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On the Performance of Porous Covalent Organic Polymers for CO_2 Capture Process at Elevated Pressures

Water and Energy Workshop

Organized by Texas A&M University at Qatar

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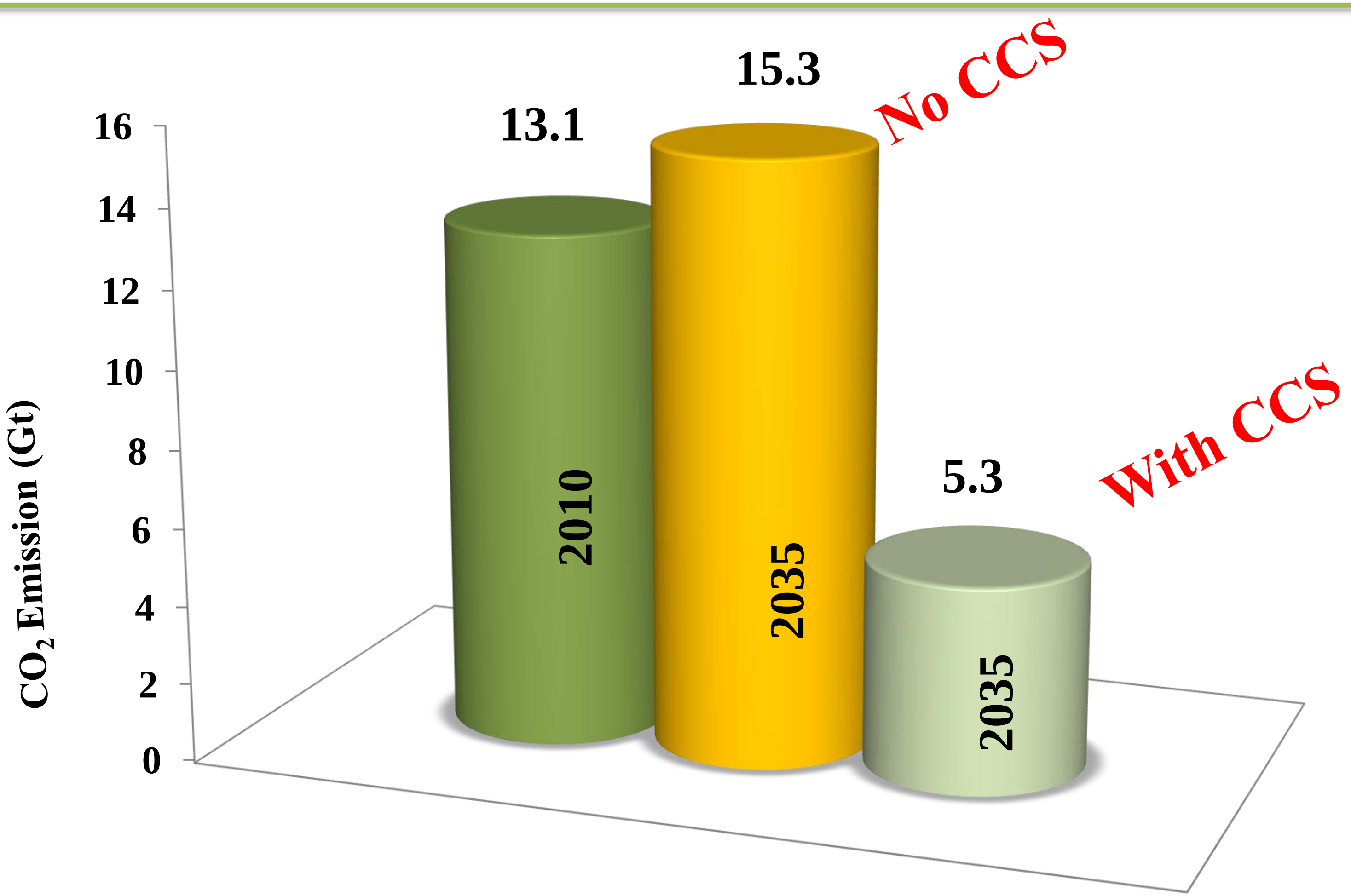
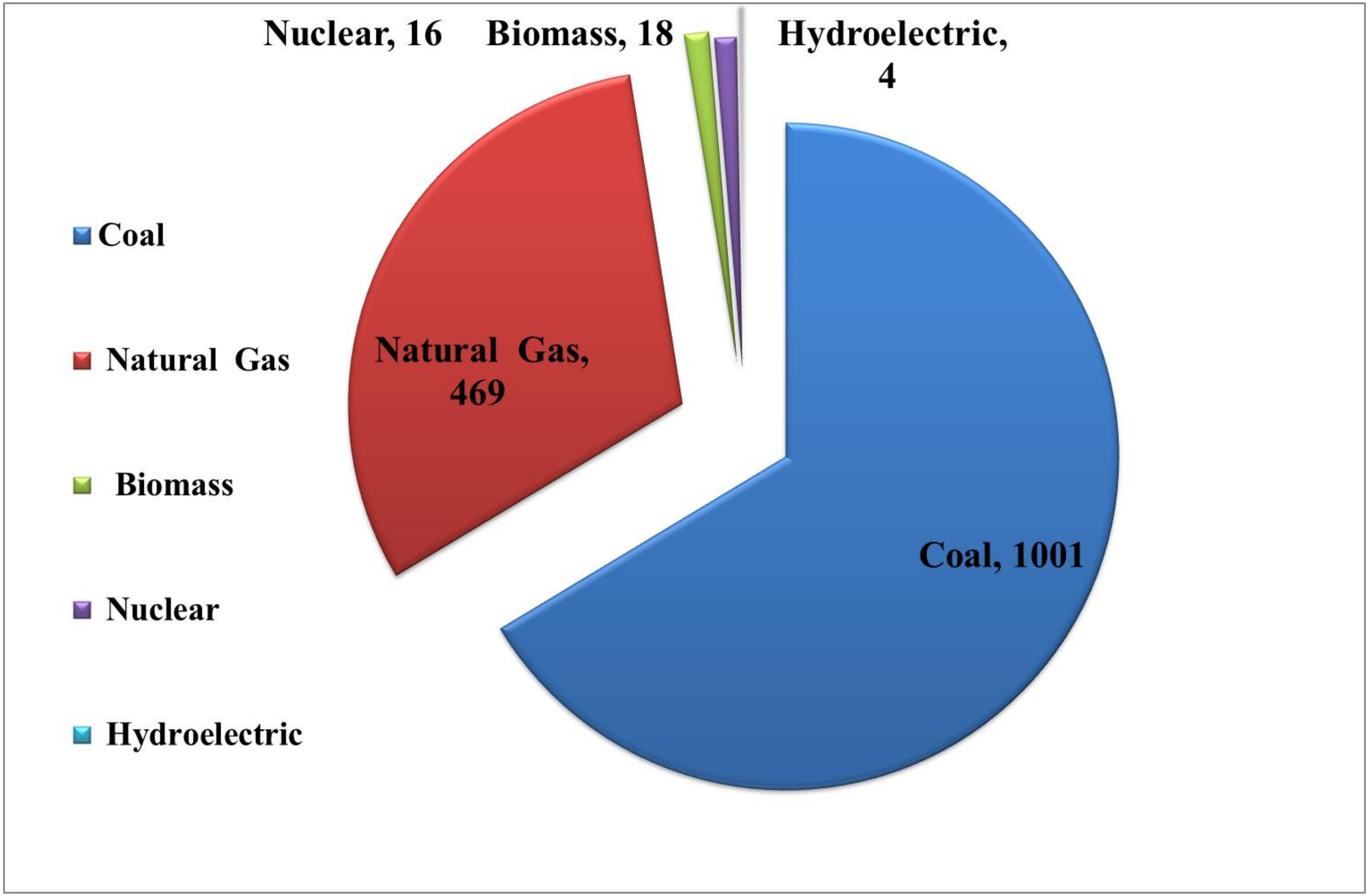
Outline

- Global concern of carbon dioxide capture and storage
- Technologies in use
- Materials selection for CO_2 capture
- Synthesis and characterization of covalent organic polymers (COPs)
- Material performance for gases capture at various temperatures and pressures
- Adsorption kinetics
- Conclusion

Global CO_2 Emission



Power Generation & CO_2 Emission



Current Technologies

- **Post combustion**

Fossil fuel or biomass is burnt and CO_2 is separated from the exhaust gases containing other gases

Pre-combustion

Fossil fuel or biomass is converted to a mixture of H_2 and CO_2, where CO_2 is separated and H_2 is used as fuel

Oxy-fuel combustion

Oxygen is separated from air and fossil fuels burnt in an atmosphere of oxygen producing water and CO_2

Capturing Technologies

- **Solvents**

  Monoethanolamine (MEA), mostly used, but, costly

  Ionic liquid are very expensive and toxic

  Deep eutectic solvents; new technology???

