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POST COMBUSTION CARBON CAPTURE USING POLYETHYLENIMINE (PEI) FUNCTIONALIZED TITANATE NANOTUBES (DE-FE0023040)

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Center for Energy & Environmental Sustainability

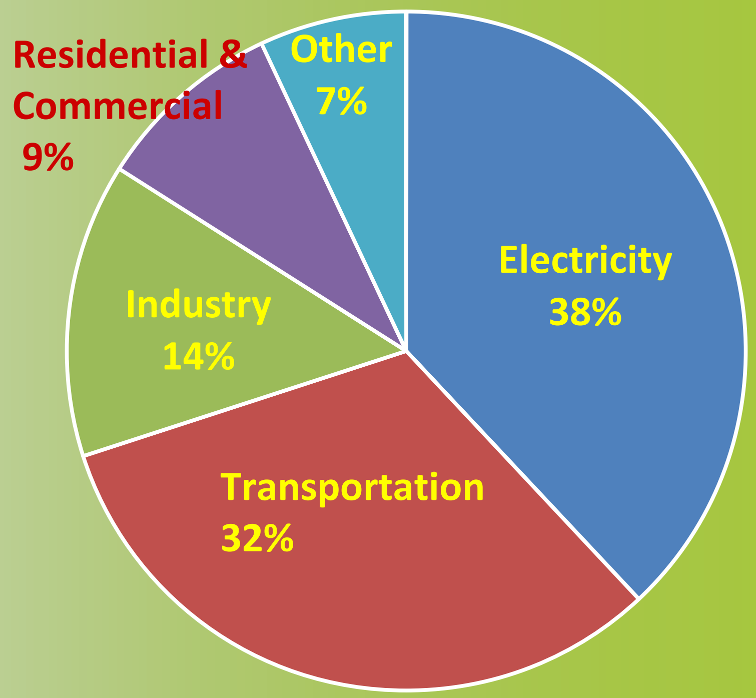
- NSF CREST Center funded in October 2010
- $5M for 5 years
- 3 research focus areas in addition to education and outreach
  - Biofuels, wind energy and Energy & Environmental Sustainability
  - 6 faculty members, 3 post-docs, and 8 grad 10-12 undergrad students per year
  - Helping to enhance the research capabilities and infrastructure

Overview

- Introduction
- Post-Combustion Capture
- Objectives
- Projects Goals and Tasks
- Timelines and Outcomes
- Participants
- Facilities and Equipment

Introduction

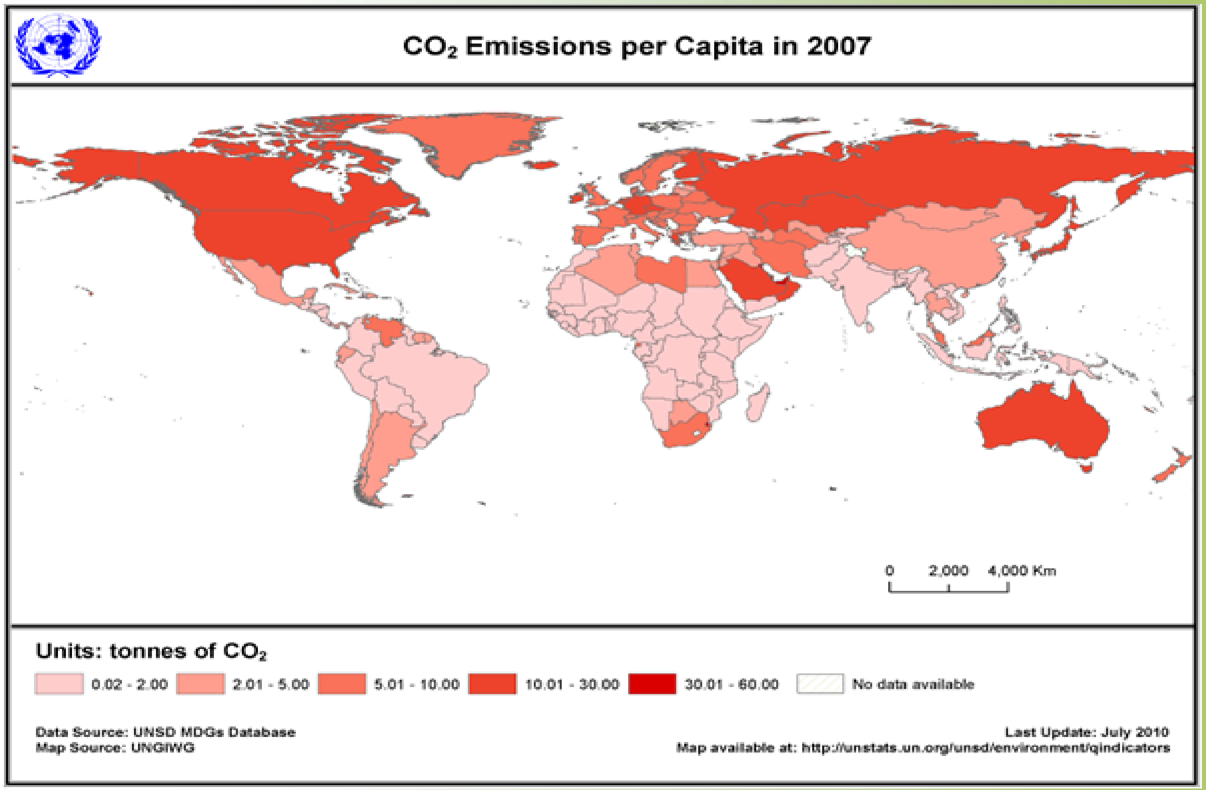
- Carbon dioxide (CO_2) is the primary anthropogenic greenhouse gas. The major human activity that produces CO_2 is fossil fuel combustion.
- The fossil fuels combustion for electricity generation accounts for about 38% of total U.S. CO_2 emissions (EPA, 2013).

