CYPRUS UNIVERSITY OF TECHNOLOGY

ENVIRONMENTAL SCIENCE AND TECHNOLOGY DEPARTMENT

Catalytic Elimination of the Ecotoxicity of Pharmaceutical Compounds using O_2/H_2 Mixtures

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OUTLINE OF PRESENTATION

1. Introduction
- Contamination of the environment from pharmaceuticals

2. State of the Art
- Catalytic Wet Air Oxidation and Oxidative Agents
- Use of Hydrogen Peroxide as an Oxidative Agent

3. Experimental and Reaction Conditions

4. Results
- Effect of Hydrogen Concentration
- Effect on Concentration of Paracetamol
- Effect on Toxicity of the Paracetamol solution before and after the reaction
- Effect of various monometallic 1% M (M= Pd, Pt, Rh, Ni, Cu, Fe and Mo) on γ-Al_2O_3
- Effect on Different Pharmaceutical Compounds

5. Future Work

6. Conclusions

How do pharmaceuticals leak into the environment

100,000-200,000 tons per year consumption of antibiotics (2007 records)

- Manufacturing Processes in pharmaceutical Factories
- Human and Animal Excretions (contamination of underground water reserves)
- Improper Disposal of Pharmaceuticals

Detection in the Environment

- Pharmaceutical compounds in trace amounts (ng/L to low μg/L) in water samples.
- The conventional technologies used in WWTP do not sufficiently remove pharmaceutical compounds.

- **Minute quantities but able to induce adverse effects.**
- **Need to find suitable methods to eliminate pharmaceutical substances from wastewater.**

Catalytic Wet Air Oxidation (CWAO)

Wet Air Oxidation

Oxidation of pharmaceuticals in water using Air/Oxygen.

Catalytic Wet Air Oxidation

- Reduces the severity of the reaction conditions compared to Wet Air Oxidation (WAO)
- More readily decomposes even refractory compounds.

Milder Operating Conditions and shorter residence time.

Consequently, reduced capital and operational costs.

Use of an oxidizing agent

Strong oxidizing agents

- Hydrogen peroxide
- Ozone
- UV radiation

Generation of Hydroxyl radical (·OH): High oxidative power. Extremely reactive and less selective than other oxidants (chlorine, molecular ozone)

Use of Hydrogen Peroxide

- Strong Oxidizing Agent.
- Produces no harmful waste.
- Low cost.

- In-situ production of hydrogen peroxide, further reduces the cost of operation. However, restrictions due to the H_2/O_2 mixture being explosive in a broad range.

- Very few research studies were published using this technique and none for studying the mechanisms of the reactions involved.

Oxidation and Reducing Ecotoxicity

- Our aim in this work is to eliminate the ecotoxicity of the Pharmaceutical Substances
- Eliminating or reducing the Ecotoxicity does not necessarily mean the substances should be completely oxidized.
- A change in their structure may be sufficient for the ecotoxicity to be reduced.

Experimental Conditions

Catalysts were prepared using a modified wet impregnation method

- 1 wt. %Pd/γ-Al_2O_3
- 1 wt. % Pt/γ-Al_2O_3
- 1 wt. % Rh/γ-Al_2O_3
- 1 wt. % Cu/ γ-Al_2O_3
- 1 wt. % Ni/ γ-Al_2O_3
- 1 wt. % Fe/ γ-Al_2O_3
- 1 wt. % Mo/ γ-Al_2O_3

Gas Feed Compositions used:

- 100% vol. O_2
- 1-5% vol. H_2/99-95% vol. O_2.
- 100% vol. H_2

Reaction Conditions

Reaction Temperature: 25^{o} C

Concentration of Paracetamol: 10 ppm

W_{cat}= 4g (dp=1.8 mm)

