Mathematical Modeling of Chemical Reactors

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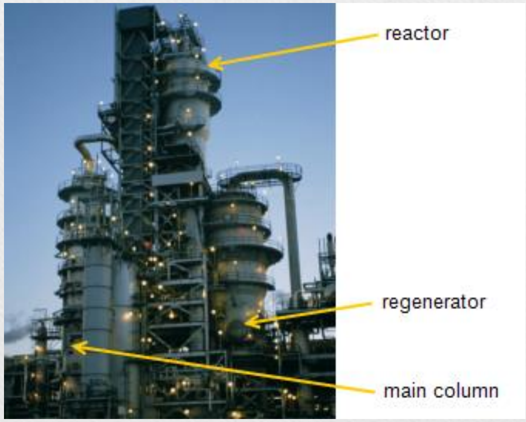
Just your garden variety chemical plants

Gandhinagar Plant

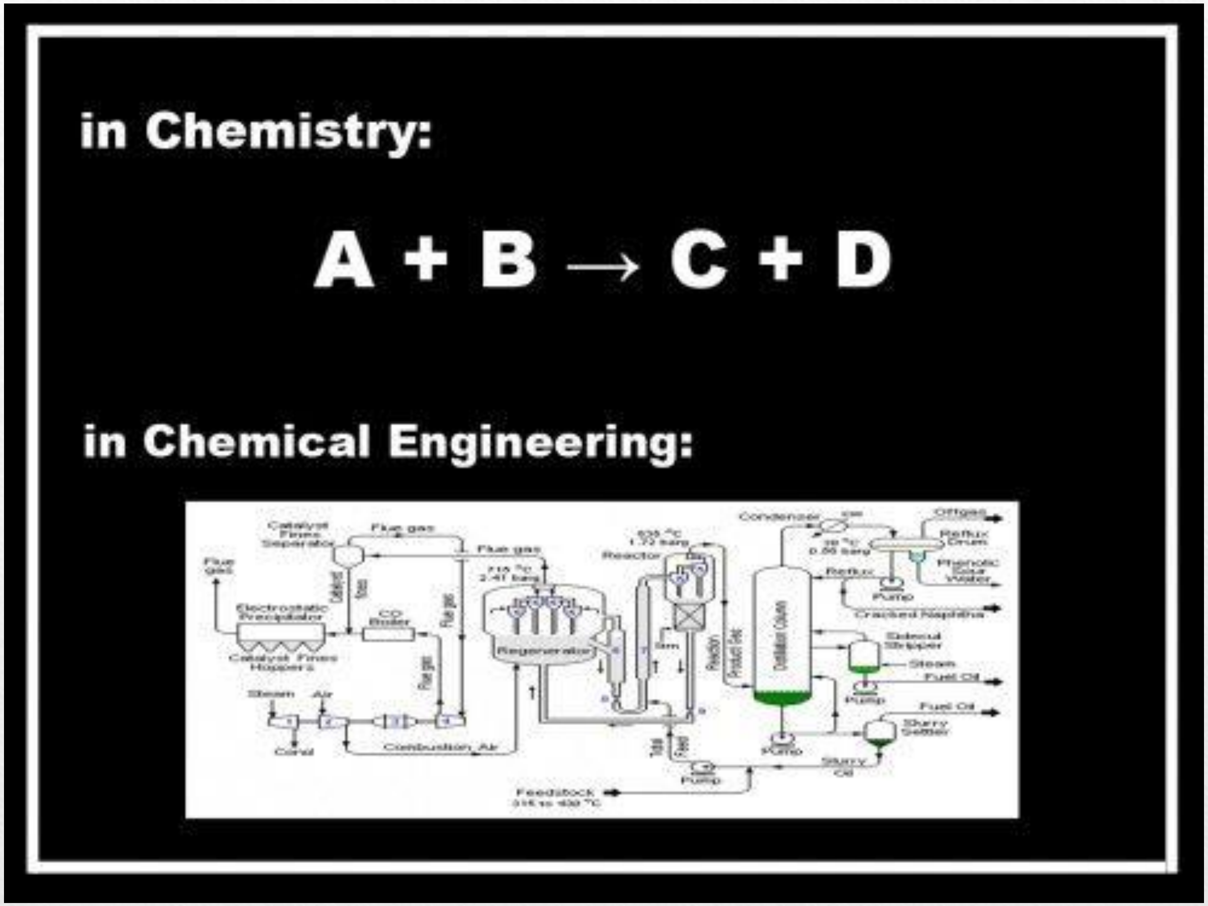
Urea manufacture plant

Jamnagar Refinery

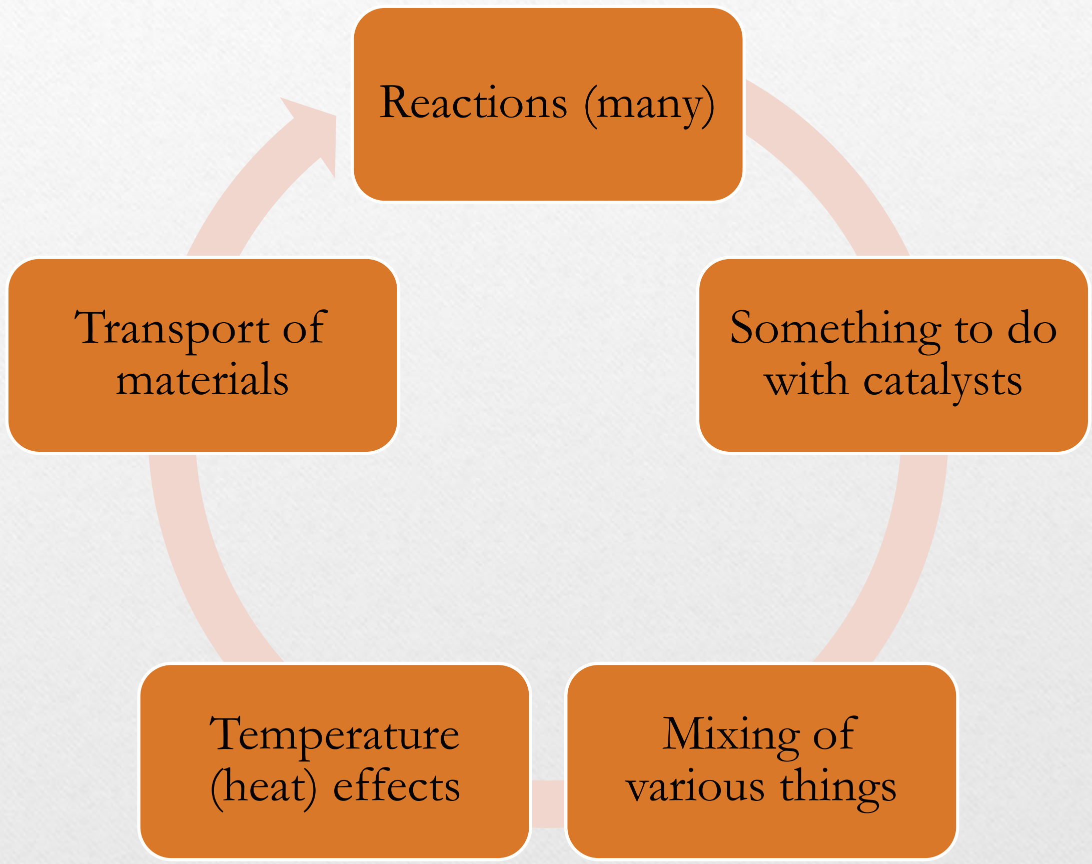


Catalytic cracking unit

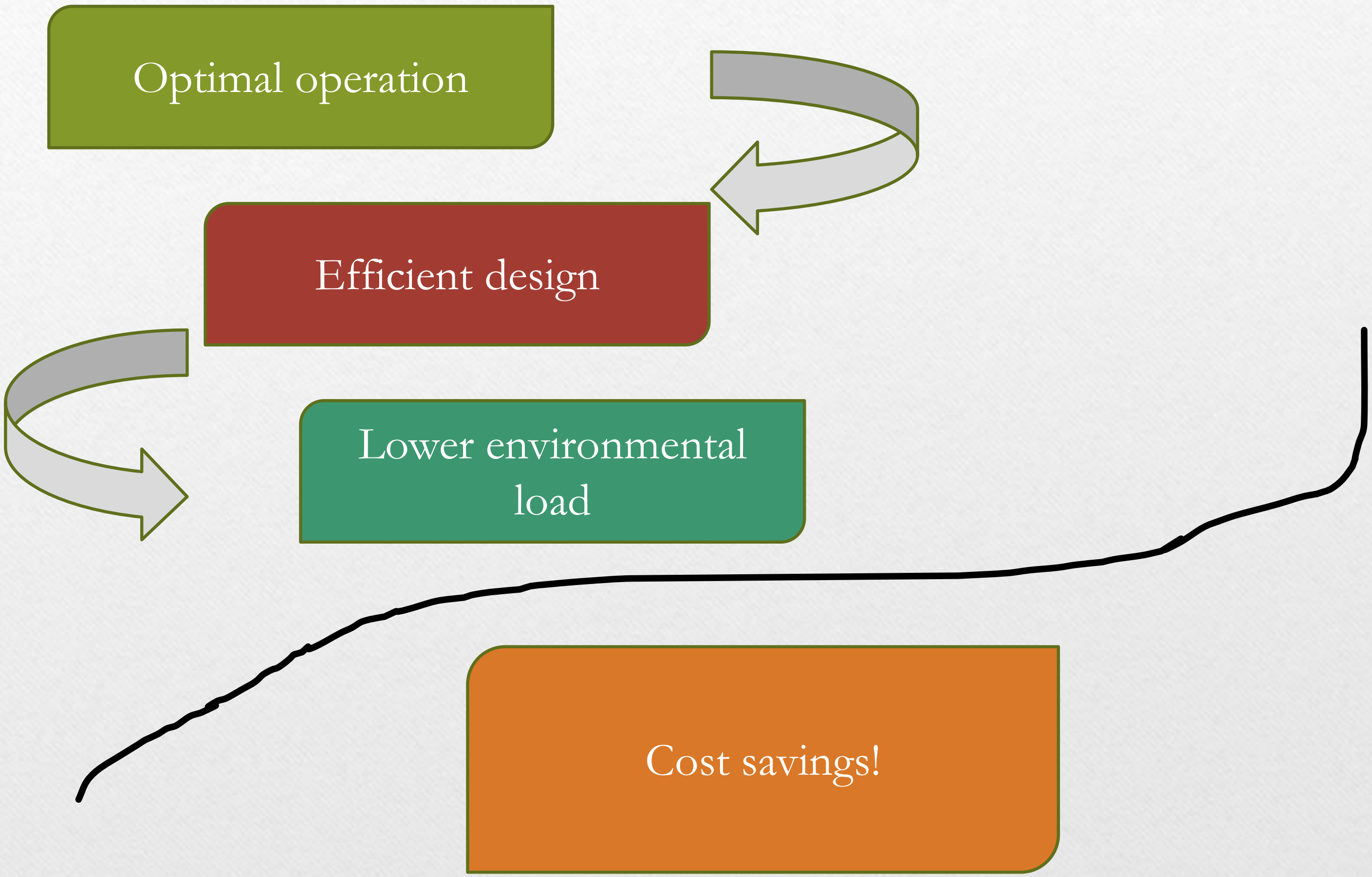
Yes, there is chemistry



Phenomena in a Chemical Reactor



Why mathematical descriptions of reactors?



Some examples from my work

Mega Goal

Our baby steps

Being kind to the environment

- Chemical routes to NOx & soot
- Catalyst-based reduction of NOx

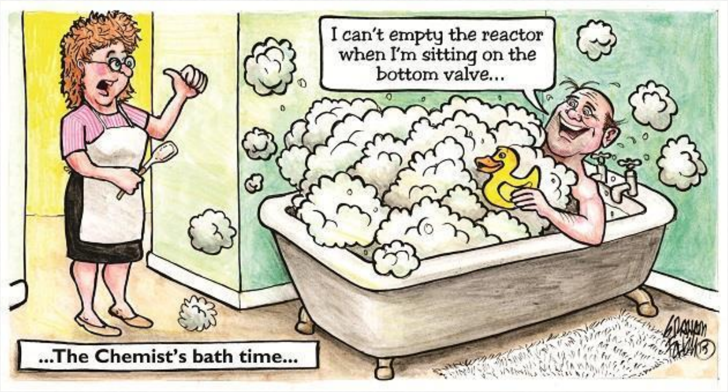
Utilising resources smartly

- Underground gasification of coal
- Production of carbon black

Some of the interesting questions we have answered-

