorption step” to enhance the “purity of CO$_2$” in the product stream. These configurations allowed to achieve “CO$_2$ purities” of 93% and 89% with recoveries of 71% and 87%, respectively (with feed condition of 30% CO$_2$ at 30°C, and regeneration at 120°C). The operation performance of the new configuration, in which less N$_2$ gas used (labelled as B), gave always better results than that of the basic one at also all the other feed conditions.

The thermal energy requirements of TSA configurations were calculated between 1.06 – 2.35 MJ/kg-CO$_2$ (46.6 – 103.4 kJ/mol-CO$_2$) depending on the feed condition and cycle configuration – a bit higher than the theoretical ones, as expected. The energy requirement values are lower than the energy requirement of amine absorption which is the mature technology of CO$_2$ post-combustion capture (176 – 264 kJ/mol-CO$_2$).

This dissertation study showed that the TSA configurations provided a substantial improvement in operation performance parameters while using a biomass based activated carbon adsorbent with “regeneration temperatures” up to 130°C and without using of vacuum. These findings are extremely promising for “TSA processes” in order to being more widely used in post-combustion capture technologies.
VSA experiments with the basic steps and known configurations were carried out to give a basis for the evaluation of results of TSA. The cyclic performance parameters of VSA configurations at all feed conditions were improved with utilizing a purge step with N₂ and introducing a pressurization step.

The “CO₂ recovery” and “CO₂ purity” of optimal VSA configuration were found 100% and 92%, respectively pressure at 0.05 kPa for 7 min evacuation and 10 mL/min N₂ purging (with feed condition of 30% CO₂ at 30°C).

Through the experimental analysis of the different TSA and VSA configurations, it was observed that higher “CO₂ purity” and “CO₂ recovery”, and accordingly higher productivity values were achieved at the lower feed temperature and higher CO₂ feed concentration.

Purity of raffinate (N₂) were similar in all the TSA/VSA configurations ranging between 87% and 99%.

A VTSA configuration was carried out at the feed condition of 30% CO₂ at 50°C, and it has been observed that combining the vacuum step with heating allows to increase the recovery to about 100%.

The comparison of the best findings among the two methods “TSA” and “VSA” showed that the cyclic performance parameters were decreased 13% in terms of “CO₂ recovery” and 3.2% in terms of “CO₂ purity” with utilizing TSA. However, considering the possibility of using available waste heat sources in the real applications, the utilization of TSA process is an encouraging method for “capturing CO₂” from post-combustion gases.

As a last word, the design of adsorption process is inherently complex and highly specific for the adsorbent used. This study evaluated the effects of “the cycle configuration” and
“the operating conditions” on “the process performance” indicators of cycles with using a biomass based activated carbon as a cheap and sustainable absorbent. Here, the process configuration has not been optimized yet to maximize the efficiency of the processes. However, it can be deducted that the TSA cycle configurations showed exceptional performance and it allows to achieve high process performances and can be announced as a encouraging method for “CO$_2$ capture” from “post combustion gases”. It is thought that this thesis study gives a contribution to fulfil the gab in the literature about the temperature driven adsorption processes for CO$_2$ capture.
Future work

The adsorption technology is not a mature technology in the CCS field. Therefore, a lot of research are needed to improve the knowledge about adsorption technologies in the literature. In order to further improve the findings from this dissertation, some future works which can be conducted are proposed in below:

- It is possible to develop a mathematical model capable of reproducing competently the cyclic experimental results provided in this dissertation.
- The performance of cyclic processes in this study is tied to the hazelnut shell derived activated carbon’s properties, it may also be possible to enhance the cyclic process performances using different adsorbents with better properties.
- The performances of the cyclic processes depend on the operating conditions selected, making it likely that the configurations will yield even better cyclic performances when optimum operating variables are used in future studies.
- More different cycle configurations should be assessed especially for TSA processes for comprehensive evaluation of the potential of the temperature driven technology to capture CO₂.
- A pilot unit can be constructed for the demonstration of the results of the cyclic adsorption processes in a large-scale.
- The performance of the adsorbent can be evaluated with the real flue gas composition including water vapour (6–15 vol.%). The effect of the concentration of “water vapour” in “flue gases” on the “CO₂ adsorption capacity” of adsorbent and cyclic process performances can be evaluated.
- A “life-cycle assessment” analysis can be conducted to evaluate environmental sustainability of the adsorption processes.
6. REFERENCES


[34] Dutcher B, Fan M, Russell AG. Amine-based CO2 capture technology development from the beginning of 2013-A review. ACS Appl Mater Interfaces


[59] Plaza MG, González AS, Pis JJ, Rubiera F, Pevida C. Production of microporous


[79] Couck S, Denayer JFM, Baron G V., Rémy T, Gascon J, Kapteijn F. An amine-functionalized MIL-53 metal-organic framework with large separation power for


6223(90)90100-D.


[173] Becnel JM, Holland CE, McIntyre J, Matthews MA, Ritter JA. Fundamentals of fixed bed adsorption processes: Analysis of adsorption breakthrough and