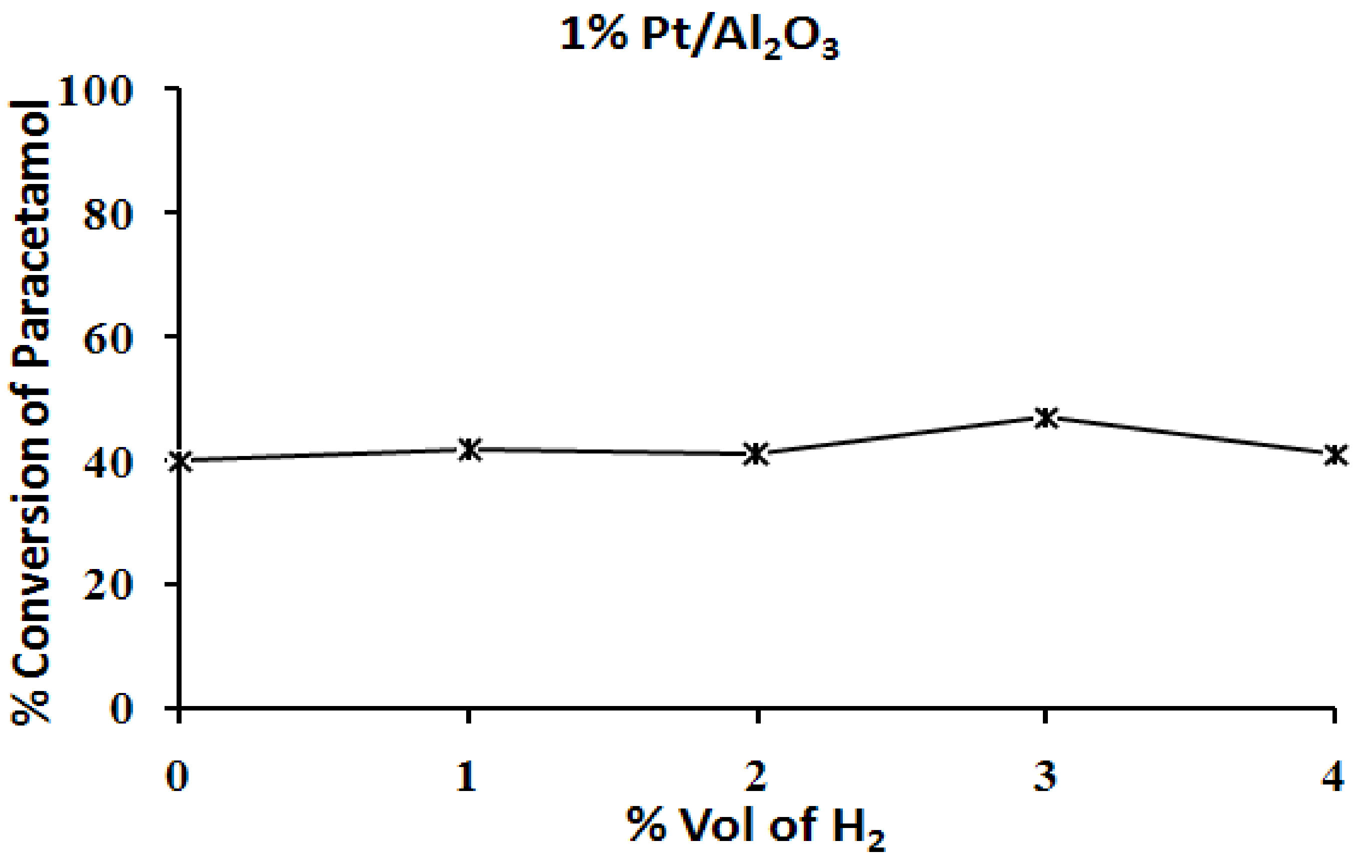
Pressure= 1.2 atm

The samples were analyzed at