1. How does NOx form in fuel-rich flames?
2. Which catalyst best controls NOx in automobile exhaust?
3. How does soot particle size distribution vary with burner configuration?
4. What are the important reactions in coal gasification?

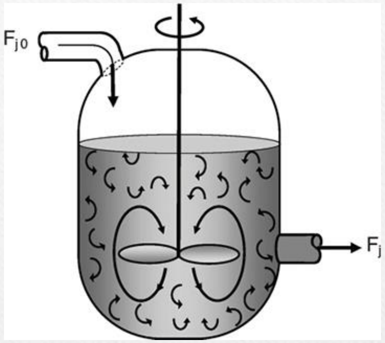
Basics of chemical reactor modeling

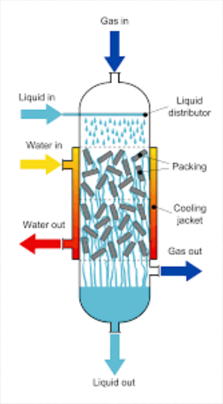


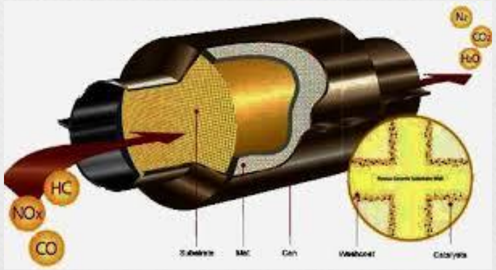
Conservation equation

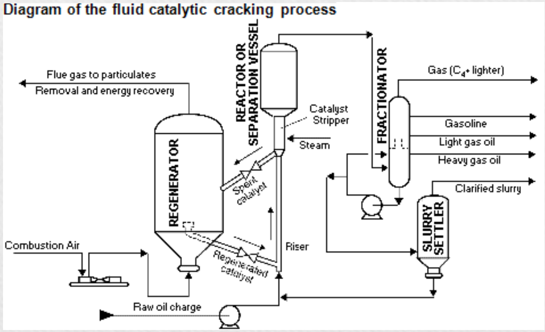
$$\boxed{\text{Accumulation} = \text{Input} - \text{Output} + \text{Generation}}$$

Because of chemical reaction



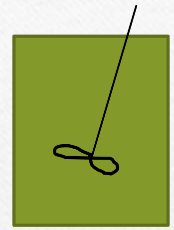






Simple examples

The Batch Reactor



What does the stirrer do?

Accumulation = ~~Input~~ – ~~Output~~ + Generation

$$\frac{dN_i}{dt} = Vr_i$$

At $t=0$, $N_i=N_{i0}$

What if more than one reaction occurs?

