WHZ Westsächsische Hochschule Zwickau
Hochschule für Mobilität

CO2 REDUCTION BY AMINE-MODIFIED STAR-SHAPED OR HIERARCHICALLY STRUCTURED SILICA ADSORBENTS IN THE AUTOMOBILES' EXHAUST

COURSE: THEORY TO PRACTICE - PTI51300

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Abstract

This paper delves into the critical issue of carbon dioxide (CO_2) emissions and their substantial role in global environmental challenges. Focusing on automobiles, which contribute significantly to global CO_2 emissions, we aim to systematically quantify emissions from various vehicle categories. Our approach involves a comprehensive methodology covering both CO_2 emission calculation and procedural steps for data cleaning and subsequent analysis using Python. Additionally, we explore the potential of Amine-Modified silica adsorbents to enhance CO_2 capture, offering benefits like high capacity, easy recovery, efficient absorption, and material stability. The broader context of climate change and global warming underscores the urgency for sustainable practices. The excessive release of CO_2, primarily from fossil fuels, necessitates innovative solutions like Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU) technologies to address environmental concerns and contribute to sustainable development.

This report is collaboratively prepared by a team consisting of Seyedeh Zahra Alavi, Bita Hamidi, Anson Kalambukattu Cijo.

1.introduction

Carbon dioxide (CO_2) emissions play a central role in discussions surrounding climate change and global environmental challenges. CO_2 is a greenhouse gas, meaning it traps heat in the Earth's atmosphere and contributes to the warming of the planet. While CO_2 is a natural component of the Earth's carbon cycle, human activities, particularly the burning of fossil fuels like coal, oil, and natural gas, have significantly increased its concentration in the atmosphere.

Cars contribute significantly to global CO_2 emissions, with passenger vehicles accounting for around 10% of global CO_2 emissions [i]. A typical passenger vehicle emits about 4.6 metric tons of CO_2 per year, with gasoline vehicles producing about 400 grams of CO_2 per mile[ii]. Luxury sports car brands like Bugatti, Rolls Royce, Lamborghini, and Ferrari are among the most polluting, emitting high levels of CO_2 per kilometer[iii]. Efforts to reduce emissions from cars include promoting fuel-efficient models, electric vehicles, and alternative transportation modes to combat climate change and improve air quality. The European Union aims to achieve a 90% reduction in greenhouse gas emissions from transport by 2050, with new CO_2 emission targets set for cars and vans to accelerate emission reductions [iv]. Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU) technologies are ways for reducing CO_2 emissions. Post-combustion is a key method, extracting CO_2 from flue gases. Despite common use, aqueous amine solutions have downsides like equipment corrosion and energy inefficiencies. In this paper, our objective is to present a systematic approach for quantifying the CO_2 emissions generated by various categories of automobiles. We aim to outline a comprehensive methodology encompassing both the calculation of CO_2 emissions and the procedural steps for data cleaning and subsequent analysis by python and then working on Amine-Modified star-shaped or hierarchically structured Silica adsorbents to improve CO_2 capture. These solid adsorbents have benefits like high capacity, easy recovery, efficient absorption, and material stability, addressing the drawbacks of traditional methods.