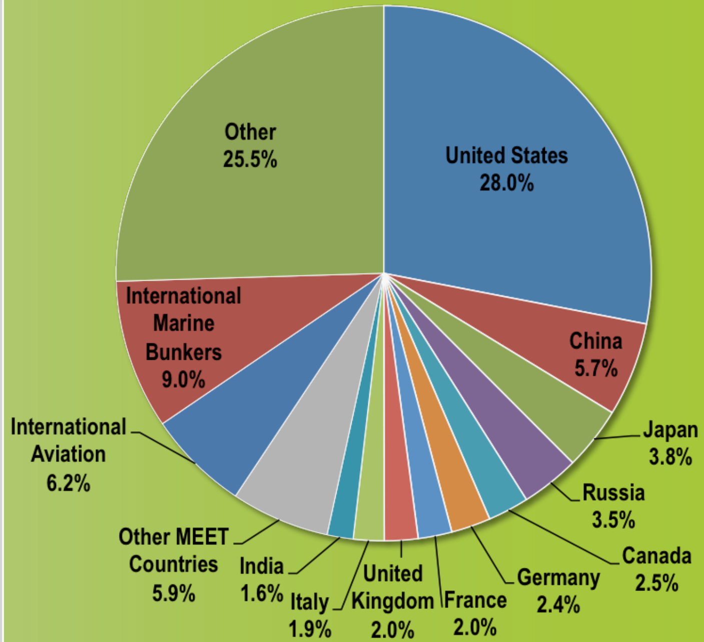


U.S. Carbon Dioxide Emissions By Source

Introduction

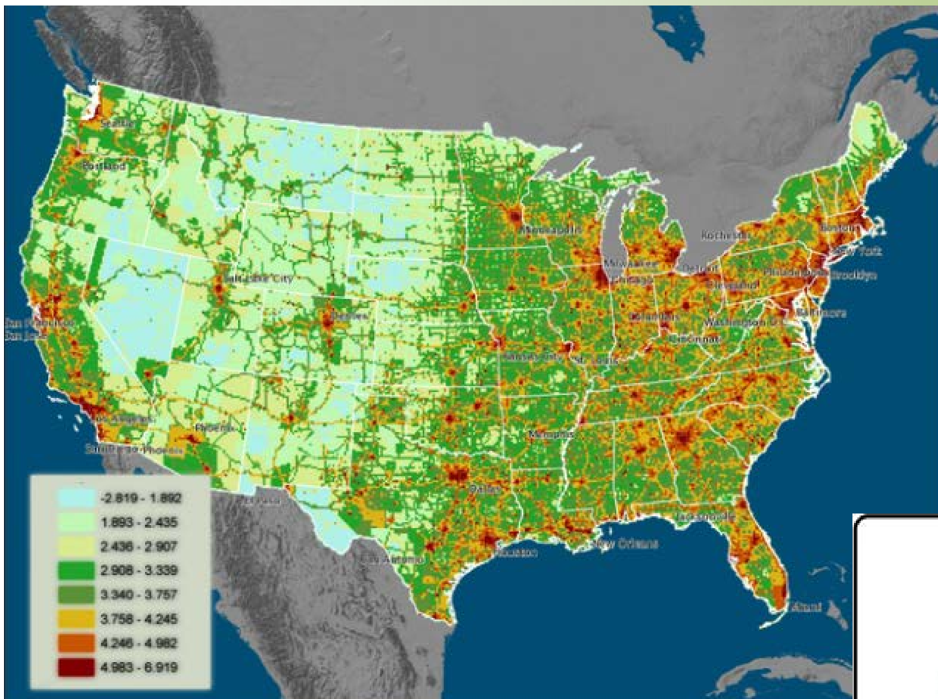
Global CO_2 Emissions





Source: mlit.go.jp

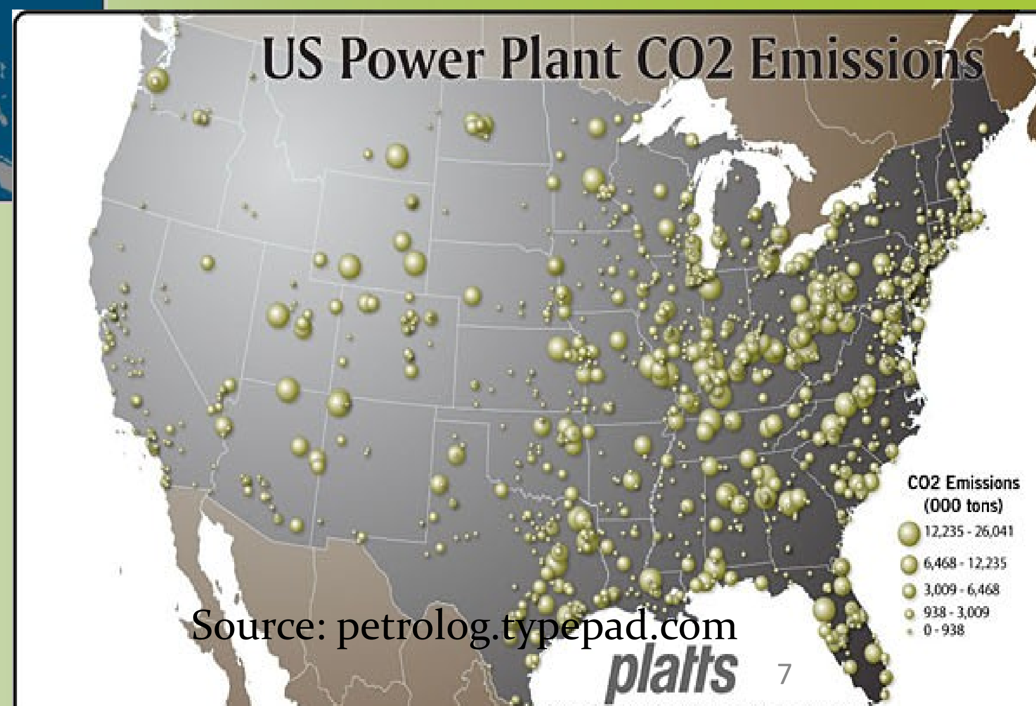
Introduction



Total CO_2 emission

Source: ohioenvironmentallawblog.com

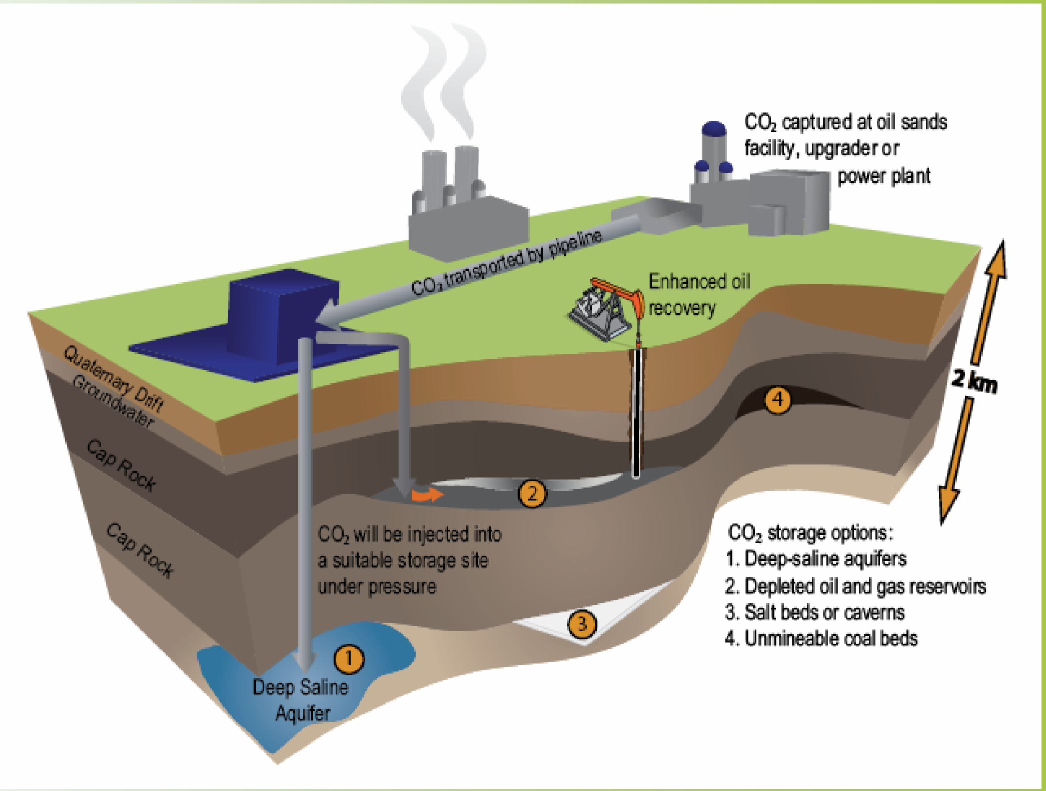
Power-plant CO_2 emission



Source: petrolog.typepad.com

Mitigation

- In order to mitigate global climate change, it is imperative that we reduce CO_2 emissions.
- One of the most effective ways to control CO_2 emissions is carbon capture and sequestration (CCS), which includes CO_2 capture, transport and storage.



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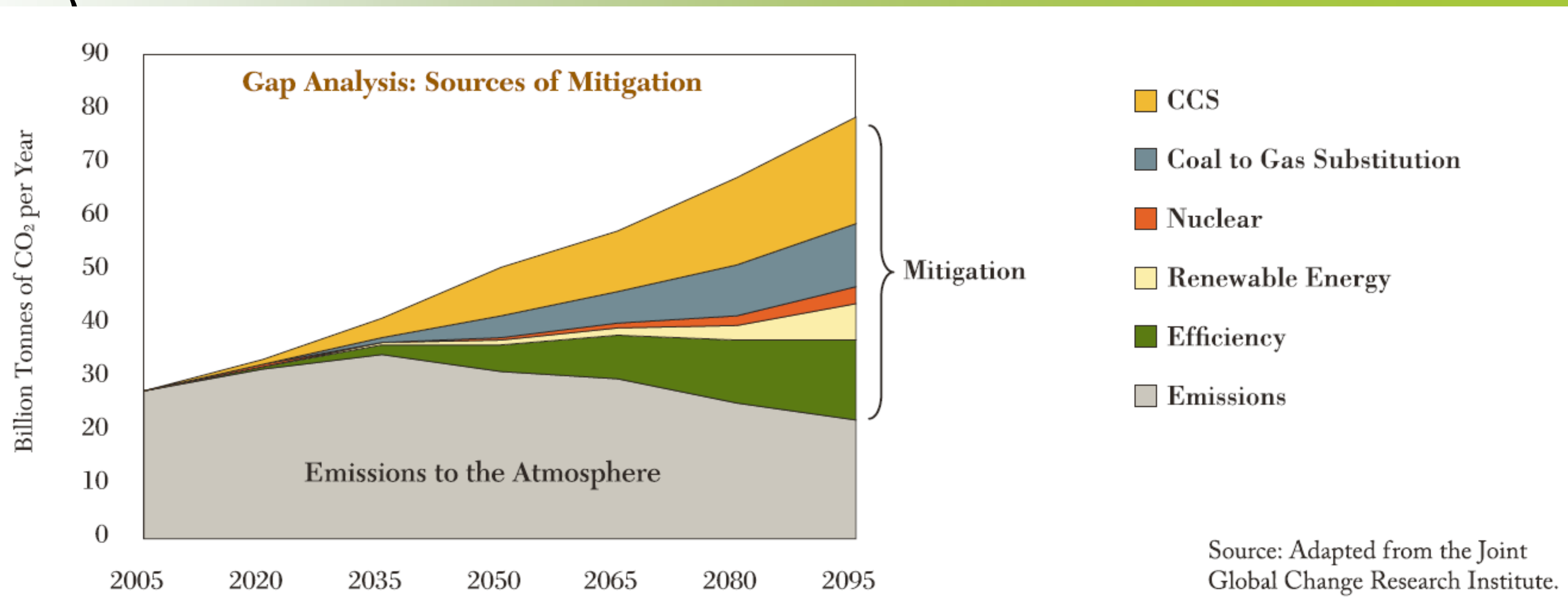
Carbon Capture and Sequestration