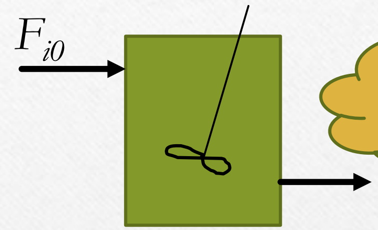
- *We write these ODEs for all the involved chemical species i*
- *r_i is of course the "rate " or speed of the reaction*
- *N_i is the number of moles and V is the reactor volume*

Do a quick unit consistency check!

(Neglecting heat effects)

The world famous perfectly stirred reactor

Also called the Continuously Stirred Tank Reactor or CSTR



Note the inlet and outlet streams

Accumulation = Input – Output + Generation

$$\frac{dN_i}{dt} = F_{i0} - F_i + Vr_i$$

At t=0, N_i=N_{i0}

What is F_{i0} then?

- *Here, the "molar flow rate" F_0 enters the picture*
- *We can also introduce "concentration" C_i*

$$\frac{dC_i}{dt} = v_0(C_{i0} - C_i)/V + r_i$$

We refer to the quantity V/v_0 as the reactor residence time

A quick summary

Isothermal

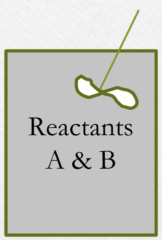
Molar flow rate $= F_A = C_A v$

Types of (ideal) reactors

$$A + B \rightarrow C + D$$
$$-r_A = kC_A C_B$$

Batch

No inlet or outlet streams



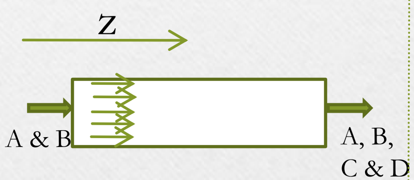
$$\frac{dC_A}{dt} = -kC_A C_B$$

Concentrations vs. time

Flow

(At steady state)

Plug flow reactor **(PFR)**

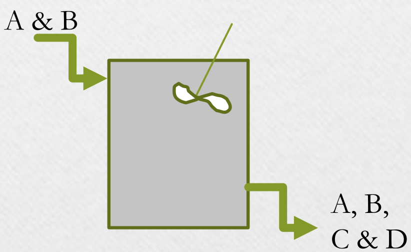


$$v_0 \frac{dC_A}{dV} = -kC_A C_B$$

$$\frac{dC_A}{d\tau} = -kC_A C_B$$

Concentrations vs. axial distance from inlet

Continuous stirred tank reactor **(CSTR)**

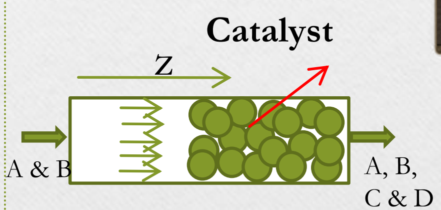


$$\frac{v_0 (C_{A0} - C_A)}{V} = kC_A C_B$$

$$\frac{(C_{A0} - C_A)}{\tau} = kC_A C_B$$

Outlet concentrations vs. flow rate, reactor volume

Packed bed reactor **(PBR)**



$$\rho_{cat} v_0 \frac{dC_A}{dW} = -k' C_A C_B$$

Concentrations vs. axial distance, catalyst weight

Developing mathematical models for chemical reactors

Reaction & reactor quantities

Independent vars: distance, time

We typically "validate" these against experiments

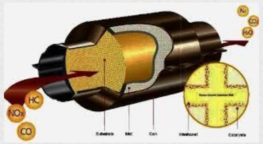
Parameters: Rate constants, flow rate, density, etc.

k_i, v_0, ρ

Dependent variables: Concentration, temperature, molar flow rate at outlet

C_i, F_i, T

Description of the performance of the chemical reactor



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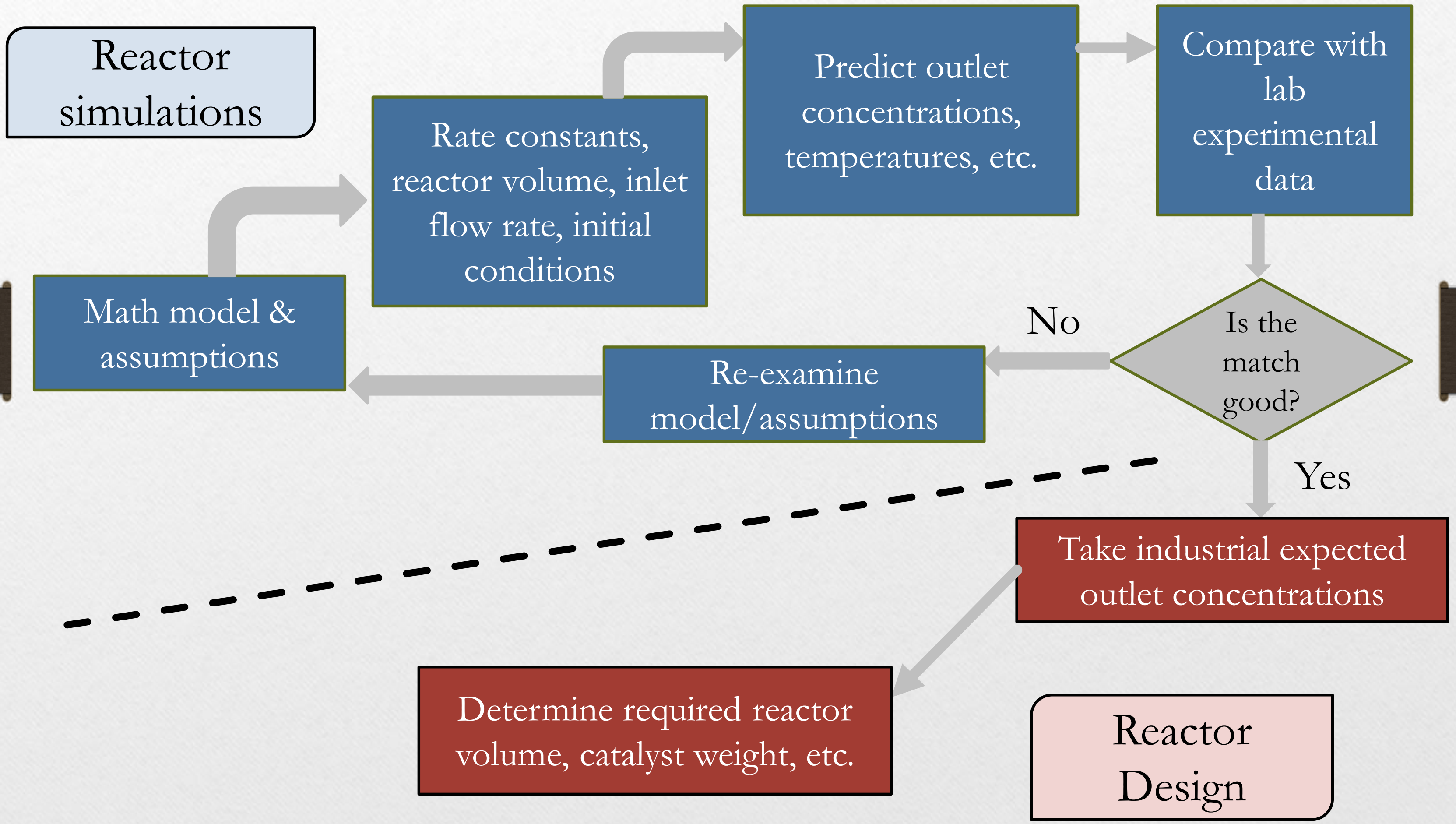
Reactor Design vs. Simulation