2.Data Collection and Initial Analysis

2.1 Explanation of Dataset on Vehicle-Related Carbon Dioxide Emissions

	A	B	C	D	E	F	G	H	I	J	K	L	M
1	Make	Model	Vehicle Class	Engine Size(L)	Cylinders	Transmission	Fuel Type	Fuel Consumptio	Fuel Consumptio	Fuel Consumptio	Fuel Consumptio	CO2 Emissions(g/)	
2	ACURA	ILX	COMPACT	2	4	AS5	Z	9,9	6,7	8,5	33	196	
3	ACURA	ILX	COMPACT	2,4	4	M6	Z	11,2	7,7	9,6	29	221	
4	ACURA	ILX HYBRID	COMPACT	1,5	4	AV7	Z	6	5,8	5,9	48	136	
5	ACURA	MDX 4WD	SUV - SMALL	3,5	6	AS6	Z	12,7	9,1	11,1	25	255	
6	ACURA	RDX AWD	SUV - SMALL	3,5	6	AS6	Z	12,1	8,7	10,6	27	244	
7	ACURA	RLX	MID-SIZE	3,5	6	AS6	Z	11,9	7,7	10	28	230	
8	ACURA	TL	MID-SIZE	3,5	6	AS6	Z	11,8	8,1	10,1	28	232	
9	ACURA	TL AWD	MID-SIZE	3,7	6	AS6	Z	12,8	9	11,1	25	255	
10	ACURA	TL AWD	MID-SIZE	3,7	6	M6	Z	13,4	9,5	11,6	24	267	
11	ACURA	TSX	COMPACT	2,4	4	AS5	Z	10,6	7,5	9,2	31	212	
12	ACURA	TSX	COMPACT	2,4	4	M6	Z	11,2	8,1	9,8	29	225	
13	ACURA	TSX	COMPACT	3,5	6	AS5	Z	12,1	8,3	10,4	27	239	
14	ALFA ROMEO	4C	TWO-SEATER	1,8	4	AM6	Z	9,7	6,9	8,4	34	193	
15	ASTON MARTIN	DB9	MINICOMPACT	5,9	12	A6	Z	18	12,6	15,6	18	359	

This dataset records information on the variations in a vehicle's CO_2 emissions based on different features. It has been sourced from the official open data website of the Canadian Government and represents a compiled version, incorporating data spanning a 7-year period. The dataset comprises a total of 7385 rows and 12 columns. Some features are represented by abbreviations, and these abbreviations are listed in table 1.

Table 1: abbreviations

<table>
<tr><td>Model
4WD/4X4 = Four-wheel drive
AWD = All-wheel drive
FFV = Flexible-fuel vehicle
SWB = Short wheelbase
LWB = Long wheelbase
EWB = Extended wheelbase</td><td>Transmission
A = Automatic
AM = Automated manual
AS = Automatic with select shift
AV = Continuously variable
M = Manual
3 - 10 = Number of gears</td></tr>
<tr><td colspan="2">Fuel Consumption
City and highway fuel consumption ratings are shown in litres per 100 kilometres (L/100 km) - the combined rating (55% city, 45% hwy) is shown in L/100 km and in miles per gallon (mpg)
CO2 Emissions
The tailpipe emissions of carbon dioxide, measured in grams per kilometer, encompass both city and highway driving.</td></tr>
</table>

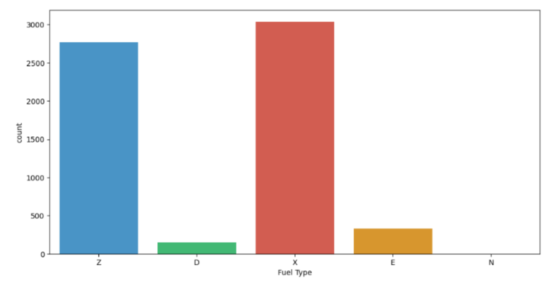
2.2 Simple Linear Regression (SLR) on Carbon dioxide emission of vehicles

Incorporating Simple Linear Regression (SLR) into our analysis focuses on unraveling the relationship between a specific factor, such as engine size or cylinders, and the associated carbon dioxide emissions from vehicles. This statistical method will provide us with a predictive equation, offering insights into how changes in the chosen factor correspond to alterations in carbon emissions. In simpler terms, it allows us to understand and quantify the influence of certain vehicle features on carbon dioxide output, aiding in predictive modeling and decision-making processes. The Python code for this analysis has been executed, explained and is available in this link:

https://colab.research.google.com/drive/1uAQxBEsHuU7bQISUa3pfECWmzB42R23m?usp=sharinghttps://colab.research.google.com/drive/1uAQxBEsHuU7bQISUa3pfECWmzB42R23m?usp=sharing

```
print(df.head())

    Make       Model Vehicle Class  Engine Size(L)  Cylinders Transmission  \
0  ACURA         ILX       COMPACT             2.0          4          AS5
1  ACURA         ILX       COMPACT             2.4          4           M6
2  ACURA  ILX HYBRID       COMPACT             1.5          4          AV7
3  ACURA     MDX 4WD   SUV - SMALL             3.5          6          AS6
4  ACURA     RDX AWD   SUV - SMALL             3.5          6          AS6

  Fuel Type  Fuel Consumption City (L/100 km)  \
0         Z                               9.9
1         Z                              11.2
2         Z                               6.0
3         Z                              12.7
4         Z                              12.1

   Fuel Consumption Hwy (L/100 km)  Fuel Consumption Comb (L/100 km)  \
0                              6.7                               8.5
1                              7.7                               9.6
2                              5.8                               5.9
3                              9.1                              11.1
4                              8.7                              10.6

   Fuel Consumption Comb (mpg)  CO2 Emissions(g/km)
0                           33                  196
1                           29                  221
2                           48                  136
3                           25                  255
4                           27                  244
```

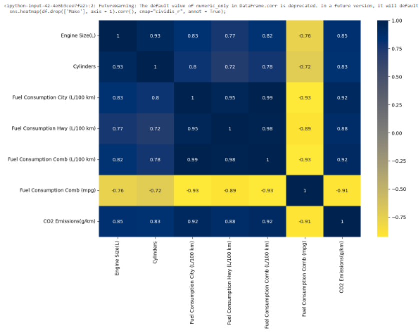
```
[36] ValueError: rotation must be 'vertical', 'horizontal' or a number, not 45
```

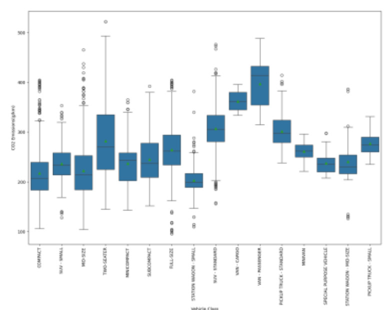


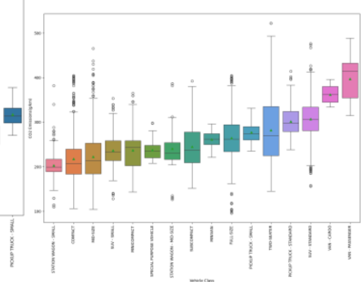

```
[37] df.describe()
```

	Engine Size(L)	Cylinders	Fuel Consumption City (L/100 km)	Fuel Consumption Hwy (L/100 km)	Fuel Consumption Comb (L/100 km)	Fuel Consumption Comb (mpg)	CO2 Emissions(g/km)
count	6282.000000	6282.000000	6282.000000	6282.000000	6282.000000	6282.000000	6282.000000
mean	3.161812	5.618911	12.610220	9.070583	11.017876	27.411016	251.157752
std	1.365201	1.846250	3.553066	2.278884	2.946876	7.245318	59.290426
min	0.900000	3.000000	4.200000	4.000000	4.100000	11.000000	96.000000
25%	2.000000	4.000000	10.100000	7.500000	8.900000	22.000000	208.000000
50%	3.000000	6.000000	12.100000	8.700000	10.600000	27.000000	246.000000
75%	3.700000	6.000000	14.700000	10.300000	12.700000	32.000000	289.000000
max	8.400000	16.000000	30.600000	20.600000	26.100000	69.000000	522.000000

```
<ipython-input-42-4e6b3cee7fa2>:2: FutureWarning: The default value of numeric_only in DataFrame.corr is deprecated. In a future version, it will default to False. Select only valid
  sns.heatmap(df.drop(['Make'], axis = 1).corr(), cmap="cividis_r", annot = True);
```