- **Membranes**

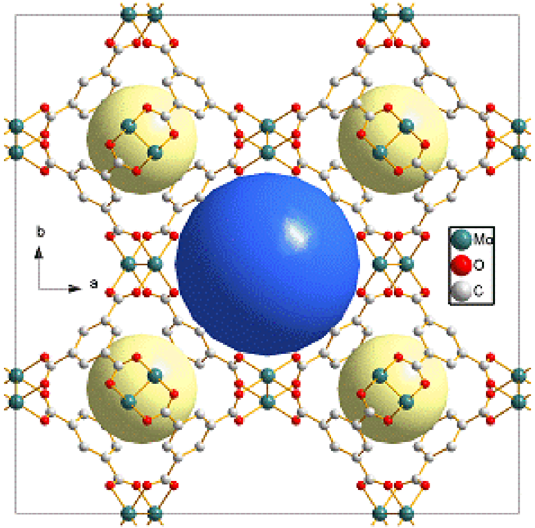
  Polybenzimidazole, need to be selective and tough

- **Adsorbents**

  Activated Carbon and MOF, need highly porous structure with high surface area

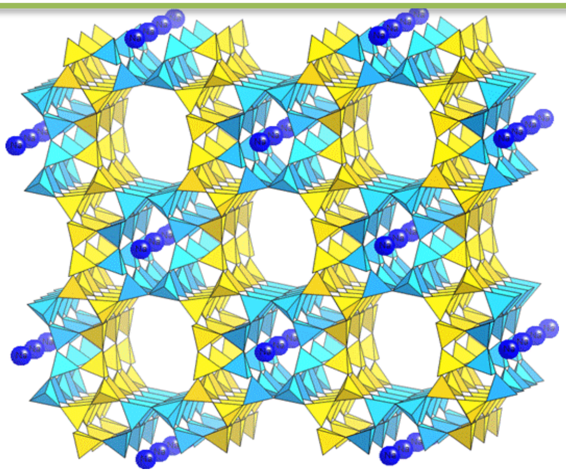
  Organic Polymer ???

Material Selection (MoF)



- Metal Organic Frame Work
- Surface area: 4530 m^2/g
- Pore volume: 3.59 cm^3/g
- Maximum CO_2 uptake at 50 bars and 298k
- **54.5 mmol/g**
- Oxidation and cost of materials are big issues

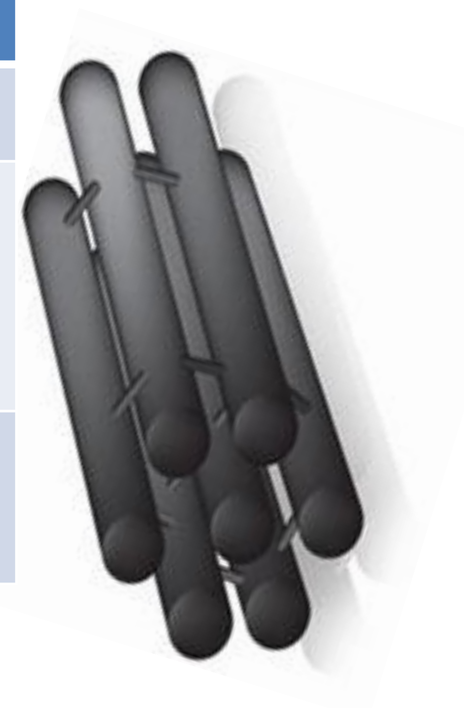
Material Selection (Zeolite)



- Surface area: 2400 m^2/g
- Pore volume: 0.167 cm^3/g
- Maximum uptake at 1 bar and 273K: **8.6 mmol/g**
- Maximum uptake at 20 bars 0.0051 mmol/g
- Hydrophilic in nature
- Needs high regeneration temperature (300 ^oC)

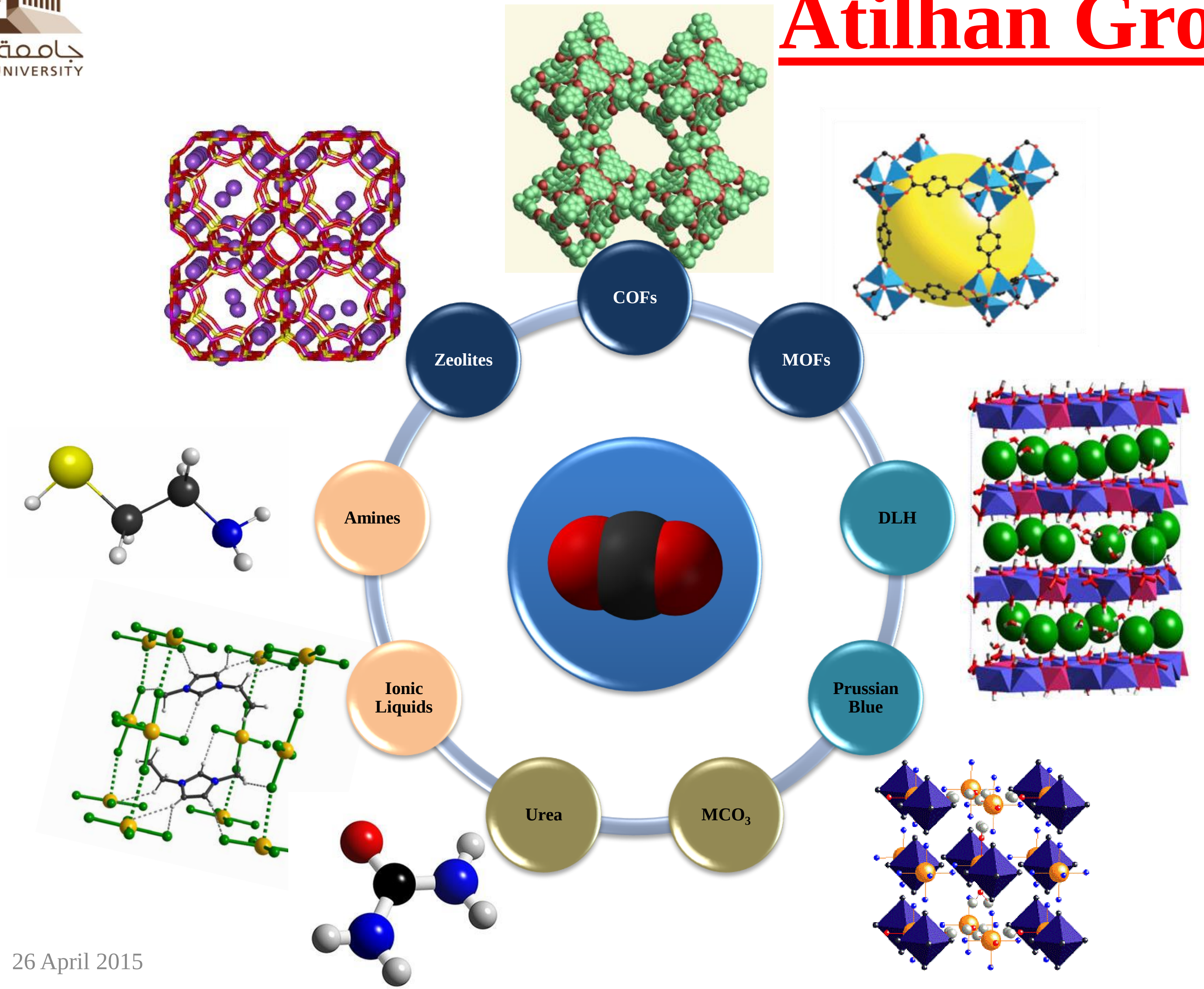
Material Selection (Activated Carbon)