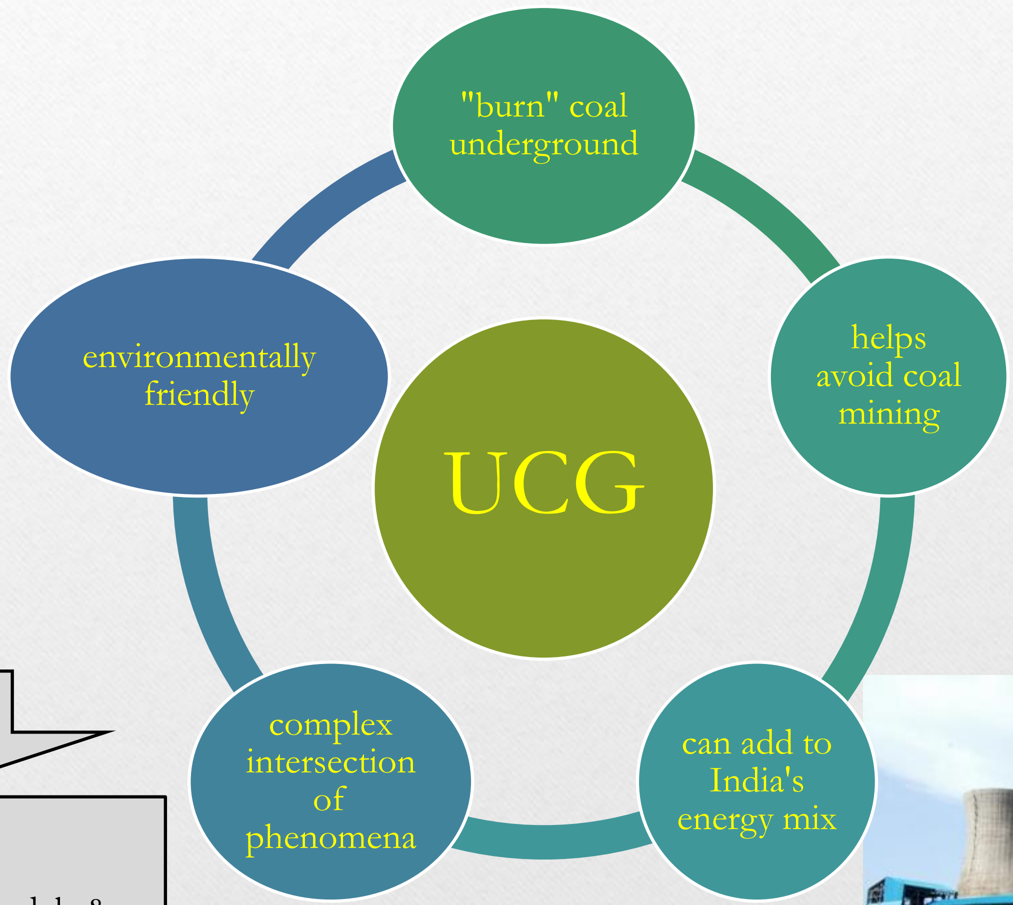
Some case studies

1. *Underground Coal Gasification*

2. *Understanding Automotive Soot*

3. *Catalytic Control of NOx*

Underground Coal Gasification



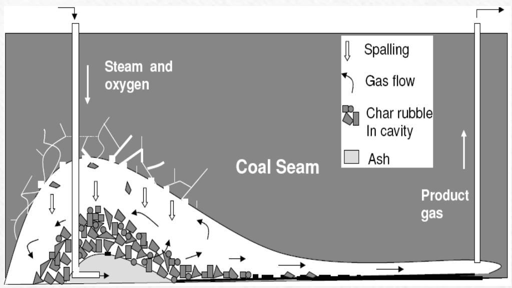
Conventional coal plant

In my lab

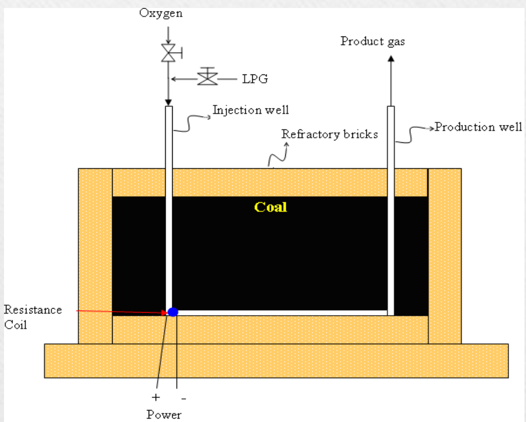
- Conducted experiments
- Developed models & insights

" Shape" of the UCG reactor

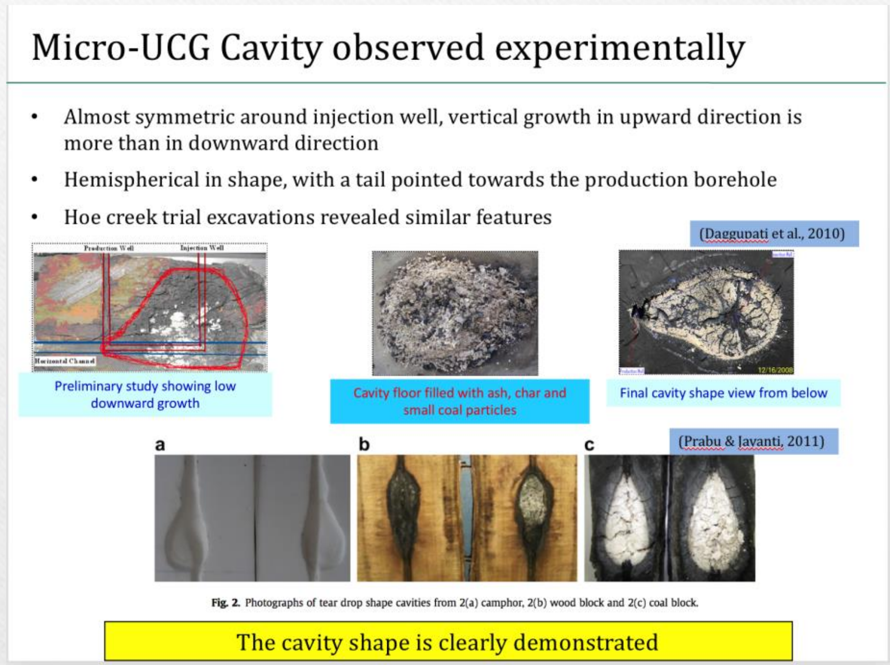
Injection Bore Hole *Production Bore Hole*



Expected visual of UCG



Our lab set-up



Some photos of what we saw

The Phenomena in UCG

Coal Particle

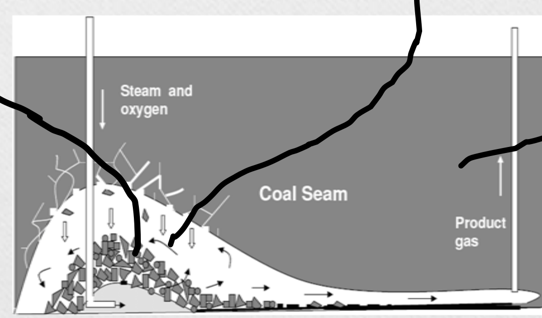
- Coal Drying
- Pyrolysis
- Gasification
- Combustion
- Other reactions

UCG Cavity

1. Evolution of cavity size & shape
2. Heat and mass transport of reactants in the cavity
3. Chemical reactions

Seam

- Coal spalling
- Surface subsidence
- Water influx



All these have to be incorporated in math models for UCG!