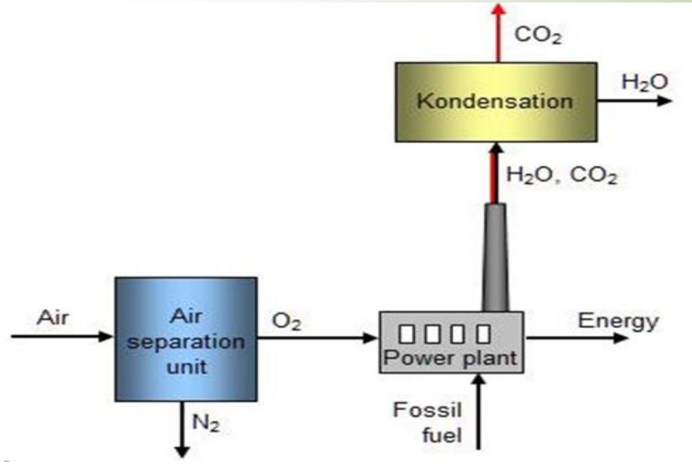
- CCS contributes one-sixth of the total CO2 emissions reductions required by 2050 and 14% of the cumulative emissions reductions through 2050 against business-as-usual scenario (International Energy Agency, 2014).
- The figure below indicates the economically efficient mix of CO2 mitigation measures to stabilize atmospheric CO2 concentrations at 550 ppm on using MiniCAM. (Logan et al., 20



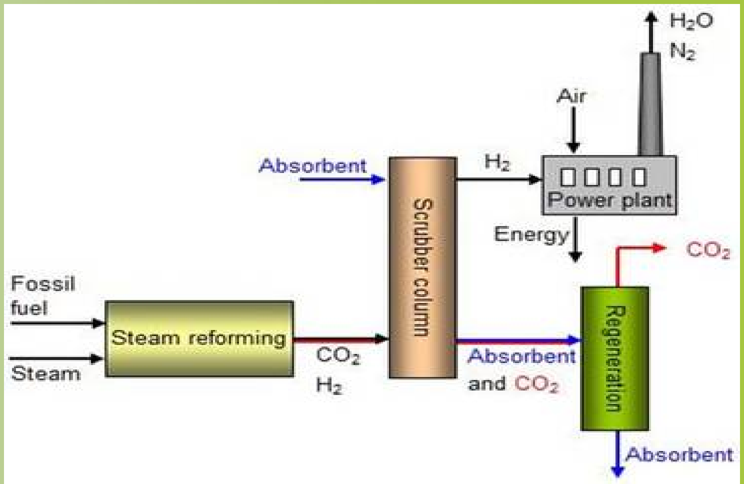
Carbon Capture and Sequestration

- The current major CO_2 capture technologies include oxy-combustion capture, pre-combustion capture, and post-combustion capture (Lee et al., 2012; Spigarelli and Kawatra, 2013).
- Each have advantages and limitations
- Post-combustion technologies are the focus here