Pore size	Micropoers	Mesopores	Macropores
Diameter	< 20 nm	20-50nm	>50 nm
Pore volume (cm^3/g)	0.15—0.5	0.020.1	0.5
Surface area(m^2/g)	100-1000	10-100	0.5-2

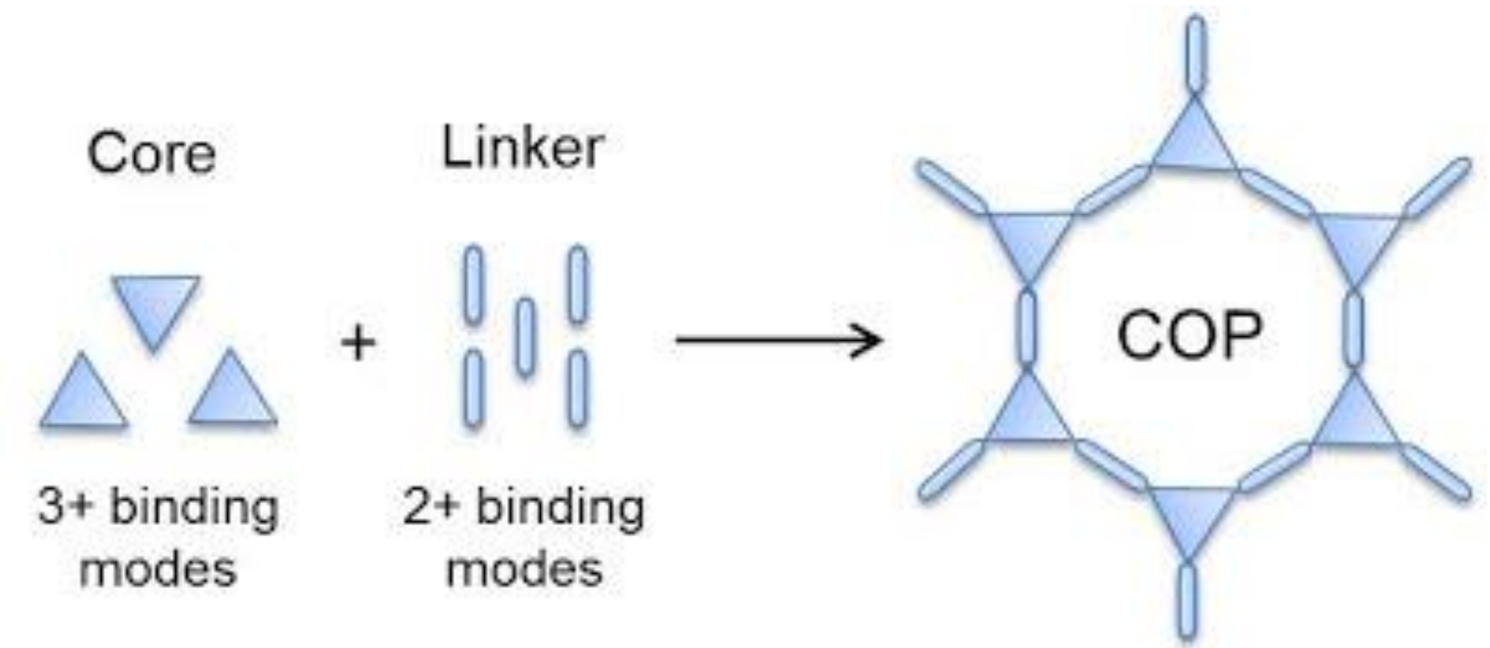


- Surface area: 2900 m^2/g
- CO_2uptake at 50 bar: **47 mmol/g**
- Limitation at high pressure

Atilhan Group



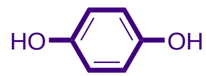
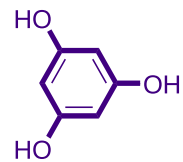
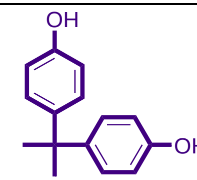
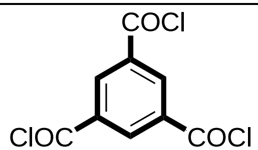
Engineering Polymers



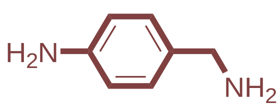
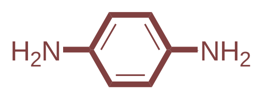
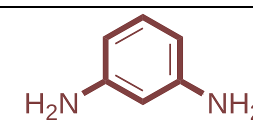
-
    - Pore structure/ connectivity
    - Dimensionality and symmetry
    - Adsorbate site interactions
- Porous solid adsorbent material can be designed to be highly size- and shape-selective.

Polymer Synthesis

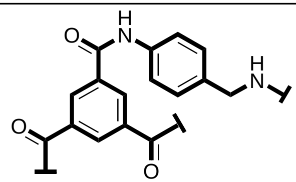
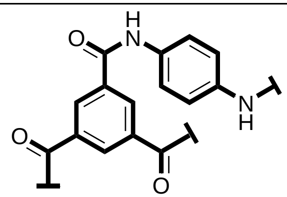
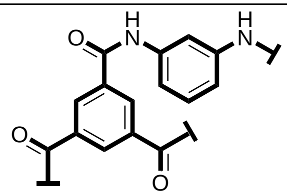
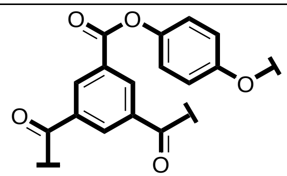
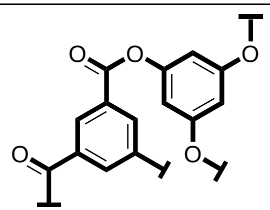
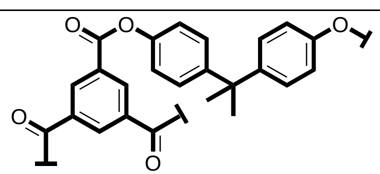
Ester (O=C-O) COPs

Core / Linker	 Hydroquinone			 Phloroglucinol			 Bisphenol A	
 Benzene tricarbonyl trichloride	**COP-35**	SA_{BET}: 5.4 m^2/g $SA_{Lang.}$: 7.5 m^2/g		**COP-36**	SA_{BET}: 11.1 m^2/g $SA_{Lang.}$: 15.4 m^2/g		**COP-37**	SA_{BET}: 54.2 m^2/g $SA_{Lang.}$: 75 m^2/g