3.Global Strategies for CO2 Capture: From Industry to Automotive Solutions

Climate change has become a widely debated global concern due to its potential harm to sustainable development. The significant emission and accumulation of greenhouse gases in the atmosphere, particularly CO2, are recognized as a major factor in causing global warming. The increasing demand for energy, driven by rapid economic growth, is closely tied to the elevated use of fossil fuels such as oil, coal, and natural gas. Burning these fuels leads to notable CO2 emissions, causing environmental damage. Noteworthy approaches for reusing CO2 waste involve Carbon Capture and Storage (CCS) and Carbon Capture and Utilization (CCU) technologies. CCS involves separating CO2 from industrial sources, compressing it, and transporting it to storage sites, ensuring secure containment in geological or oceanic locations instead of releasing it into the atmosphere. This method is particularly well-suited for large sources like power or cement plants.

CCS and CCU technologies employ three main methods for capturing CO_2: post-combustion, pre-combustion, and oxy-fuel combustion. Post-combustion, which involves extracting carbon dioxide from flue gases after combustion, is the easiest to implement and is commonly used as an upgrade to existing facilities. Figure 1 provides a categorization of carbon dioxide capture technologies. The most popular method involves absorbing carbon dioxide using aqueous amine solutions, known for high efficiency but accompanied by drawbacks such as equipment corrosion, inefficient absorbent regeneration, and notable energy losses.

To address these issues, scholars are increasingly exploring the synthesis of amine-modified solid adsorbents like Amine-Modified star-shaped or hierarchically structured Silica adsorbents for CO_2 capture. This approach offers advantages such as high adsorption capacity, easy recovery and handling, efficient absorption in humid conditions, and material stability. Figure 2 illustrates various types of CO_2 adsorbents and their adsorption capacity based on adsorption temperature.

It is imperative to capture CO_2 emissions from cars because of their substantial role in climate change and air pollution. The transportation sector, particularly cars, significantly contributes to CO_2 emissions, emphasizing the necessity to adopt carbon capture technologies to alleviate their environmental impact. One effective approach involves utilizing Amine-Modified star-shaped or hierarchically structured Silica adsorbents for capturing CO_2 in the exhaust emissions from cars.[v],[vi]