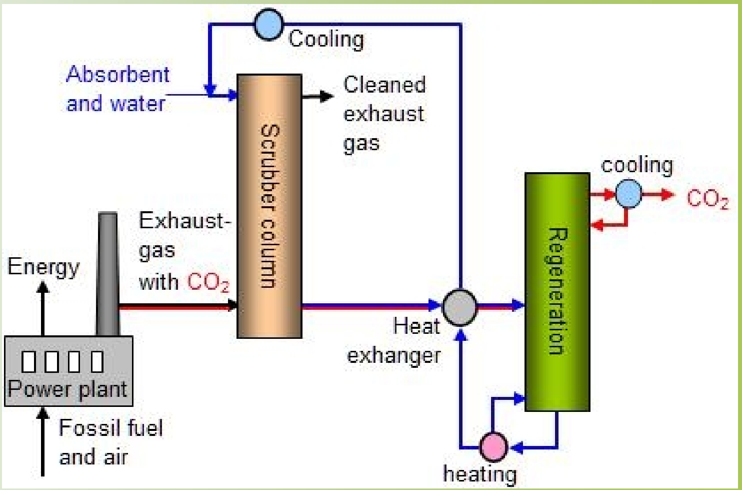
CO_2 Capture Technologies



- **Oxy-combustion capture**



- **Pre-combustion capture**

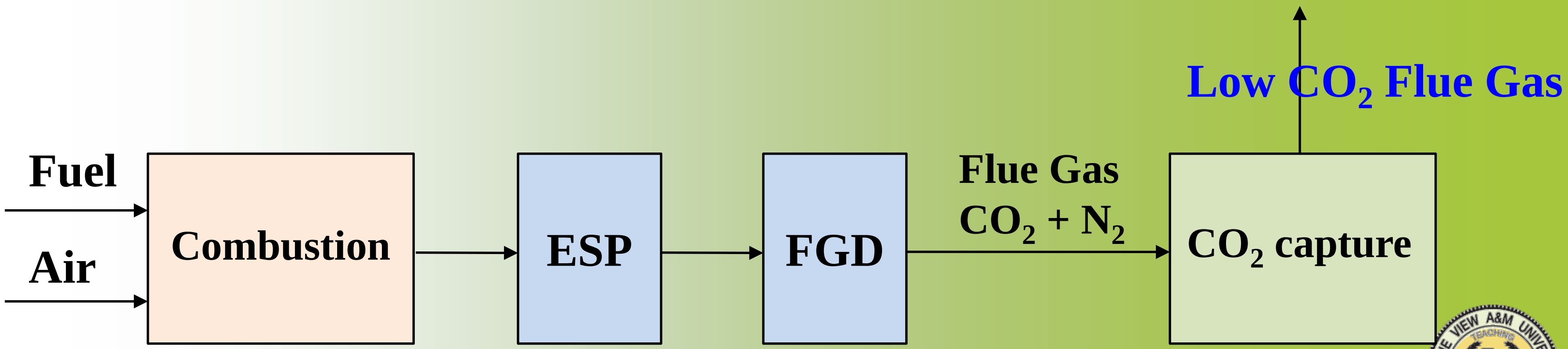


- **Post-combustion capture**

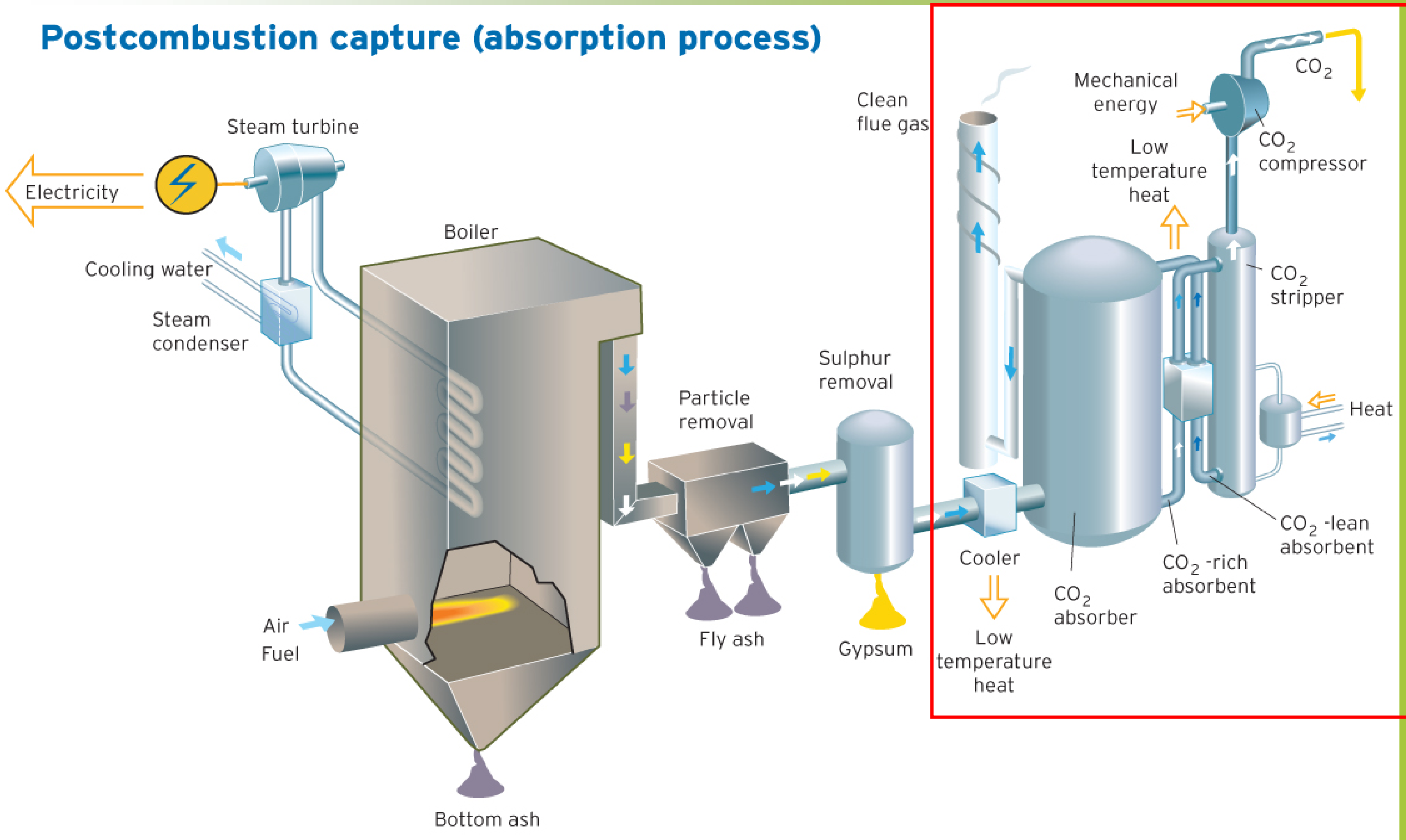
Source: Bellona Environmental CCS http://bellona.org/ccs/technology/capture/oxyfuel.html

Post Combustion CO_2 Capture Technologies

- Post-combustion carbon capture is especially desirable due to its potential to retrofit existing power plants with reasonable cost. A simplified schematic of post-combustion carbon capture for a coal-fired power plant is shown as following:
- CO_2 is captured after the flue gases are cleaned up by Electro Static Precipitator (ESP) and Flue Gas Desulfurization (FGD).



Post-Combustion CO2 Capture



Source: millicentmedia.com

Post-Combustion CO_2 Capture Technologies

- **Absorption**
  - **Chemical absorption**
    - ✓ Amines
    - ✓ Caustics
  - **Physical absorption**
    - ✓ Selexol
    - ✓ Rectisol
- **Adsorption**
  - **Chemical adsorption (TSA)**
    - ✓ Metal oxides
  - **Physical adsorption (PSA, TSA)**
    - ✓ Zeolites
    - ✓ Carbons
    - ✓ Si/Al gels

Source: Lee and Park, 2014; Spigarelli and Kawatra, 2013

Post-Combustion CO_2 Capture Technologies Continued..

- **Membrane**
  - **Organic membrane**
    - Polysulphone
    - Polyamide
    - Cellulose derivatives
  - **Inorganic membrane**
    - Metallic
    - Ceramics
  - **Enzymatic membrane**
- **Cryogenics**
- **Others**
  - **Chemical looping**
  - **CO_2 hydrate**
  - **Electrochemical pump**
  - **Microbial/Algae**

Source: Lee and Park, 2014; Spigarelli and Kawatra, 2013

Post-Combustion CO_2 Capture Technologies

- In post-combustion capture, CO_2 is removed from the flue gas after the combustion of the fossil fuel with air (DOE, 2010), and the flue gas usually has low CO_2 content and low pressure (about 1 bar).
- Current technologies for post-combustion CO_2 capture focus mainly on solvent-based absorption, however, the low pressure of the power plant flue gas would result in additional cost for CO_2 compression, transportation and storage.
- Other disadvantages of absorption include degradation in an oxidizing atmosphere, more energy intensive during regeneration, has limited CO_2 loading capacity, and are corrosive with foaming and fouling characteristics (Sreenivasulu et al., 2015).

Post-Combustion CO_2 Capture Technologies

Continued…

- To solve the challenge of processing a large-volume, low-pressure flue gas, many recent researchers have focused on the separation of CO_2 using porous solid adsorbents. The high surface areas and specific adsorption sites of porous materials make them good candidates for application in CO_2 capture.
- Nanoporous materials are porous materials with pore diameter of 100 nanometers or less, their high surface area and light weight make them promising for carbon capture application.

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Post-Combustion CO_2 Capture Technologies

Continued..

- Significant focus on nanoporous materials functionalized with amines for carbon capture due to their high selectivity and efficiency for carbon capture from flue gas.

- Synthesizing highly efficient amines-functionalized nanoporous materials is still a big challenge; more efforts need to be put on the investigation of optimal parameters for synthesizing economic and effective nanomaterial for CO_2 capture..

Relevant Literature

- Only one study (Liu et al. 2012) was obtained from the literature that was relevant to our project
- The use of modified protonated titanate nanotubes (PTNTs) in combination with PEI was examined
- The larger specific surface area (320.4 m^2/g) and pore volume (1.07 cm^3/g) of PTNTs proved to beneficial to the introduction of PEI with little hindrance, thereby, guaranteeing a high loaded capacity.
- The functionalized PTNTs with 50 wt.% PEI loading exhibited a high adsorption capacity of 130.8 mg/g-sorbent at 100^0C .

Objectives

The specific objectives of the proposed research are:

- Establish a knowledge base on the synthesis of TiO_2 nanotubes and adsorption characteristics of Polyethylenimine (PEI) and also the various protocols available for the impregnation of PEI.
- Develop optimized protocols for synthesis of TiO_2 nanotubes impregnated with PEI.
- Characterize the impregnated nanotubes and use it for refining the parameters for synthesis such as temperature, concentration and time.

Objectives (continued)

- Develop computational fluid dynamic (CFD) simulations of the carbon capture process in the reactor to optimize the reactor conditions for high carbon capture efficiency.
- Demonstrate the efficiency of impregnated TiO_2 tubes for carbon capture under various environmental conditions such as temperature and concentration,
- Establish a validated CFD model and a standard operating procedure for carbon capture using PEI impregnated TiO_2 nanotubes.

Project Tasks

- The proposed research will be carried out in a series of 7 tasks:

Project Task 1.0

Task 1.0 – Project management and planning

- A Project Management Plan (PMP) was completed and submitted to NETL, we will manage and report on activities in accordance with the plan.

Project Task 2.0

Task 2.0 – Literature review and identification of materials and protocols

- A comprehensive literature review on (i) current nanomaterial synthesis and technology for carbon capture as well as (ii) current reactor designs and optimizations that are being used will be conducted to facilitate the material synthesis and reactor design and fabrication.
- Special attention will be placed to identify innovative methods to efficiently and economically synthesize the materials and design the carbon capture reactors.