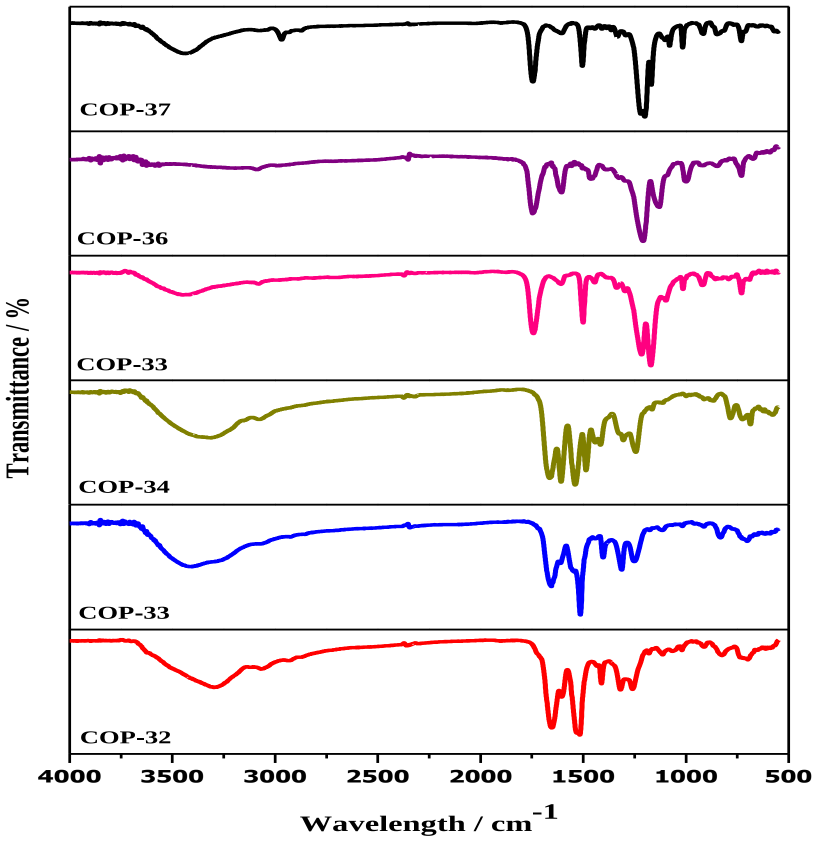
Amide (O=C-N) COPs

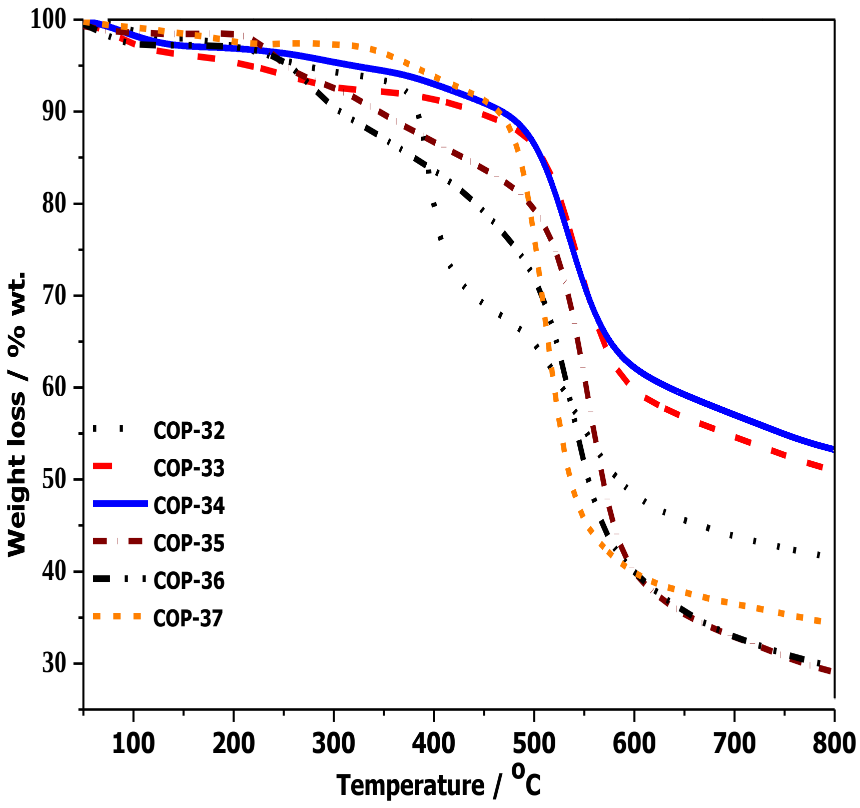
 4-aminobenzylamine		 p-phenylenediamine			 m-phenylenediamine		
COP-32	SA_{BET}: 46 m^2/g $SA_{Lang.}$: 63.8 m^2/g		**COP-33**	SA_{BET}: 53.2 m^2/g $SA_{Lang.}$: 73.4 m^2/g		**COP-34**	SA_{BET}: 33.4 m^2/g $SA_{Lang.}$: 46.2 m^2/g

Physical Properties of COPs

Sample code	Structure	Surface area, m^2/g	Pore volume (cm^3/g)	Tapped bulk density, cm^3/g
COP-32		BET = 46 Langmuir = 63.8	0.1389	0.19
COP-33		BET = 53.2 Langmuir = 73.4	0.2	0.156
COP-34		BET = 33.4 Langmuir = 46.2	0.095	0.253
COP-35		BET = 5.4 Langmuir = 7.5	0.011	0.125
COP-36		BET = 11.1 Langmuir = 15.4	0.031	0.22
COP-37		BET = 54.2 Langmuir = 75	0.19	0.2

COPs Characterization





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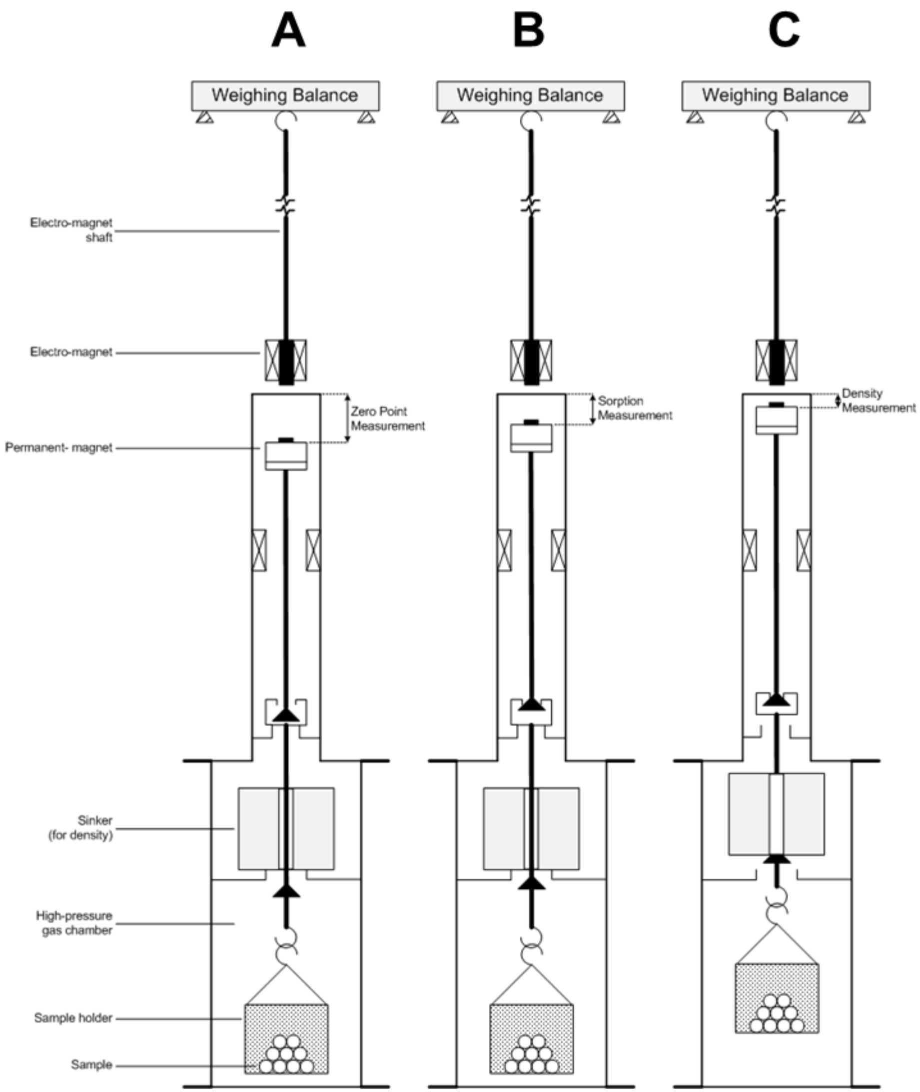
CO_2 Solubility Measurements