0, 30, 60 and 120 min after reaction using UV/vis

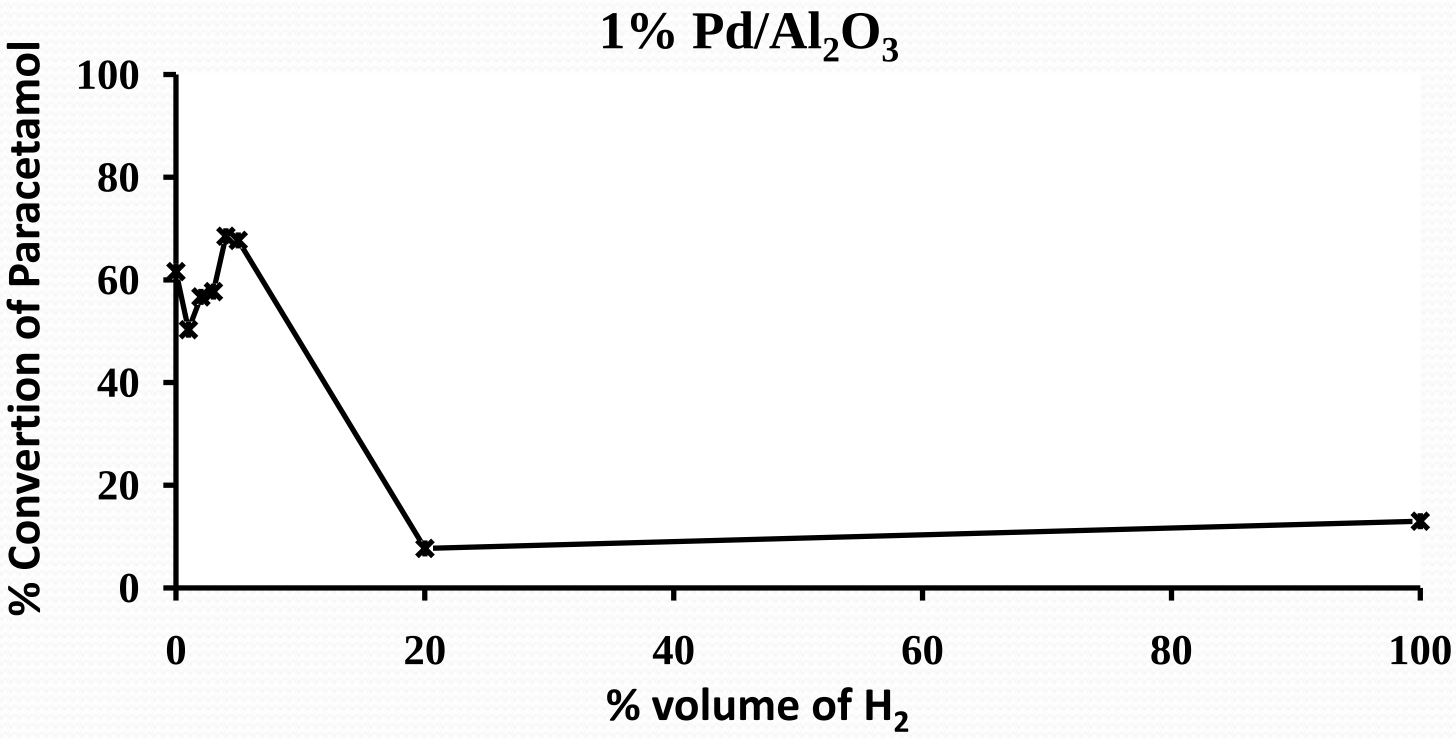
spectrophotometry at 243nm.