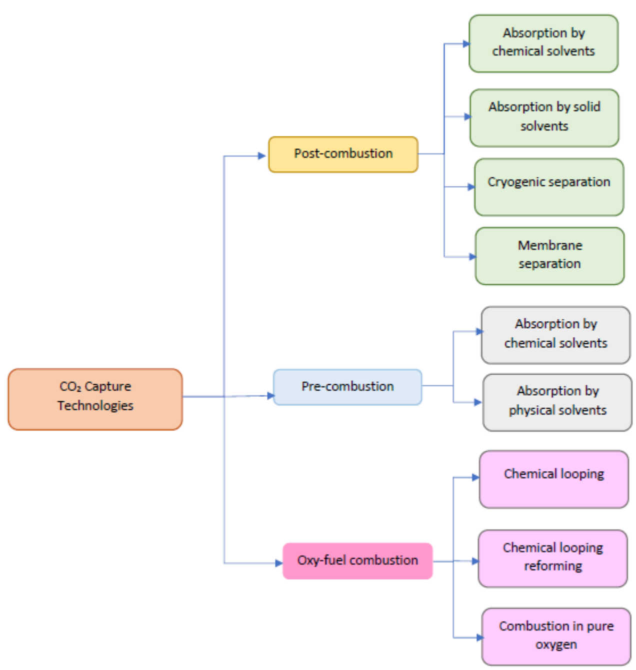


Fig. 1. CO_2 capture technologies

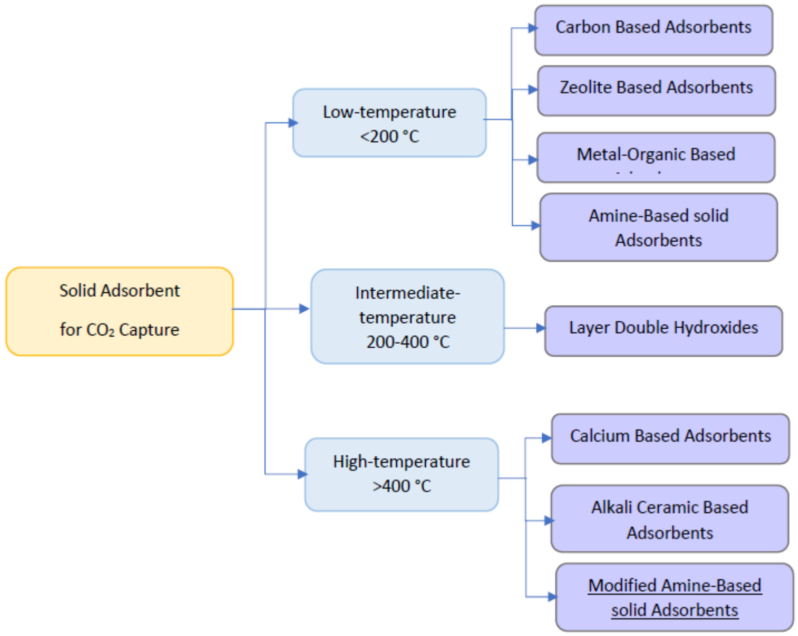


Fig. 2. Type of CO_2 adsorbents

4.Methodology for Reducing CO2 Emissions in Vehicles

Highlighting the significance of capturing CO2 emissions from cars is emphasized by the substantial impact of the transportation sector on worldwide carbon emissions. Carbon dioxide is recognized as a key contributor to global warming, and the share of carbon dioxide emissions from vehicles is approximately 65%, surpassing other emission sources. Given the impending strict emission standards, it is imperative to address this issue effectively.[vii]

From 2013 to 2022, there has been an observed increase in CO2 emissions, as indicated in Figure 3. From 2013 to 2022, there has been an observed increase in CO2 emissions, as indicated in Figure 3. To anticipate CO2 emissions for 2023 and 2024, we plan to use Python based on the data available on "www.kaggle.com." Subsequently, we aim to implement Amine-Modified star-shaped or hierarchically structured Silica solid adsorbents, taking into account essential parameters for effective adsorption in vehicle exhaust. This specific adsorbent is a type of synthesized amine-modified solid adsorbent designed to capture and diminish CO2 emissions. Consequently, we can compare the levels of CO2 emissions with and without the application of this adsorbent to assess the reduction achieved.