Modelling of UCG

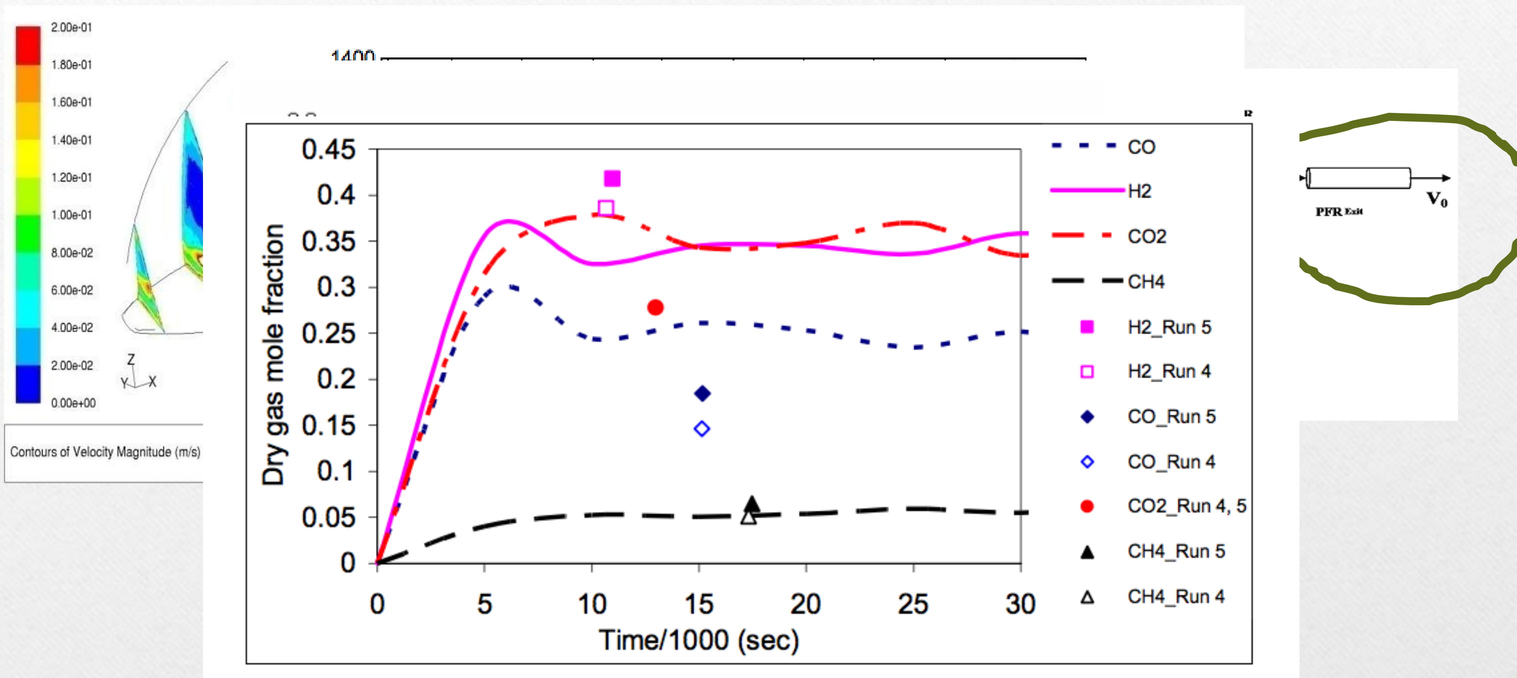


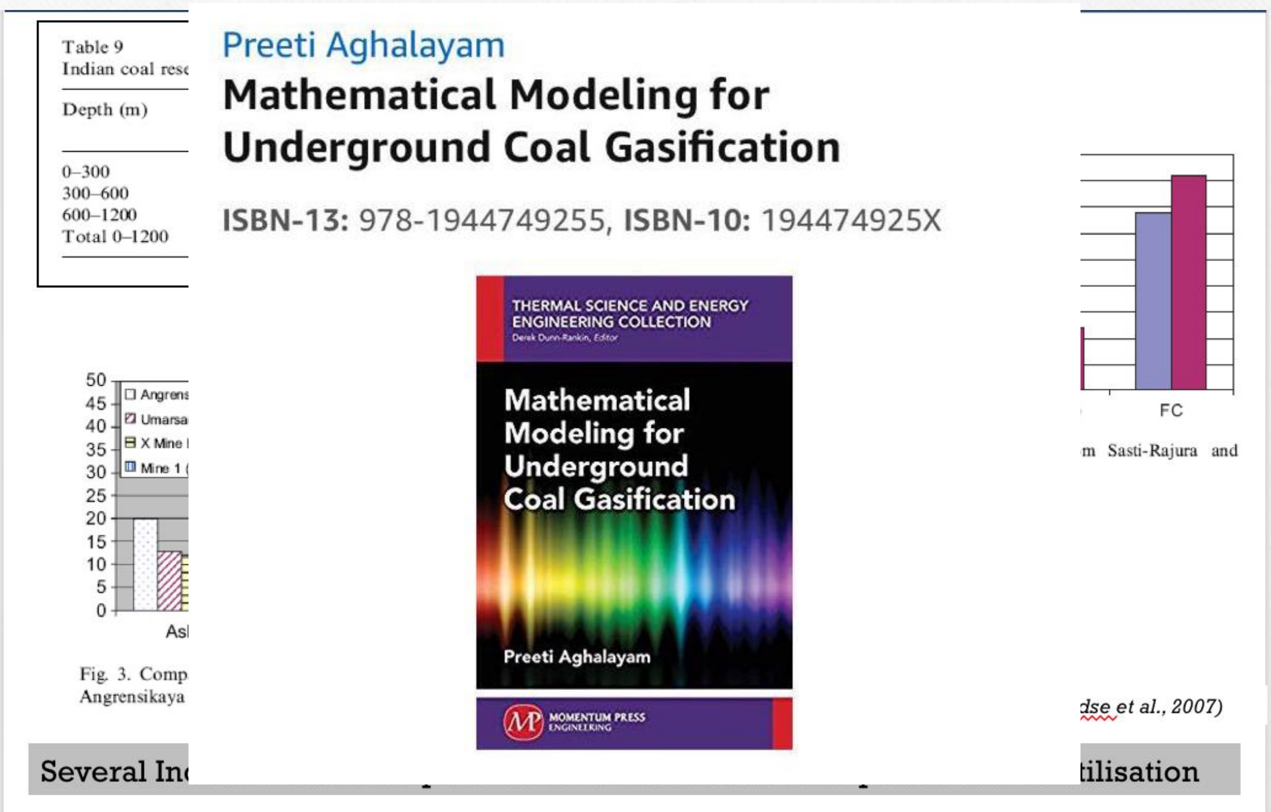
Figure 11. Comparisons of dry gas compositions with experimental results from Thorsness et al., (1978).

Figure 5. Temperature profiles along the reactor length at different time

The math model of UCG is an idealized picture of the complex process, but has good ability to predict experimental data

UCG in India

- Our simulations of the UCG reactor have yielded good results!