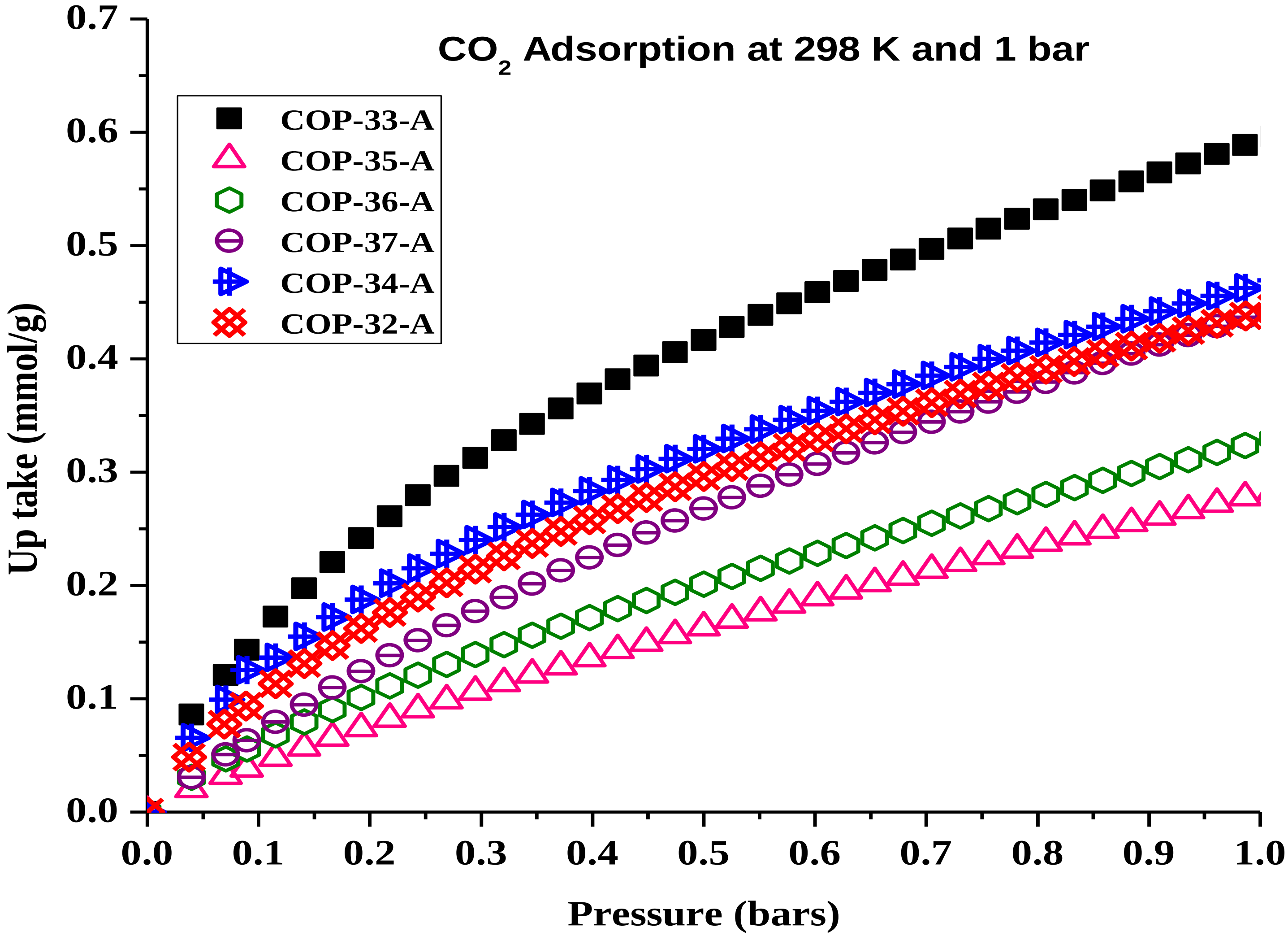
- We used Rubotherm® sate-of-the-art gas sorption apparatus.
- Two isotherms are used: 25 °C and 50 °C
- Three pressures ranges were used i.e. 1 bar, 10 bars and 200 bars.
- Buoyancy correction has been taken care of.

Operating Principle



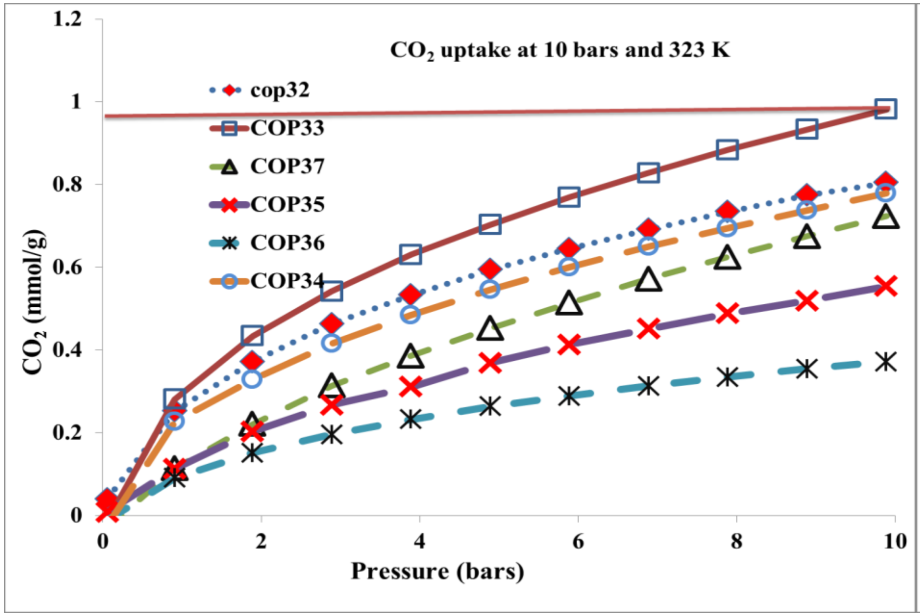
Schematics of magnetic suspension sorption apparatus operating principle. (**A**) sample loaded to measuring basket in high pressure cell; (**B**) Measurement point 1 (MP1) – magnetic coupling is on and mass of the sample is measured; (**C**) Measurement point 2 (MP2) – in–situ density of the adsorbed gas is measured.