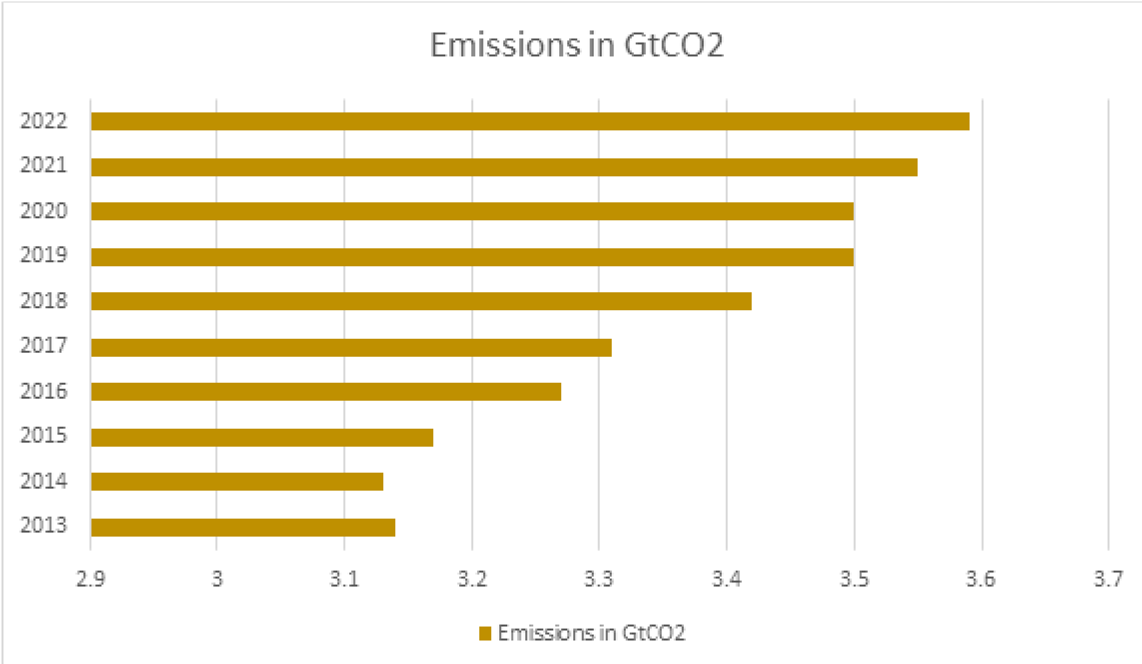


Fig. 3: CO_2 emissions from cars and vans worldwide from 2013-2022

In this experiment, a specified quantity of silica adsorbents, modified with amines and designed in either a star-shaped or hierarchically structured configuration, will be introduced into the exhaust systems of diverse types of vehicles. The primary objective is to diminish and capture CO_2 emissions. Subsequently, an analysis of the experimentally calculated CO_2 emission and reduction for the years 2023-2024 will be conducted. This innovative technology holds the potential to transform emissions reduction practices across various modes of transportation, including trucks, trains, planes, and boats, by establishing a connection between vehicles and CO_2 distribution infrastructure, enabling the capture of carbon emissions at the source. The technology operates by capturing CO_2 emissions from car exhausts through a process known as adsorption. Amines, organic compounds with the ability to chemically react with CO2, enhance the adsorption capabilities of silica, making them particularly adept at selectively capturing CO_2 from sources with low concentrations, such as vehicle exhaust and flue gas. The adsorption process involves the following sequential steps:

- **Adsorption Process:** As the exhaust gas, containing CO_2, traverses through the adsorbent, a chemical reaction with CO_2 occurs, enabling the adsorbent to selectively capture the CO_2 from the gas stream.
- **Storage or Utilization**: The captured CO_2 can be stored for subsequent disposal or utilized in various industrial processes, thereby contributing to emissions reduction.

- **Regeneration**: Once the adsorbent reaches saturation, regeneration becomes imperative to restore its capacity. This involves desorbing the captured CO_2 molecules, typically achieved through processes such as heating, vacuum treatment, or purging with inert gases [viii].

To evaluate high-performing amine-modified star-shaped or hierarchically structured silica adsorbents for CO_2 capture in car's exhaust, consider the following key parameters:

1. Selection of Materials: Choose appropriate silica materials with star-shaped, hierarchically, or mesoporous structures, such as MCM-41, HMS, or SBA-15, recognized for their expansive surface area and adjustable pore sizes. Additionally, opt for suitable amine molecules, including polyethylenimine (PEI), tetraethylenepentamine (TEPA), or monoethanolamine (MEA), based on their reactivity and efficiency in capturing CO_2.
2. Surface Area Consideration: The elevated surface area of adsorbents in car exhaust facilitates an augmented presence of active sites, enhancing the potential for CO_2 adsorption.
3. Pore Size Impact: The size of pores in Amine-Modified star-shaped or hierarchically structured Silica adsorbents is a key determinant of their CO_2 adsorption capability and efficiency. An optimal pore size and volume enable the effective diffusion of CO_2 molecules into the star-shaped or hierarchically structured matrix. Smaller pores generally result in greater CO_2 adsorption capacities, attributed to intensified interactions between CO_2 molecules and the internal surface of the adsorbent. However, smaller pores may concurrently raise mass transfer resistances, placing a limitation on the adsorption rate. Although smaller pores contribute significantly to CO_2 adsorption, larger pore volumes enhance the permeation of CO_2 molecules throughout the adsorbent matrix, promoting mass transfer and elevating overall adsorption performance. Therefore, determining an optimal pore size range is crucial for achieving a balance between high adsorption capacities and swift adsorption kinetics. Consequently, the selection of an ideal pore size can be guided by experimental testing involving varying pore sizes of adsorbents.[ix]
4. Amine Loading Importance: The quantity of amine loading stands as a pivotal factor when assessing amine-modified star-shaped or hierarchically structured silica adsorbents for CO_2 adsorption in car exhaust systems. The concentration of amine groups present on the surface of the silica material significantly influences the CO_2 adsorption capacity.Through the optimization of amine loading, researchers can enhance the adsorption performance of star-shaped or hierarchically structured silica adsorbents, leading to heightened CO_2 capture