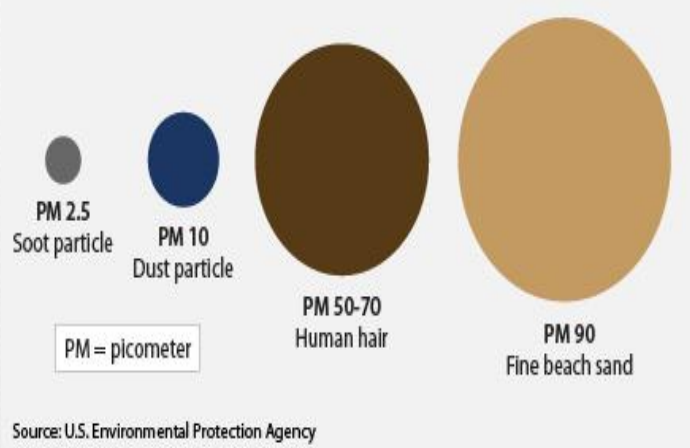


But, honestly…

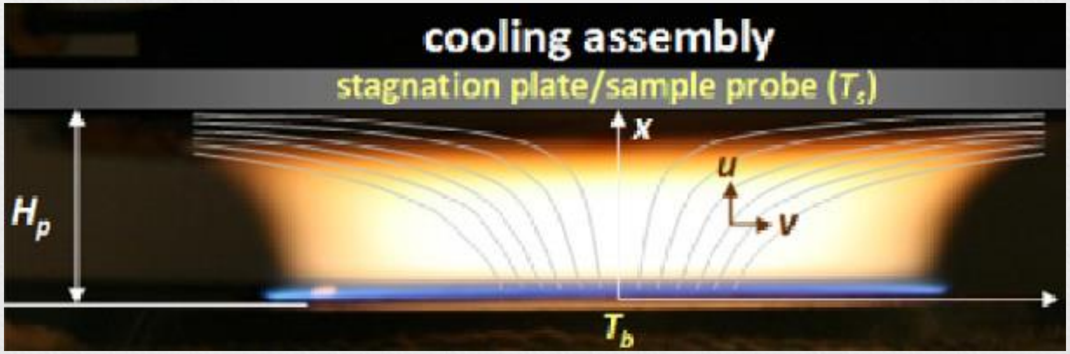
A number of law-suits have also been filed against UCG!

Formation of Soot in Flames

Regulations on PM emissions from vehicles prompt us to examine this problem.



Soot – Carbonaceous particles with aliphatics & aromatics.
Fuel - H/C Ratio – 2
Soot – H/C Ratio – 0.1

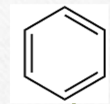


Premixed flame impinging on ona stagnation plate

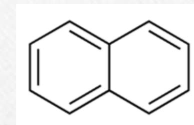
Modeling Soot

Soot, assumed to be coronene ring i.e. …romatic ri…

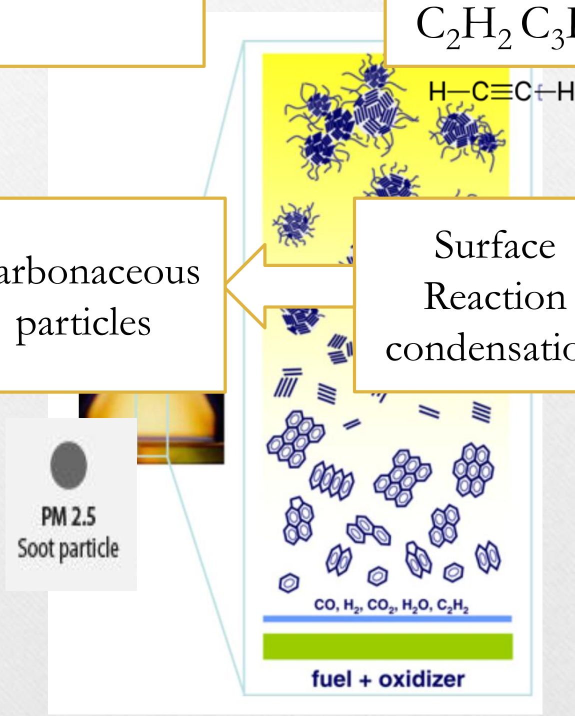
Fuel → PAH precursor C_2H_2 C_3H_3 → First Aromatic Ring → PAH $C_{10}H_8$



A7 - Coronene

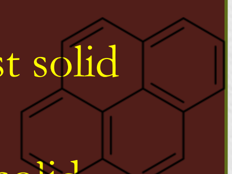


Nucleation → Coagulation → Surface Reaction condensation → Carbonaceous particles

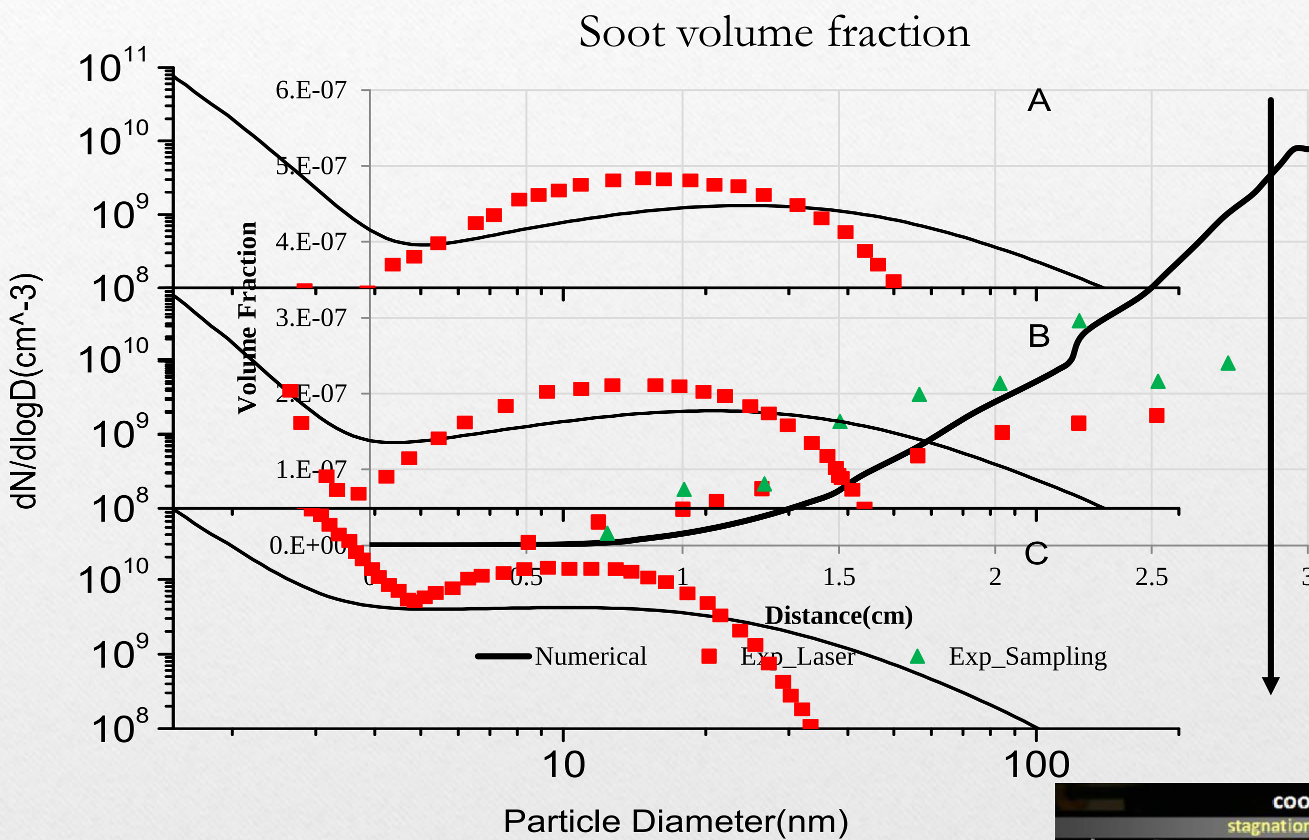


A… hemic… is in… ng so…

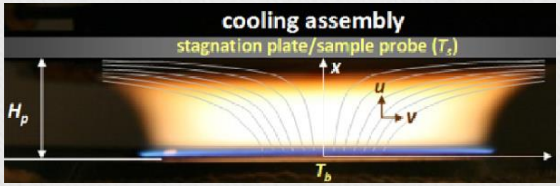
- …action… soot precursors"
- Nucleation forming the first solid particle
- Condensation reactions as solid particle grows