Effect of Hydrogen Concentration



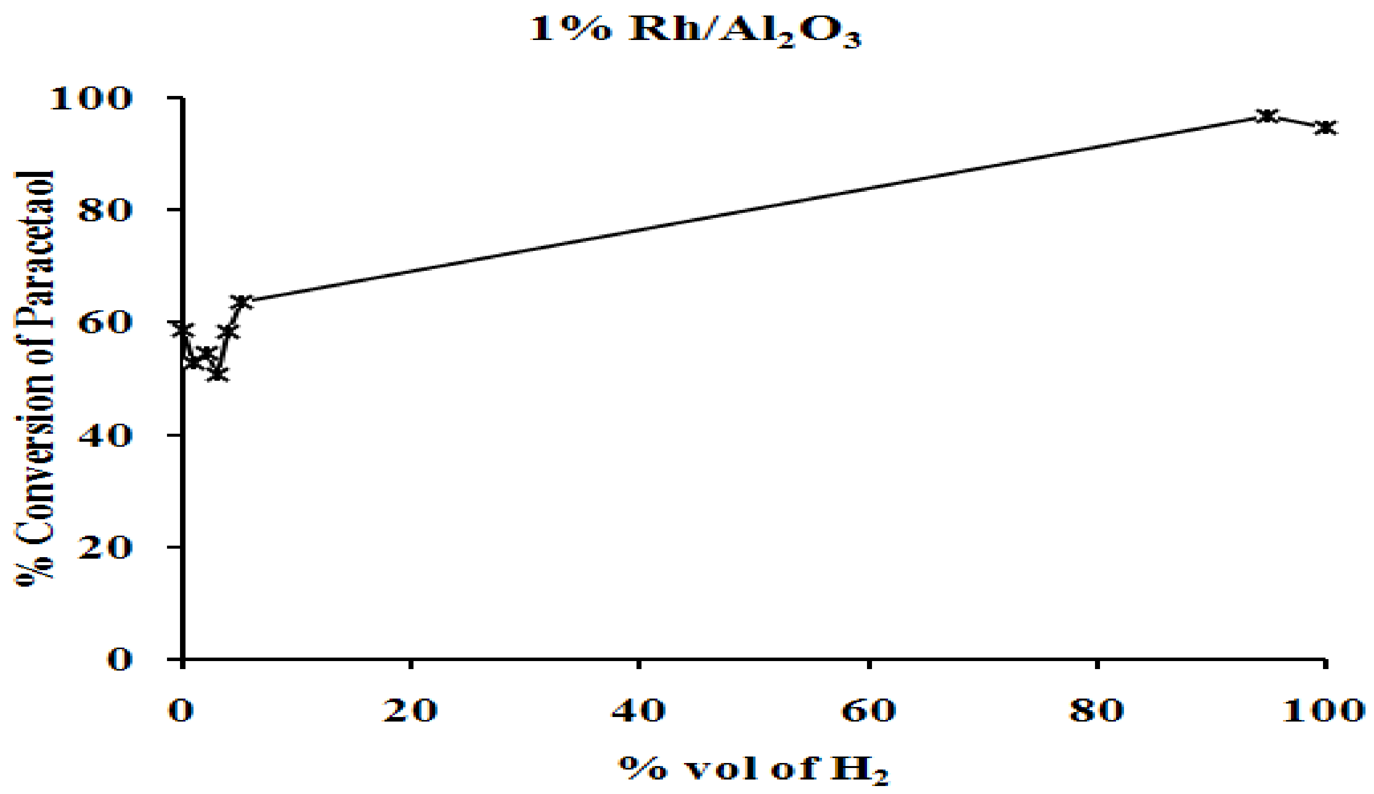
- No change in the conversion of Paracetamol
- Around 40-50% conversion of Paracetamol in 2 hours