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Project Task 3.0

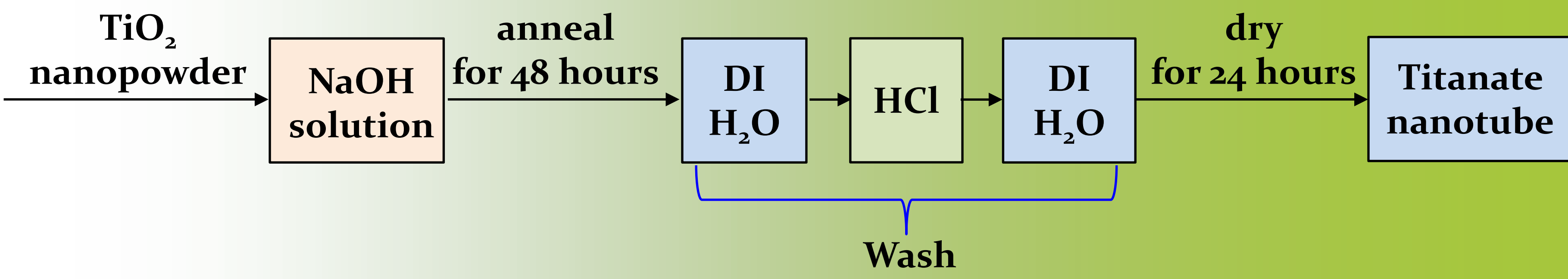
Task 3.0 – Synthesis of PEI impregnated Titanate nanotubes

- A novel nanomaterial with the unique porous properties of Titanate nanotube and the adsorption features of impregnated polyethylenimine (PEI) will be developed to efficiently capture CO_2 from the flue gas effluent from fossil energy power generation.
- Specifically, Polyethylenimine (PEI) functionalized Titanate nanotube will be synthesized using impregnation method.
- The synthesis process includes two subtasks: (i) Preparation of Titanate nanotube, (ii) Polyethylenimine (PEI) functionalization.

Project Task 3.0 (continued)

(i) Preparation of Titanate nanotube

- Hydrothermal reaction method will be used to prepare Titanate nanotube.
- The hydrothermal method is a widely used technique for preparation of Titanate nanotubes.
- A typical hydrothermal synthesis procedure:



Project Task 3.0 (continued)

(i) Preparation of Titanate nanotube (continued)

- The reaction environments such as temperature, solvent concentrations, hydrothermal duration, and the subsequent washing times, as well as washing acid concentration are critical factors that affect the characteristics of Titanate nanotubes products.
- The above parameters will be tested to acquire the optimal materials for the Polyethylenimine (PEI) functionalization step.

Project Task 3.0 (continued)

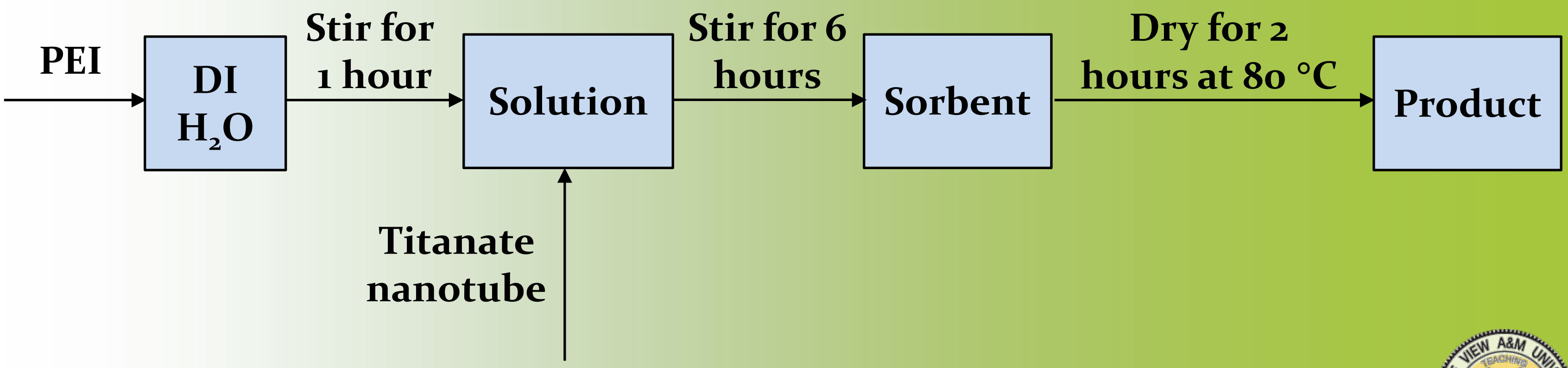
(ii) Polyethylenimine (PEI) functionalization

- Polyethylenimine (PEI) functionalization will be conducted using impregnation method, which is commonly used for amine functionalization.
- Several reaction conditions such as temperature, concentration and other parameters will be studied in order to try to optimize this functionalization procedure.

Project Task 3.0 (continued)

(ii) Polyethylenimine (PEI) functionalization (continued)

- A desired amount (amount will be varied) of PEI is dissolved in DI water by stirring for 1 hour, and then the previously made TiO2 nanotubes are added to the solution and stirred for 6 hours to obtain the sorbent. The produced material is dried at 80°C for 2 hours and kept in sealed container until use.



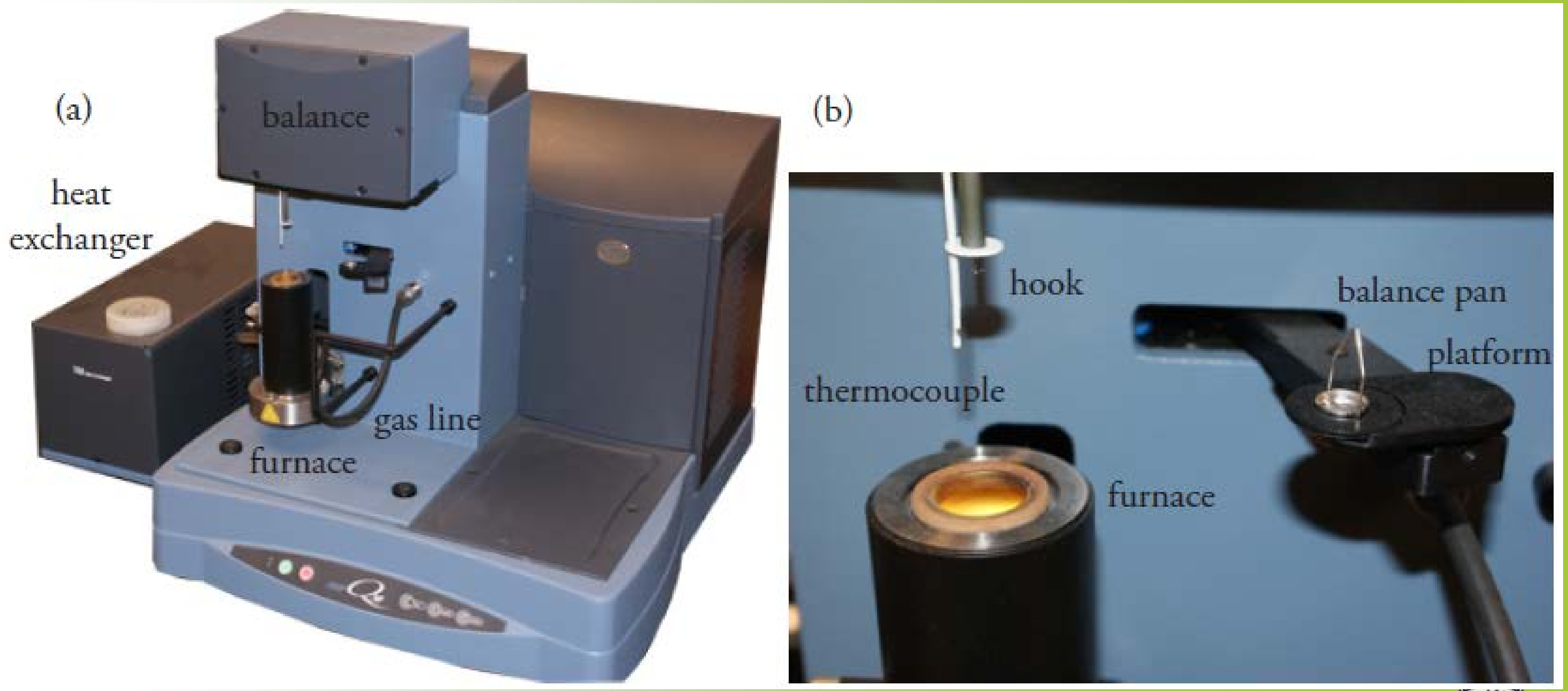
Project Task 4.0

Task 4.0 – Characterization of the PEI impregnated Titanate nanotubes and optimization of synthesis protocol

- The thermal stability of the synthesized material will be studied using Thermogravimetric analysis (TGA) to determine weight differences associated with thermal changes.
- The influence of PEI loading on CO2 adsorption performance will be measured by TGA.
- The material morphologies will be observed using transmission electron microscopy (TEM), and the structure of crystal phases will be analyzed by X-ray diffraction (XRD).