CO_2 Up take

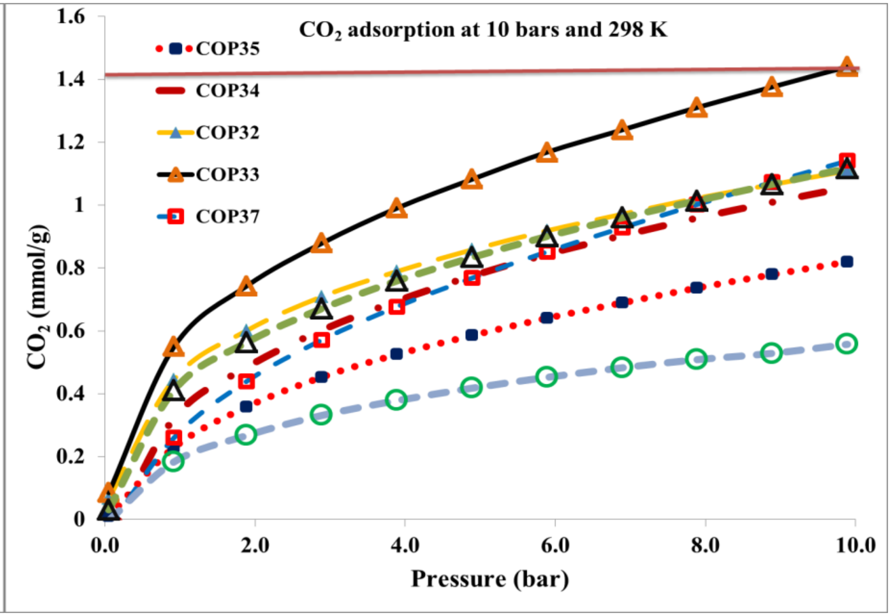


CO2 Adsorption at 298 K and 1 bar
COP-33-A
COP-35-A
COP-36-A
COP-37-A
COP-34-A
COP-32-A
Up take (mmol/g)
Pressure (bars)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0

CO_2 Up take

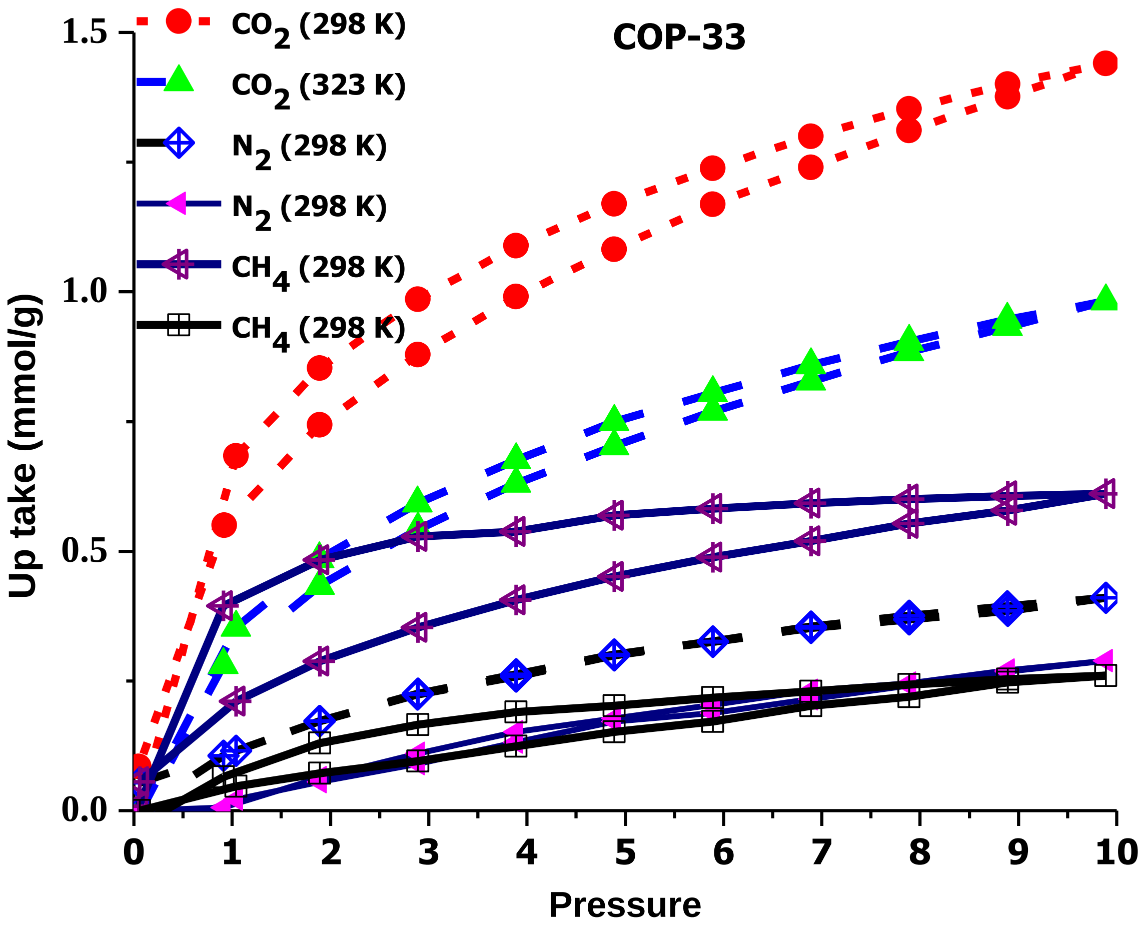


CO2 uptake at 10 bars and 323 K
cop32
COP33
COP37
COP35
COP36
COP34
CO2 (mmol/g)
Pressure (bars)

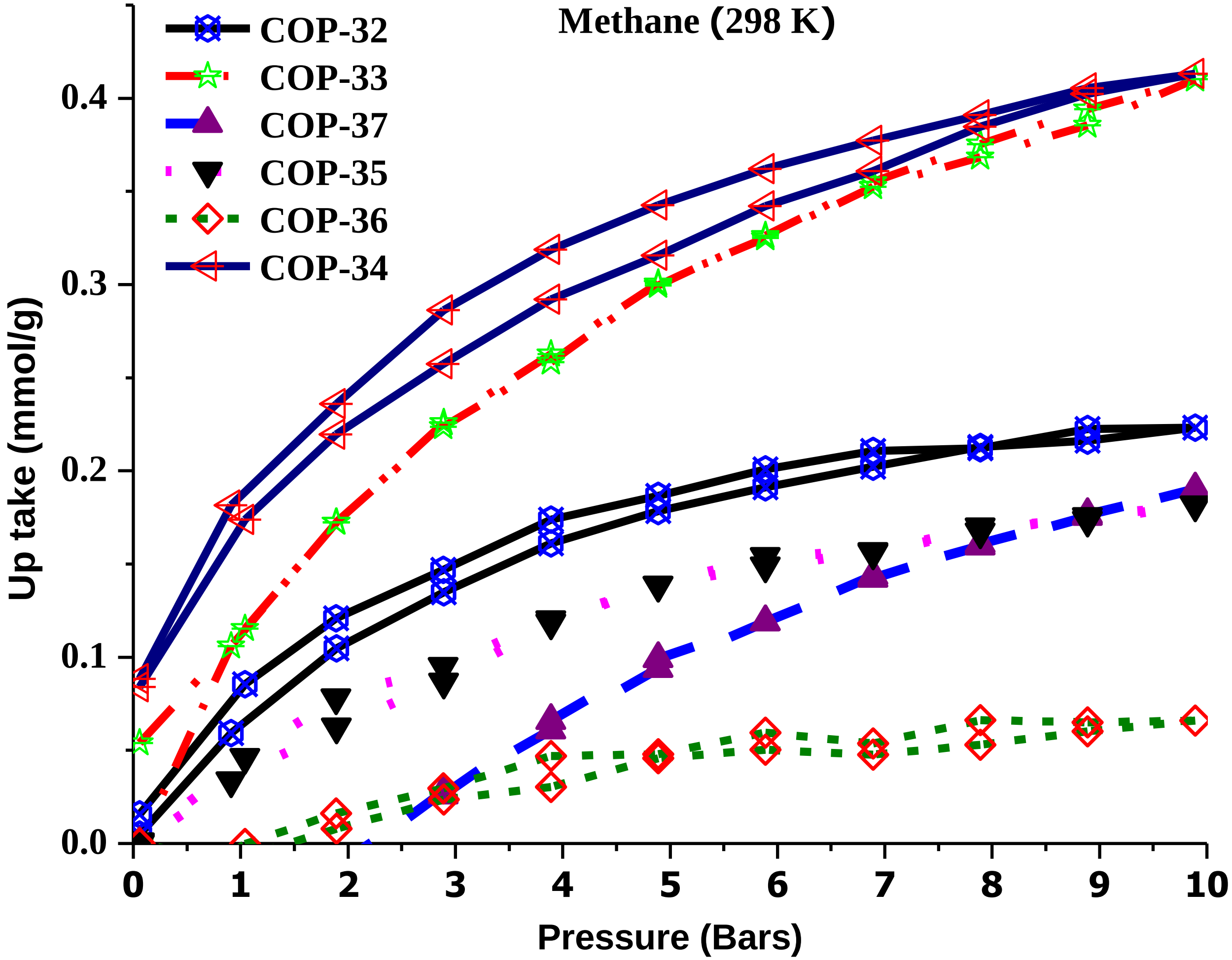


CO2 adsorption at 10 bars and 298 K
COP35
COP34
COP32
COP33
COP37
CO2 (mmol/g)
Pressure (bar)