Effect of Hydrogen Concentration



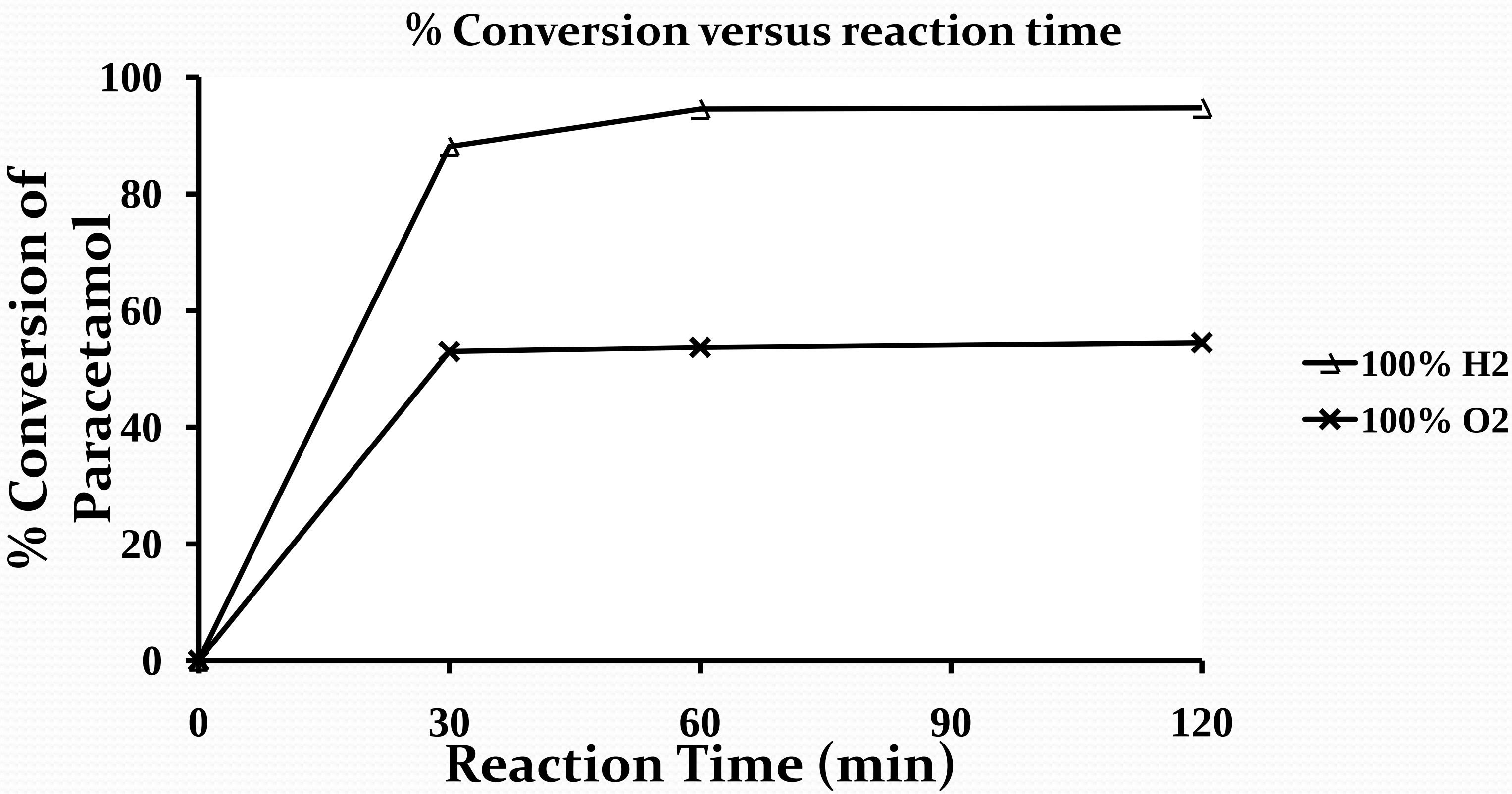
- ≥ 5% H_2 slight increase in Paracetamol % Conversion
- For 20 and 100 % H_2 – Very low conversion
- Up to 70% conversion in 2 h