Validation of model results



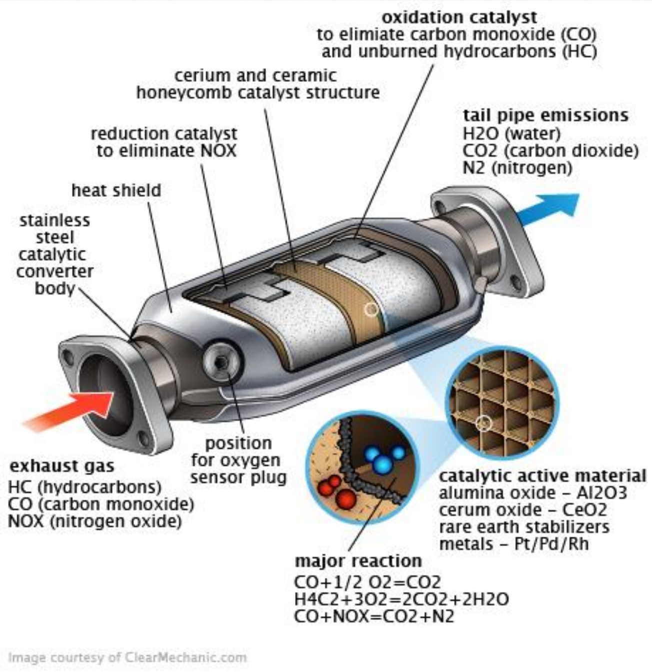
Increasing height above burner



But, honestly…

Appearances can be deceptive!

Control of NOx using Catalysts

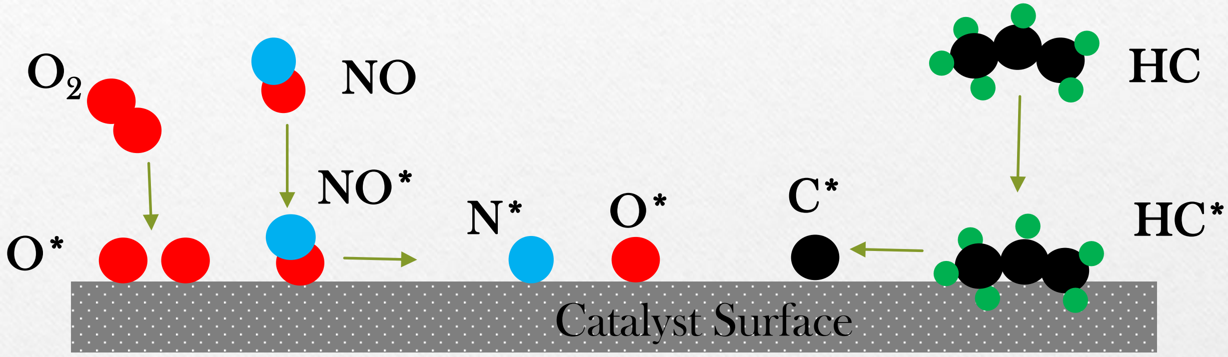


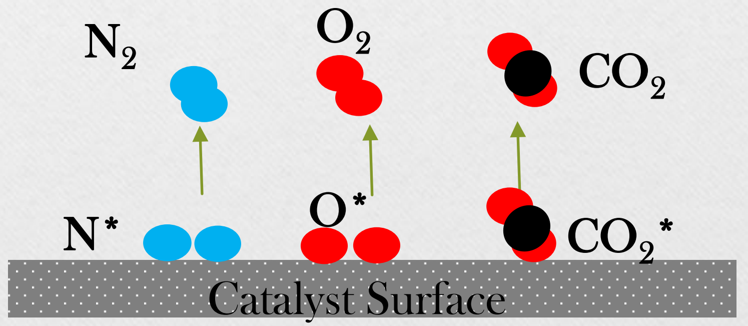
Catalytic converters are used to reduce NOx in automobiles

But they have drawbacks- cold start, lean burn engines…

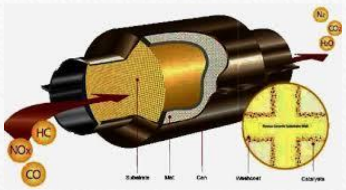
Selective catalyic reduction, Lean NOx trap are proposed for this.