Project Task 4.0 (continued)

- The material morphologies such as textural properties before and after PEI functionalization will be investigated to optimize the parameters of the material synthesis.



http://chemwiki.ucdavis.edu/Analytical_Chemistry/Analytical_Chemistry_2.0/08%3A_Gravimetric_Methods/8C_Volatilization_Gravimetry

Project Task 4.0 (continued)

http://microscopy.tamu.edu/instruments

Transmission Electron Microscopy

- The material morphologies will be observed using transmission electron microscopy (TEM).
- Figure shows the the FEI Tecnai G2 F20 ST TEM in the Microscopy and Imaging Center at Texas A&M University.

Project Task 4.0 (continued)

X-ray Diffractometer

- The structure of crystal phases will be analyzed by X-ray diffraction (XRD).
- Figure shows the Bruker-AXS SMART1000 CCD three-circle X-ray Diffractometer in the X-ray Diffraction Laboratory at Texas A&M University.

http://xray.tamu.edu/instruments.php

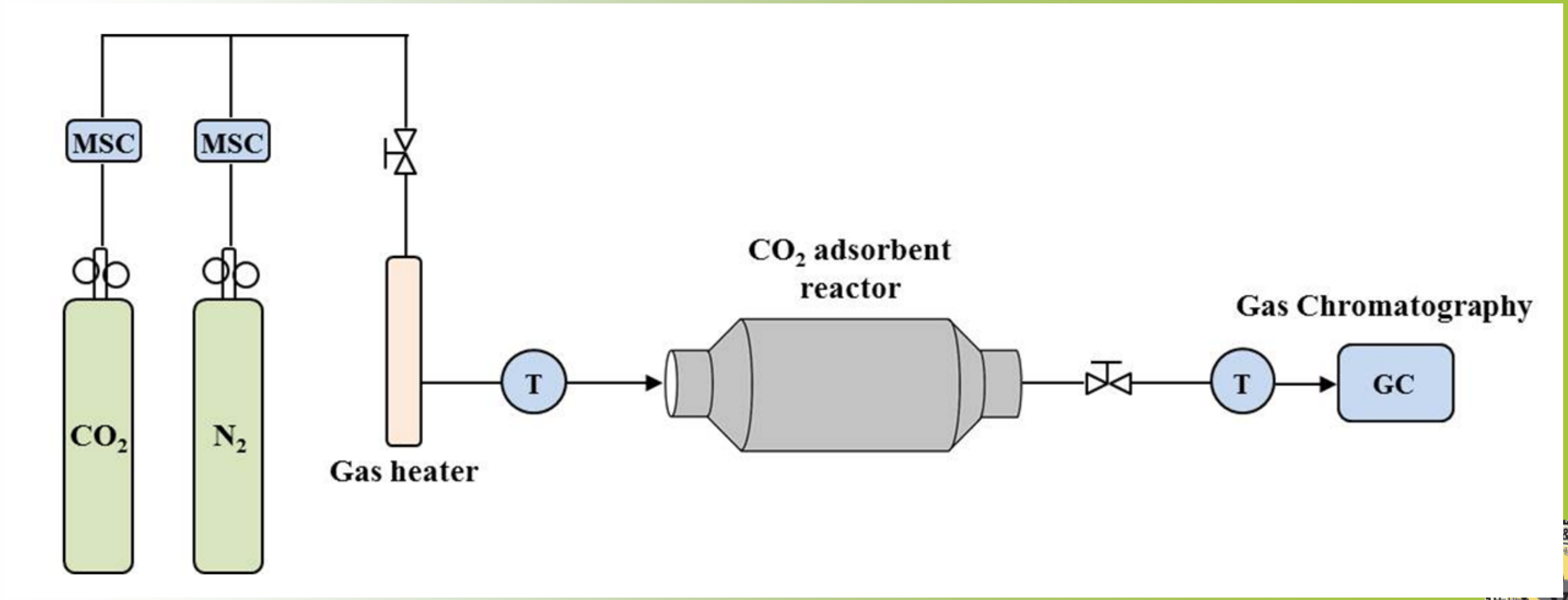
Project Task 5.0

Task 5.0 – CFD modeling of the carbon capture reactor

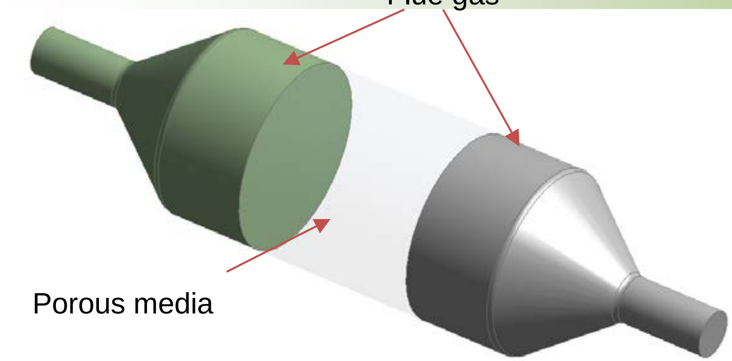
- Computational fluid dynamics (CFD) simulations will be performed using several commercial CFD codes for post combustion CO_2 capture process using the porous media concept to model the developed nanomaterial used in this study.
- Good predictions of the pressure drop and the mass transfer characteristics in the reactor are critical for scaling up the reactors and the validated CFD simulations will help in predicting the optimum design parameters for large scale applications.

Project Task 5.0 (continued)

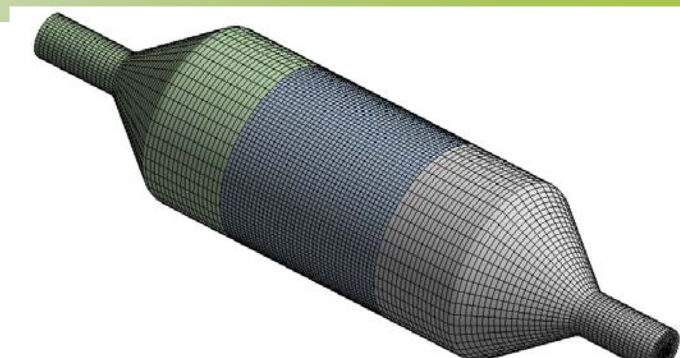
- By modeling the exhaust gas flow, the pressure drop and the uniformity of flow through the porous media can be determined. To simulate the CO_2 adsorbing reactor using CFD analysis, porous media for fixed-bed reactors will be considered.