efficiency and overall effectiveness in reducing emissions from car exhausts. Research indicates that increased amine loading is associated with a higher CO_2 adsorption capacity.

5. Temperature and Pressure Influence: Elevated temperatures and pressures typically augment the adsorption kinetics and capacity of CO_2 for amine-based adsorbents, attributed to heightened molecular mobility and reaction rates. Research has demonstrated that at higher temperatures and pressures, both the adsorption capacity and rate increase, consequently enhancing the efficiency of CO_2 capture.[x]
6. Regeneration Strategy: The adsorbent should be easily regenerated without significant loss of CO_2 adsorption capacity. there are several approaches aimed at maintaining the adsorbent's CO_2 adsorption capacity without significant loss (Kawamoto, 2021)[xi] . Some of these methods include:

6.1 Thermal Desorption: Heating the adsorbent to release the CO_2 molecules, followed by cooling to restore the original structure and functionality.

6.2 Chemical Regeneration: Applying chemical agents to remove the adsorbed CO_2, such as washing with water or acid solutions.

6.3 Combination of thermal and chemical treatments: A hybrid approach that involves both heating and chemical treatment to achieve better regeneration results.

Research endeavors have concentrated on formulating effective regeneration methods for Amine-Modified star-shaped or hierarchically structured Silica adsorbents, with the goal of reducing the depletion of CO_2 adsorption capacity and sustaining long-term stability. It is imperative to scrutinize the most suitable regeneration conditions tailored to each particular adsorbent to guarantee its enduring and sustainable performance in capturing CO_2 emissions from car exhausts.

5. Calculation and Experiments

We would like to use Python to predict the amount of CO_2 emission in 2023 and 2024 based on the available data in different years. Then, the amount of CO_2 emission with considering Amine-Modified Silica adsorbent will be calculated and compared with the predicted amount.

Calculation of required surface area:

For the calculation of required surface area using the BET (Brunauer–Emmett–Teller) equation, which is commonly used for porous materials like MCM-41. The formula for calculating the BET surface area is as follows:

$$S_{BET} = \frac{6}{C} \sum \frac{ni}{\left(\frac{Pi}{P0}\right)\left(1-\left(\frac{Pi}{P0}\right)\right)} \qquad (1)$$

Where:

- S_{BET}= BET surface area
- C = constant related to the adsorbate used
- ni = amount of gas adsorbed at pressure
- Pi = equilibrium pressure
- P0 = saturation pressure
- n = number of data points

For a particular Amine-Modified star-shaped or hierarchically structured Silica adsorbent, such as amine-functionalized MCM-41, experimental information regarding gas adsorption under varying pressures can be gathered. Employing the BET equation and determining the constant C through fitting this data enables the calculation of the adsorbent's surface area. This approach offers valuable insights into the material's adsorption capacity and efficiency concerning the capture of CO_2 emissions in car exhausts.