CO_2 Up take of COP-33



CH_4 Up take of COP



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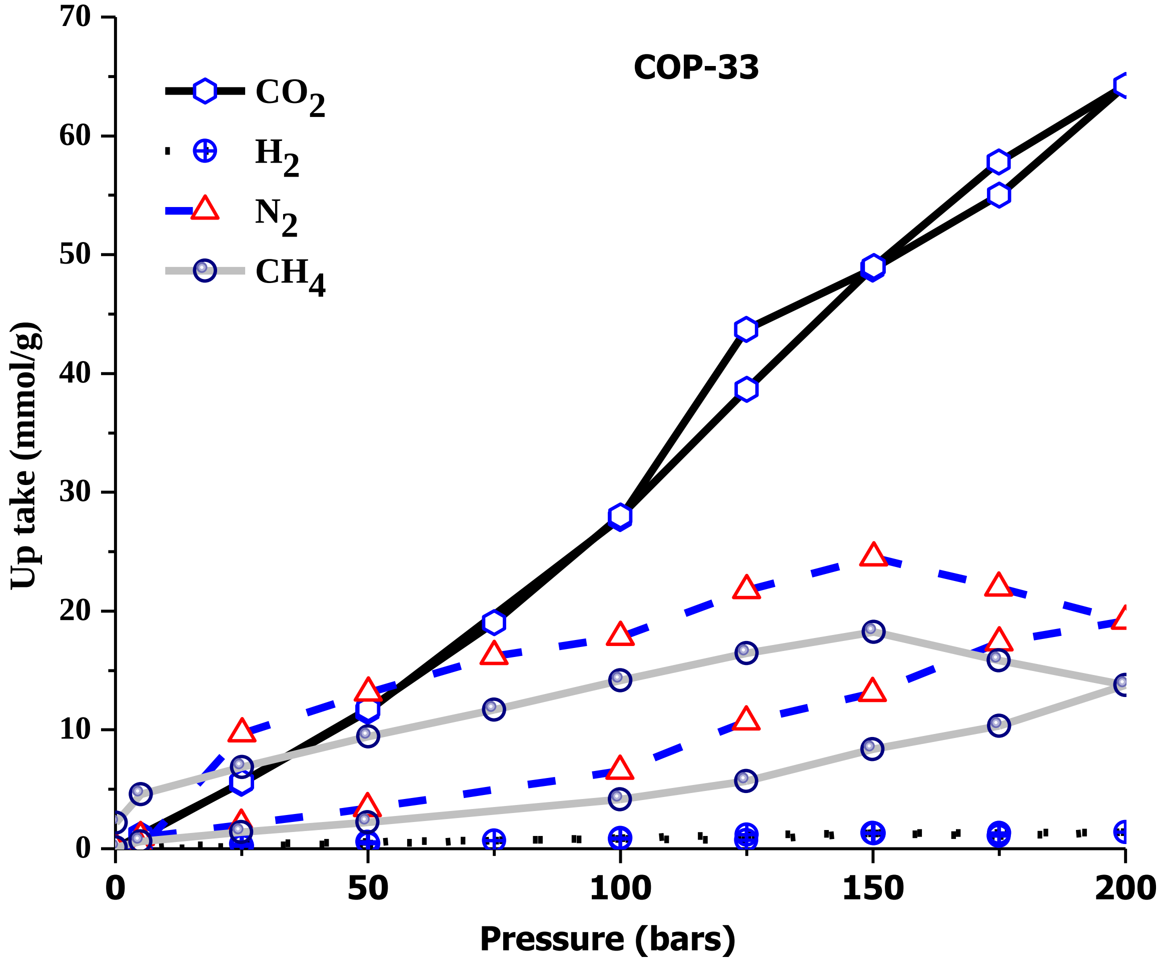
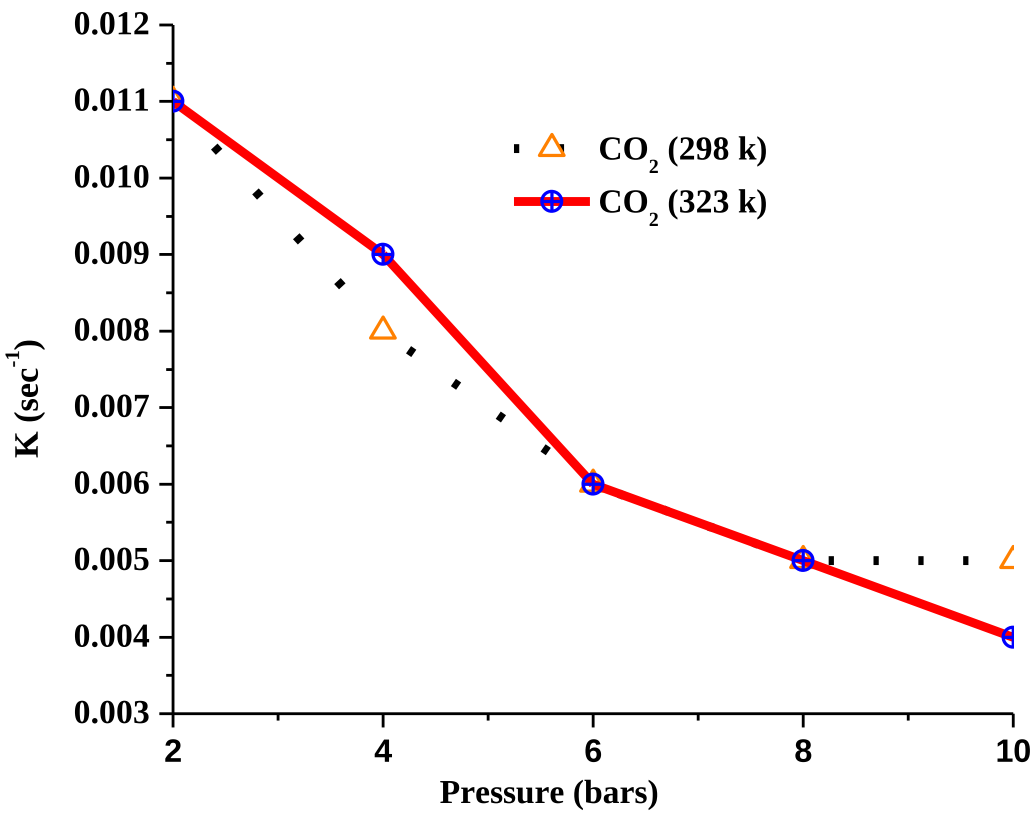
CH_4, N_2 and CO_2 Up take

Maximum adsorption of N2, CO2 and CH4 by COP						
	CO2 (mmol/g)		Methane (mmol/g)		N2 (mmol/g)	
Temp/Material	**298K**	**323K**	**298K**	**323K**	**298K**	**323K**
COP32	1.109213	0.804201	0.223124	0.081515	0.080872	0.037786
COP33	**1.440349**	**0.981784**	**0.410248**	**0.289082**	**0.61099**	**0.259958**
COP34	1.116972	0.778442	0.41324	0.188905	0.177384	0.05648
COP35	0.819419	0.554221	0.18187	0.130621	0.08249	0.059161
COP36	0.557371	0.3717	0.0659	0.018713	0	0
COP37	1.140691	0.723342	0.190126	0.107208	0.212632	0