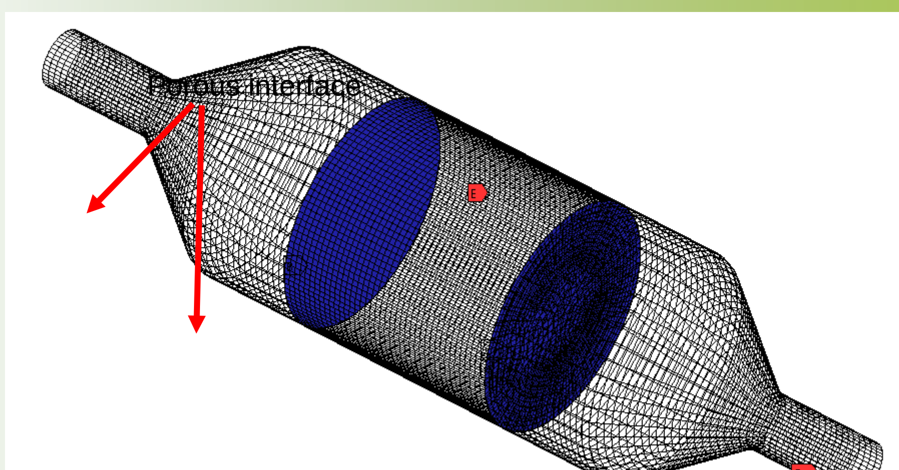
CFD Modeling : Porous Media



<Geometry model>



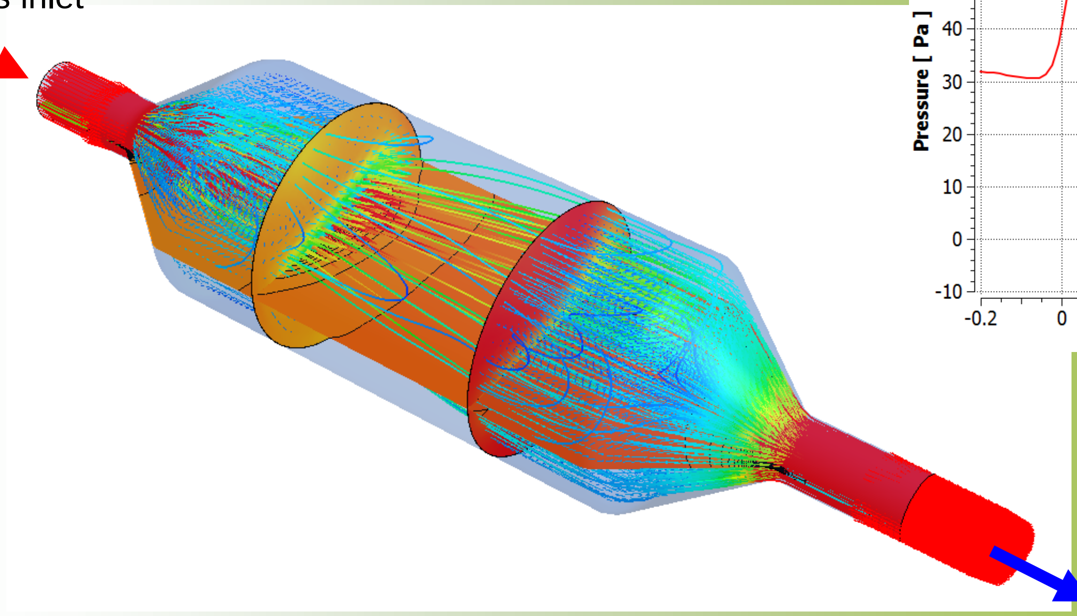
<Mesh model>



<Mesh model>

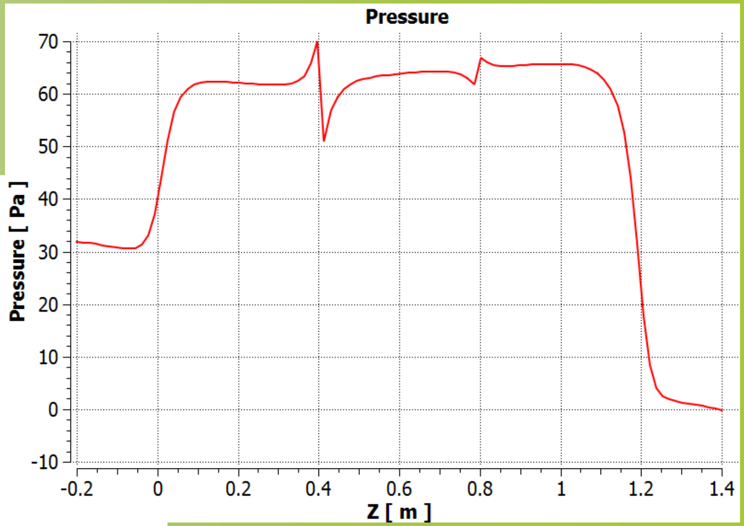
CFD Modeling : Porous Media

Flue gas inlet



<CFD result (velocity, pressure)>

Flue gas outlet



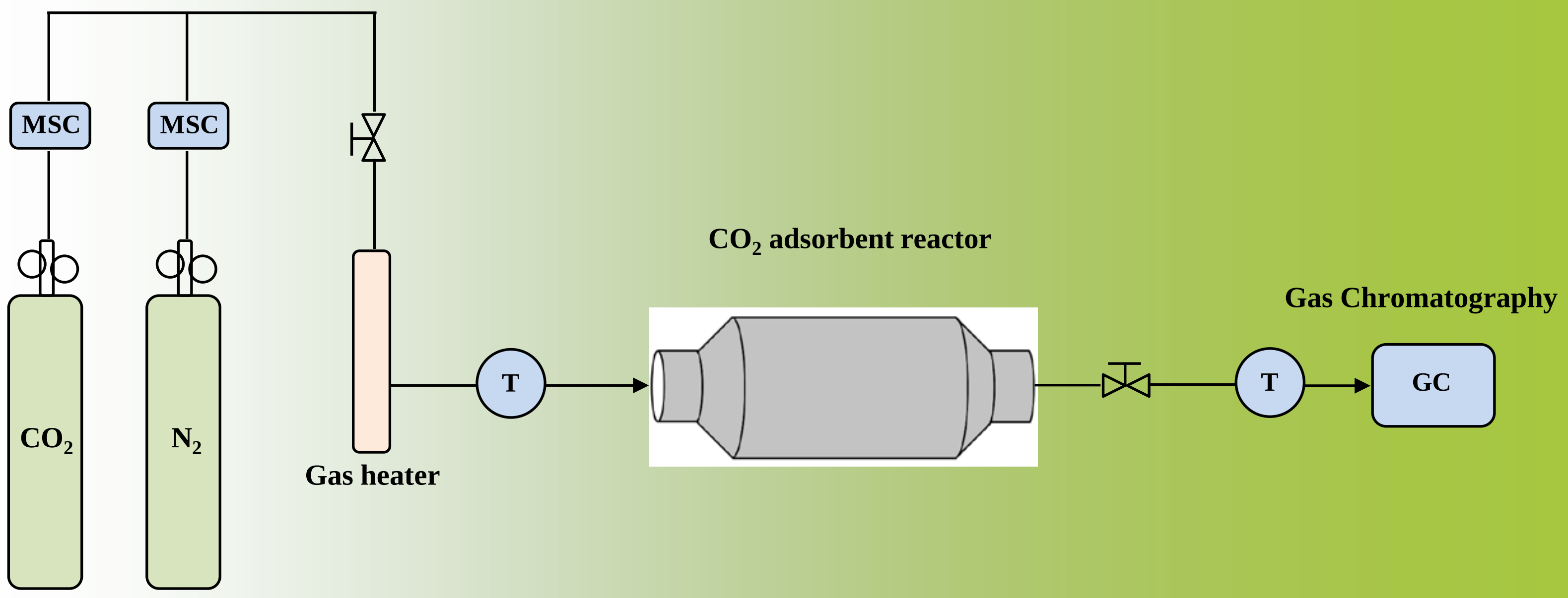
<Pressure drop chart>

Project Task 6.0

Task 6.0 – Experimental testing of the carbon capture reactor

- The capture of carbon dioxide from the carbon dioxide and nitrogen gas mixture will be tested in a customized fixed-bed CO_2 adsorbent reactor.
- The CO_2 adsorption capacities at various pressure and temperature will be tested and calculated.
- In the desorption phase, the temperature is increased, and the gas flow will be changed to N_2.
- The adsorption and desorption cycle will be conducted multiple times to test the performance of prepared material.

Project Task 6.0 (continued)



- A Shimadzu GCMS-QP2010 Ultra gas chromatograph with mass spectrometer will be used to measure the flue gas content.