Hypothesised reaction mechanism



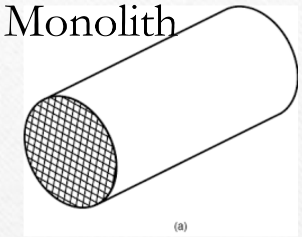


A plug flow reactor model



Cat Converter

Monolith



Plug flow reactor

Mass balance for surface intermediates

$$\sum_{j=1}^{nrxns} \nu_{ij} R_j = 0$$

Mass balance for gas-phase species

$$\frac{(C_i^0 - C_i)}{\tau} = -a_v * (\sum_{j=1}^{nrxns} \nu_{ij} R_j)$$

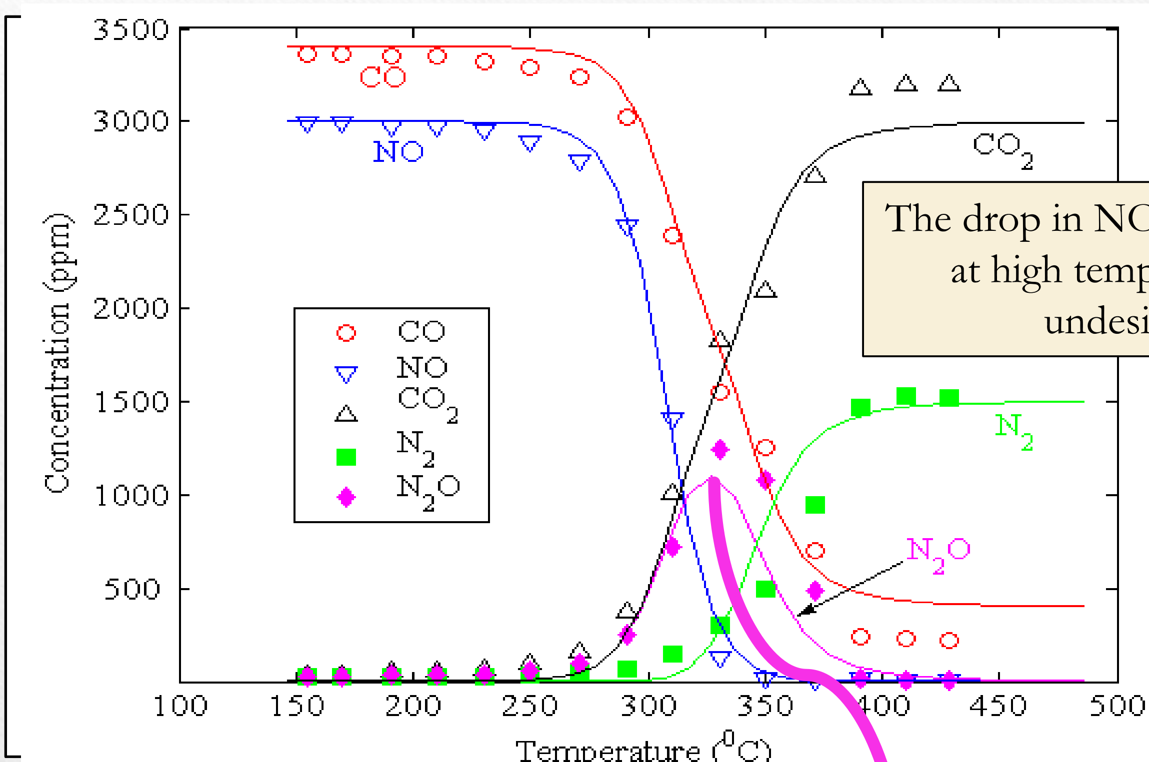
Catalyst site conservation

$$\sum_{i=1}^{nsurface} \theta_i = 1$$

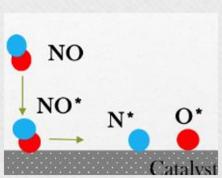
Elementary Reactions	Activation barrier (kcal/mol)				
	Pt	Rh	Pd	Ru	Ir
NO + * → NO*	0.0	0.0	0.0	0.0	0.0
NO* →NO + *	26.0	26.0	32.0	34.2	30.7
NO* → N* + O*	12.5	6.6	9.0	0.0	7.7
N* + N* → N_2+ 2*	26.6	26.6	42.8	48.5	39.3
NO*+N* → N_2O* + *	21.2	21.2	30.0	42.2	28.7
N_2O* → N_2O + *	12.2	10.0	17.0	12.0	14.0
CO + * → CO*	0.0	0.0	0.0	0.0	0.0
CO* → CO + *	32.0	32.0	34.0	34.0	34.0
CO* + O* → CO_2 + 2*	23.2	24.3	24.4	27.0	24.9
O_2 + 2* -> 2O*	0.0	0.0	0.0	0.0	0.0
2O* -> O_2 + 2*	51.0	85.0	55.0	121.0	54.0

Predicting experimental data

Catal Today,119, 98-93 (2007)
IJCRE, V5, A1 (2007).



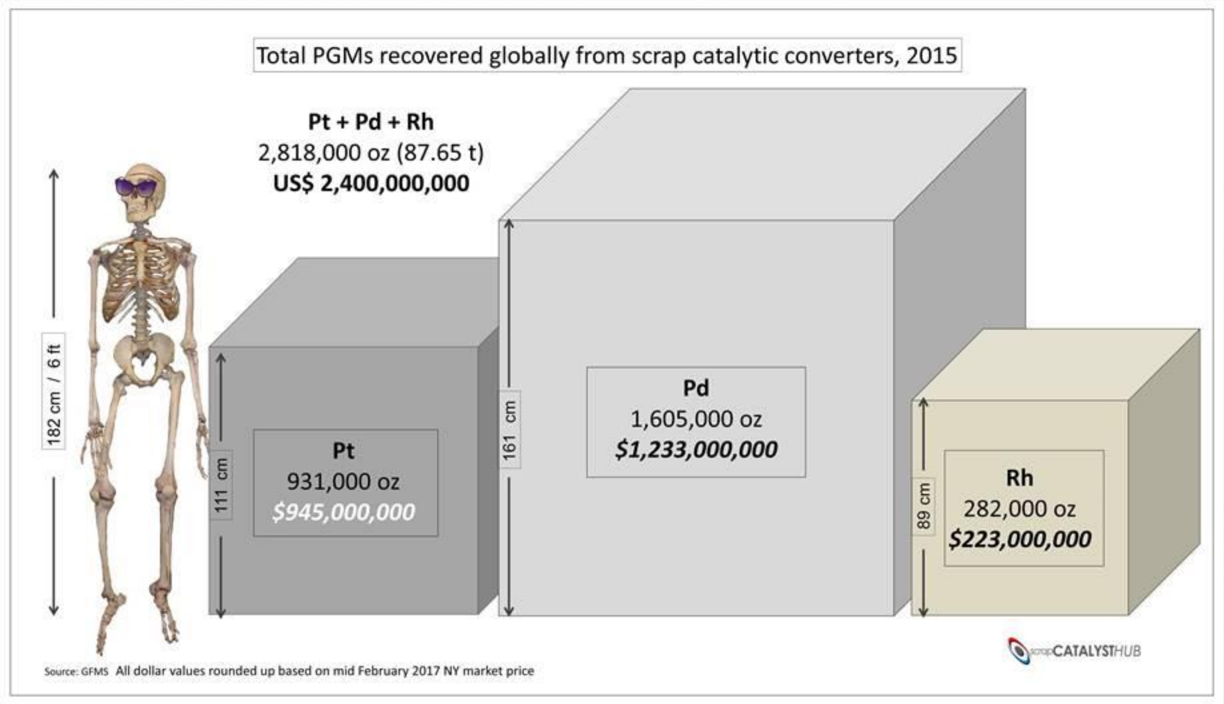
The drop in NO "conversion" at high temperatures is undesirable



Important reaction

This high N_2O production is undesirable

But, honestly…



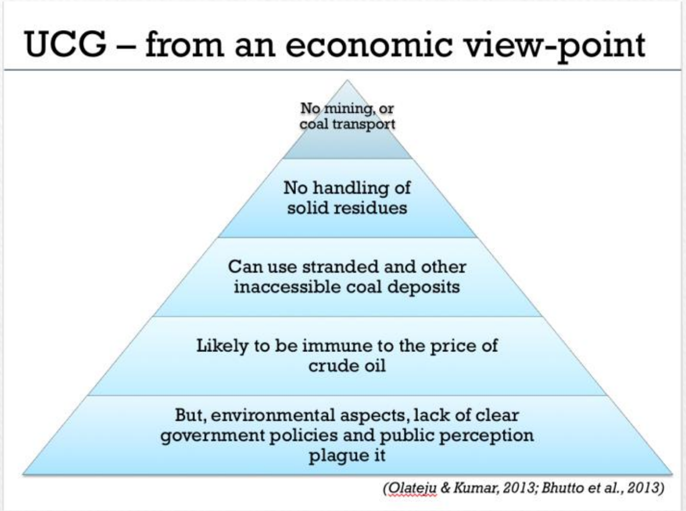
http://www.scrap-catalyst-hub.com/precious-metals/scrap-catalytic-converter-industry-size/

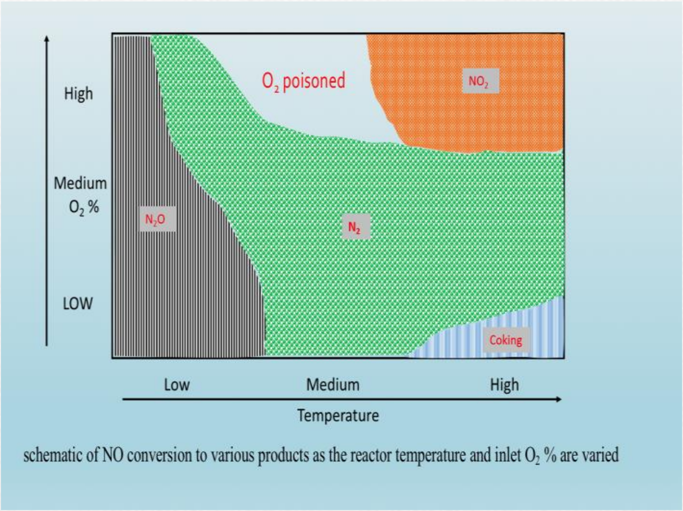
The catalyst metals are humongously expensive!

What we have found so far

- Predictive process model for UCG → that super interesting shape of the UCG reactor
- Validated model for soot formation → the truth about bimodal soot
- Catalytic reaction mechanisms → the problem of N_2O formation in cat converters

But this is just the beginning!





Models that account for economic & safety aspects

Studies on the effects of practical operating conditions

Discoveries of new and improved catalysts

To conclude

- Math modeling of chemical reactors is a rich field
- I presented stuff I work on, there is TONS more
- Hope some of you will be interested in working in these areas in the future!

Want to discuss anything? Write to me

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