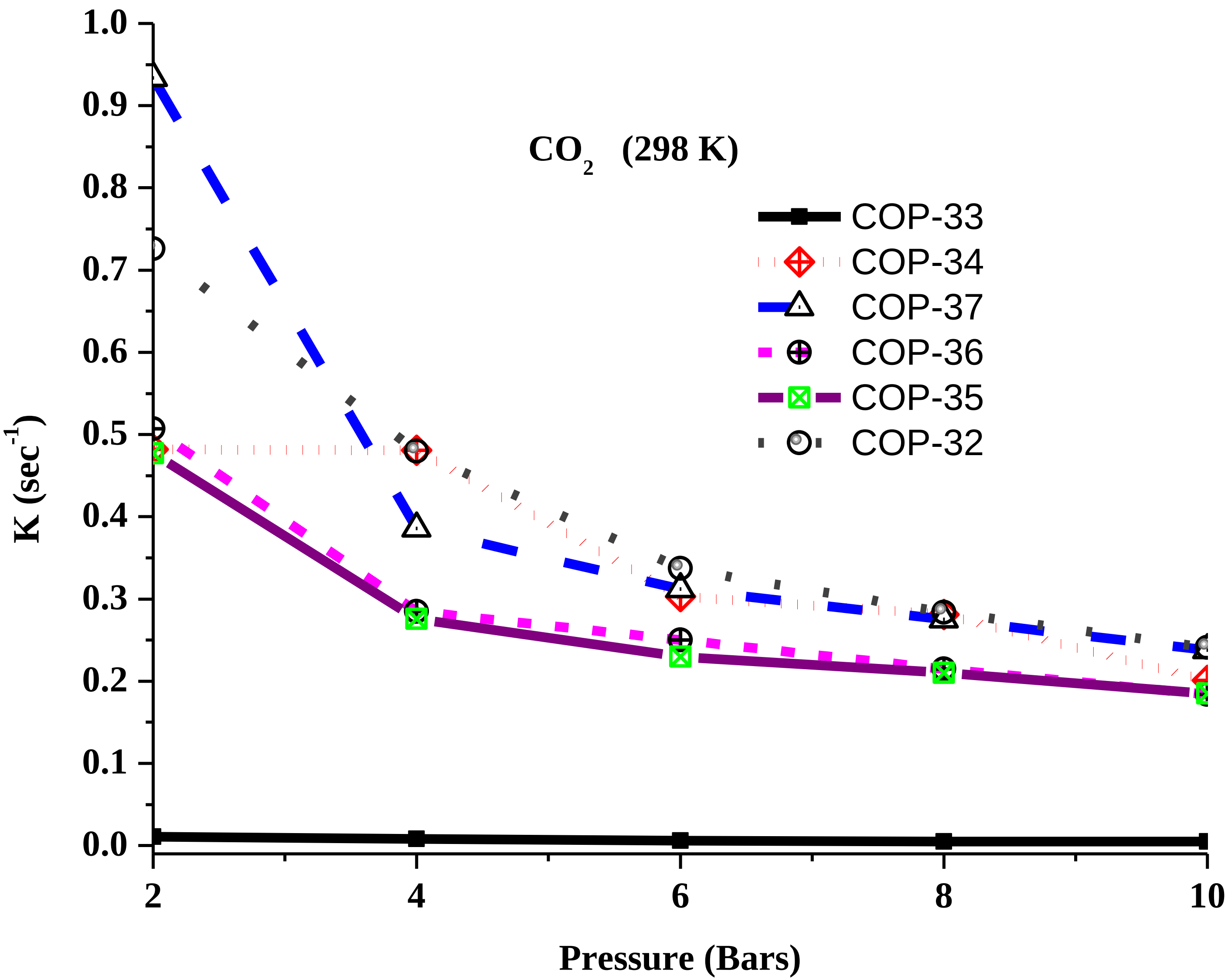
CO_2 Up take of COP-33



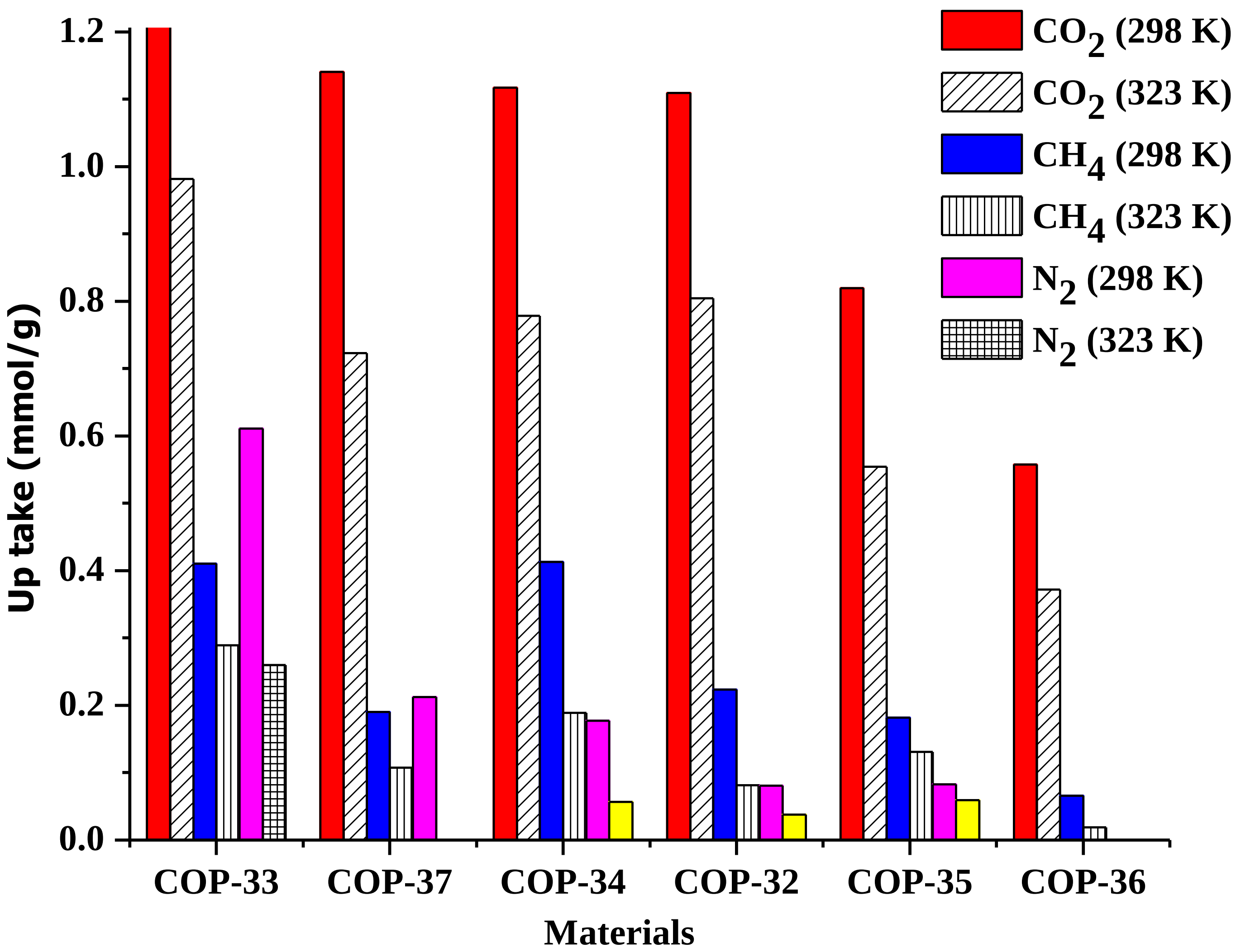
Mass transfer co efficient (k)



Mass transfer co efficient (k)



Over all performance



Group…

Funding

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