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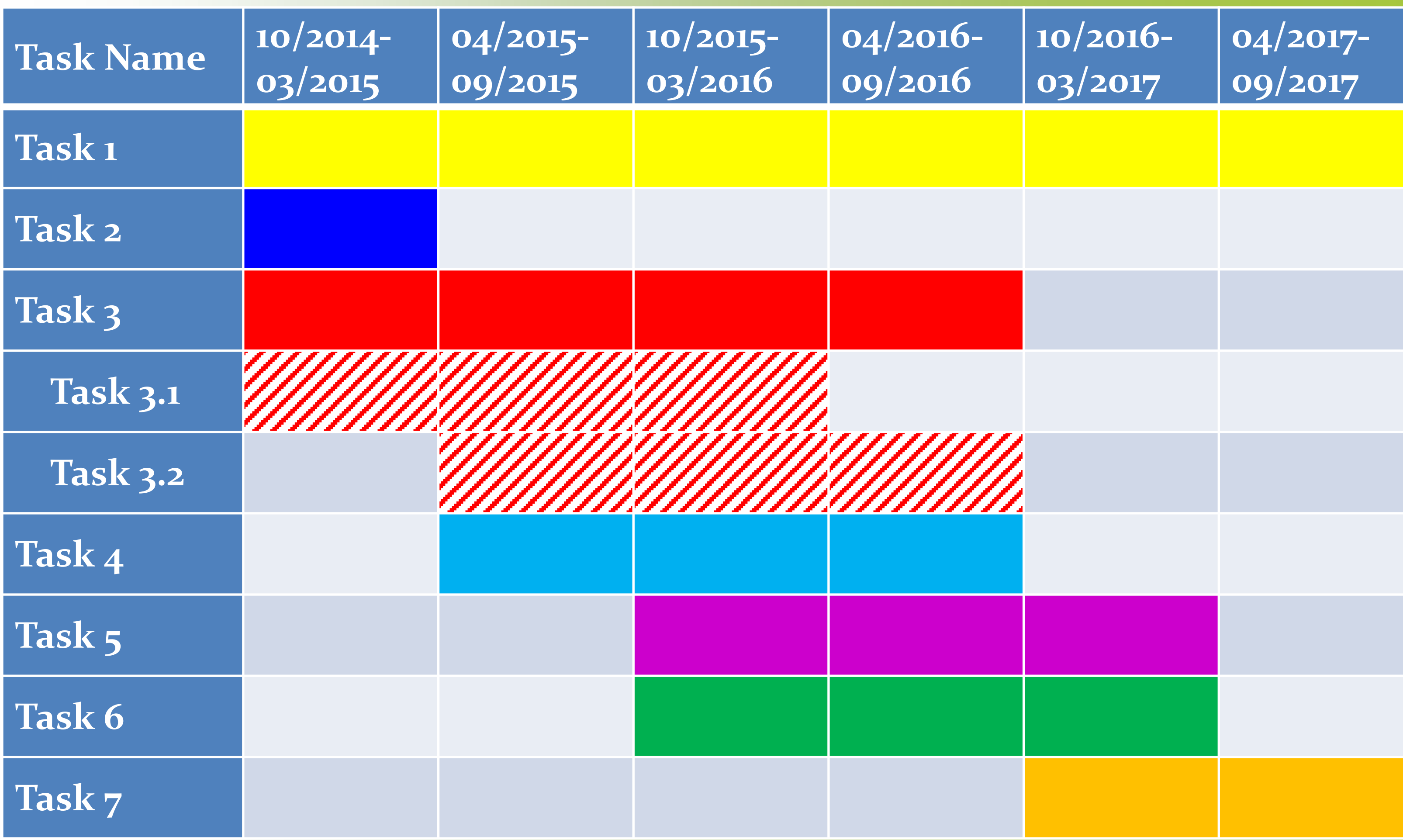
Project Task 7.0

Task 7.0 – Standard operating procedure for lab scale carbon capture reactor using PEI impregnated TiO_2 nanotubes and validated CFD Model

- Final optimized parameters for fabricating TiO_2 nanotubes using hydrothermal method and further functionalization by Polyethylenimine (PEI) using impregnation method
- CFD model simulations will be validated using the experimental results and optimized reactor parameters will be established.
- An optimized and functioning CFD model as well as a standard operating procedure for designing, fabricating and operating a carbon capture reactor will be developed.

Project Timetable



Relevance & Outcomes/Impacts

- A unique and Innovative Method.
- Two materials (TiO_2 and Polyethylenimine (PEI) that are commonly used for many purposes separately but in this study we are impregnating TiO_2 nanotubes with PEI to provide a highly selective nano- porous material with a very large surface area to capture carbon.
- The study will optimize the procedures for synthesizing the nanotubes and the impregnation protocols and develop standard operating procedures for carbon capture at different temperatures and concentrations.
- A successful outcome from this proposed study will provide a very high efficiency and low cost method to capture CO_2 from effluents of advanced fossil energy systems.

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Relevance & Outcomes/Impacts

- The proposed study will be conducted at Prairie View A&M University, a Historically Black College/University (HBCU).
- Roy G. Perry College of Engineering will have an opportunity to enhance our research capabilities into energy research and particularly into carbon capture technologies.
- This will also enhance our educational training infrastructure to include these topics into our newly established Energy Engineering minor.
- This will have impact on many students from the underrepresented group here on PVAMU campus.
- The proposed research will train and support at least 2 undergraduate and one to two graduate students to engage in the challenging energy research.

Roles of Participants

- Prof. Raghava R. Kommalapati (Ph.D., Louisiana State University, 1995) will serve as Principal Investigator for this project and he will coordinate all aspects of the research project.
- Dr. Kommalapati is the Director of NSF CREST Center for Energy & Environmental Sustainability (CEES) and Professor of Civil and Environmental Engineering at Prairie View A&M University.
- Dr. Kommalapati has many years of experience in environmental engineering research, particularly in the area of air quality, air-fog interactions and environmental impact of various energy technologies.

Roles of Participants

- Co-PI, Dr. Xinhua Shen (Ph.D., Colorado State University, 2011) was a post-doctoral researcher at PVAMU and currently an assistant professor at University of Northern Iowa.
- She has two patents on developing porous materials for high temperature gas purification, including "Method of preparing iron-aluminum based metal compound microporous filter element, and its application", "Porous catalytic filtering metal material and its preparation".
- Dr. Shen will participate in material synthesis, material characterization and experimental testing to optimize CO_2 capture.

Roles of Participants

- Co-PI, Dr. Ziaul Huque (Ph.D., Oregon State University, 1991) is a professor of Mechanical Engineering at Prairie View A&M University.
- Dr. Huque has many years of experiences in computational fluid dynamics (CFD) simulations. Dr. Huque will oversee the CFD simulation.
- Dr. Kyoungsoo Lee (Ph.D., Inha University, South Korea 2009) is a Post-Doctoral Researcher in CEES, and has many years' experiences of using CFD to develop the aerodynamic analysis on the wind energy and structural area.
- Dr. Lee will work on the CFD simulation to optimize the operational parameters and conditions.

Roles of Participants

- Dr. Akhil Kadiyala, recently joined CEES as a post-doctoral researcher and will participate in the project to coordinate the laboratory experiments
- One (possibly two) graduate student and two undergraduate students at Prairie View A&M University will participate in the planned literature review, material synthesis, material characterization and experimental testing.

Facilities and Other Resources

- Material synthesis and characterization will be performed in the laboratories of the Center for Energy & Environmental Sustainability and Civil & Environmental Engineering.
- Part of the material characterization will be conducted in the labs available in Department of Mechanical Engineering,
- CFD simulations and experimental tests will be conducted using the computing facilities in the Center for Energy & Environmental Sustainability.
- A Total of more than 5,000 sq ft of laboratory space is available for this research. Two technicians are also available in the College of Engineering for any assistance needed with material synthesis.

Equipment

- The primary pieces of equipment that will be used for this study include;
- Thermogravimetric Analyzer (TGA Q500 TGA with Auto sampler made by TA Instruments)
- Transmission Electron Microscopy (TEM)
- X-ray diffraction (XRD) instrument
- Shimadzu GCMS-QP2010 Ultra gas chromatograph with mass spectrometer .
  - TGA and GC-MS are available in the Roy G. Perry College of Engineering. The PIs have ongoing relationship with several researchers at our system university, Texas A & M University and they have access to TEM and XRD and will be available for our use at nominal cost.

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Equipment

Other Equipment

- High performance 48 noted cluster in the center for CFD simulations.
- 4 – 16 nodes HP workstations for computing

Other Equipment (continued)

- Agilent 1200 series HPLC
- Dionex ICS 5000, Ion chromatograph
- Shimadzu TOC-L Total Organic Carbon Analyzer
- Shimadzu UV-1800 UV Spectrophotometer
- Thermo-Orion 720A pH Meter
- Ohaus AS200 Analytical Balance
- Fisher Scientific FS140H Tabletop Ultrasonic Cleaner
- Thermolyne cimarec 3 HP47135 stirrer
- Thermolyne 1300 Furnace
- Water purification system.

Questions?