Calculation of the CO_2 concentration and CO_2 captured volume:

Calculation of the concentration of CO_2 outlet of the cars' exhaust, CO_2 captured volume by the adsorbent can be expressed as:

$$Q_{ads} = \frac{(F\ X\ (C\ in - C\ out) X\ t}{M} \qquad (2)$$

$$V_{co2} = F\ X\ (C\ in - C\ out) X\ t \qquad (3)$$

Where:

- Q_{ads} is the adsorption capacity (mmol CO_2/g). (should be considered ≤5.5 mmol/g)
- F is the total flow rate (mmol/minute). (it can be considered as an assumption based on typical amount or experimental data)
- C_{in} is the concentration of CO_2 entering the cars' exhaust (vol%). (it can be considered as an assumption based on typical amount or experimental data based on analyzer)
- C_{out} is the concentration of CO_2 outlet of the cars' exhaust (vol%). (will calculate)
- t is the time at which C_{out} reaches its maximum (assumption)
- M is the weight of the adsorbent (g) (assumption)
- V_{co2} is volume of CO_2 captured (m3). (already calculated)

This equation can be utilized to compute the necessary weight of the adsorbent and the volume of captured CO_2, making certain assumptions about the CO_2 adsorption capacity of the amine-based adsorbent. These assumptions are derived from measured flow rates, concentration variations, and the time needed for the process.

Calculate Percentage Reduction:

Divide the CO_2 captured using the adsorbent by the CO_2 emitted without the adsorbent, and multiply by 100 to get the percentage reduction:

$$\% \text{ Reduction} = \frac{\text{CO2 Captured}}{\text{CO2 Emitted without adsorbents}} X\ 100$$

This evaluation provides insight into the effectiveness of Amine-Modified star-shaped or hierarchically structured Silica adsorbents in capturing CO_2 emissions from car exhausts. It should mention that the accuracy of the results depends on the quality and reliability of the experimental data gathered.[xii],[xiii]

Conclusion

The utilization of Amine-Modified star-shaped or hierarchically structured Silica solid adsorbents for the capture of CO2 emissions from car exhausts presents a promising strategy to alleviate the significant impact of the transportation sector on climate change and air pollution. Crucial factors influencing effective adsorption encompass material selection, surface area, pore size, amine loading, temperature and pressure, and the regeneration strategy. The BET equation proves useful in determining the required surface area of the adsorbent. Simultaneously, the concentration of CO2 in the outlet of cars' exhausts and the volume of captured CO2 enable the calculation of the achieved percentage reduction. By optimizing these parameters, researchers can enhance the adsorption capabilities of the adsorbents, resulting in heightened CO2 capture efficiency and overall effectiveness in curbing emissions from car exhausts.

Testimony and contribution

My experience in programming, especially with Python, modestly contributed to the project's success. I aimed for professionalism through dedication, a sense of responsibility, and adherence to high standards, fostering a collaborative and smoothly progressing environment.

Partnering with Zahra Alavi on this experimental project was an enriching experience. Zahra's understanding of Python, coupled with her dedication and scientific enthusiasm, proved instrumental in the project's success. I am confident that Zahra will not only continue to excel but also make significant contributions to the field in future endeavors.

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[i] https://earth911.com/business-policy/which-car-brands-emit-the-most-carbon-dioxide/

[ii] https://247wallst.com/special-report/2023/07/19/the-worst-new-cars-for-humans-and-the-environment/

[iii] https://www.pollutionsolutions-online.com/news/air-clean-up/16/breaking-news/what-are-the-most-polluting-cars/42314

[iv] https://www.forbes.com/sites/jimgorzelany/2021/02/24/dirty-bakers-dozen-the-13-environmentally-meanest-vehicles-for-2021/?sh=58d9c460165b

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[x] Yihe Miao, Z. H. (2021). Operating temperatures affect direct air capture of CO2 in polyamine-loaded mesoporous silica.

[xi] Kawamoto, K. (2021). Adsorption characteristics of the carbonaceous adsorbents for organic compounds in a model exhaust gas from thermal treatment processing.

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[xiii] Rossella Girimonte, F. T. (2020). Adsorption of CO2 on Amine-Modified Silica Particles in a Confined-Fluidized Bed.

(2023). Retrieved from How to calculate co2 adsorption capacity?: https://www.researchgate.net/post/How_to_calculate_co2_adsorption_capacity