Effect of Hydrogen Concentration



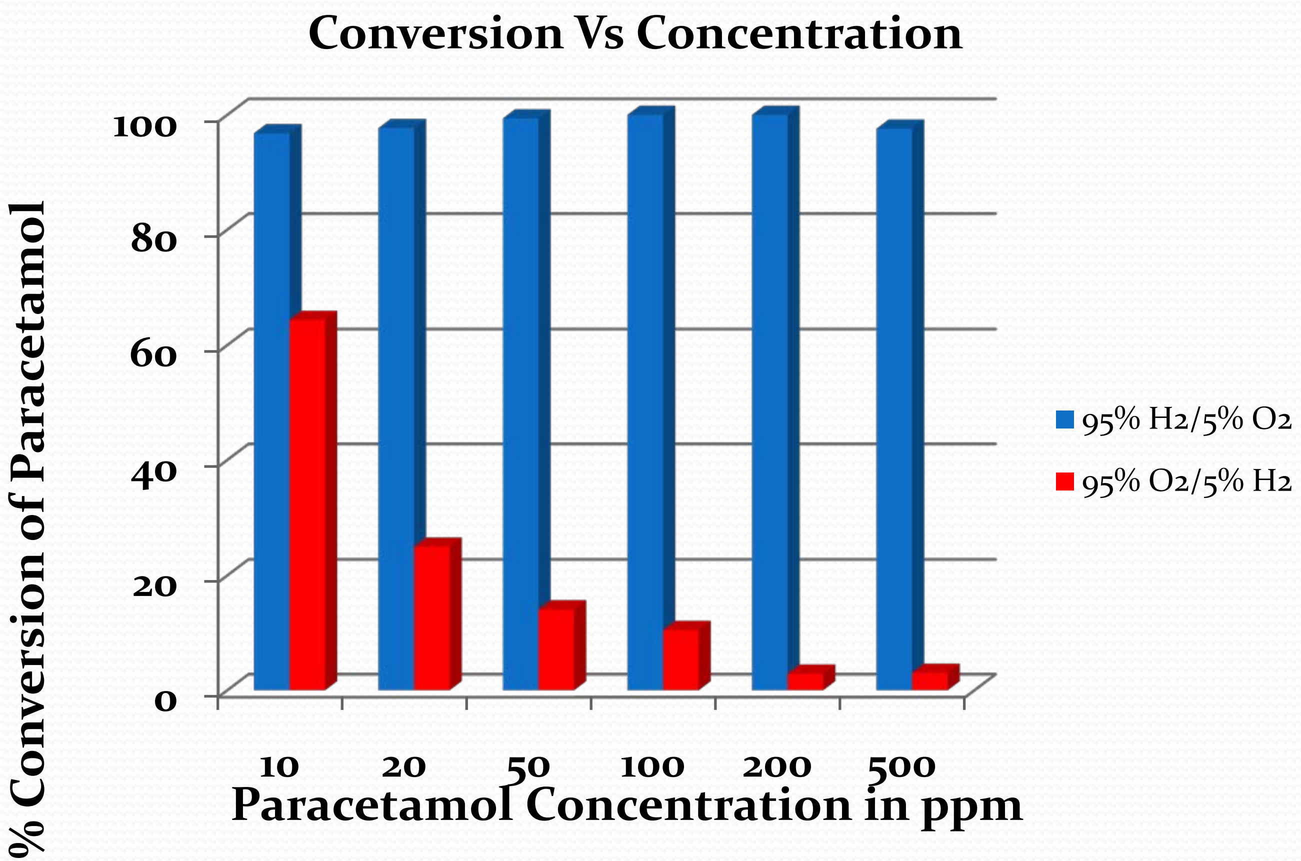
- Increase of conversion at low % vol of H_2
- Nearly 100% Conversion at 95 and 100% H_2
- Nearly 100% Conversion after 2h

Conversion of Paracetamol with time



- 88% of Paracetamol is converted in just 30 min
- Nearly 100% conversion of Paracetamol in 2 h in room T and 1.2 atm.

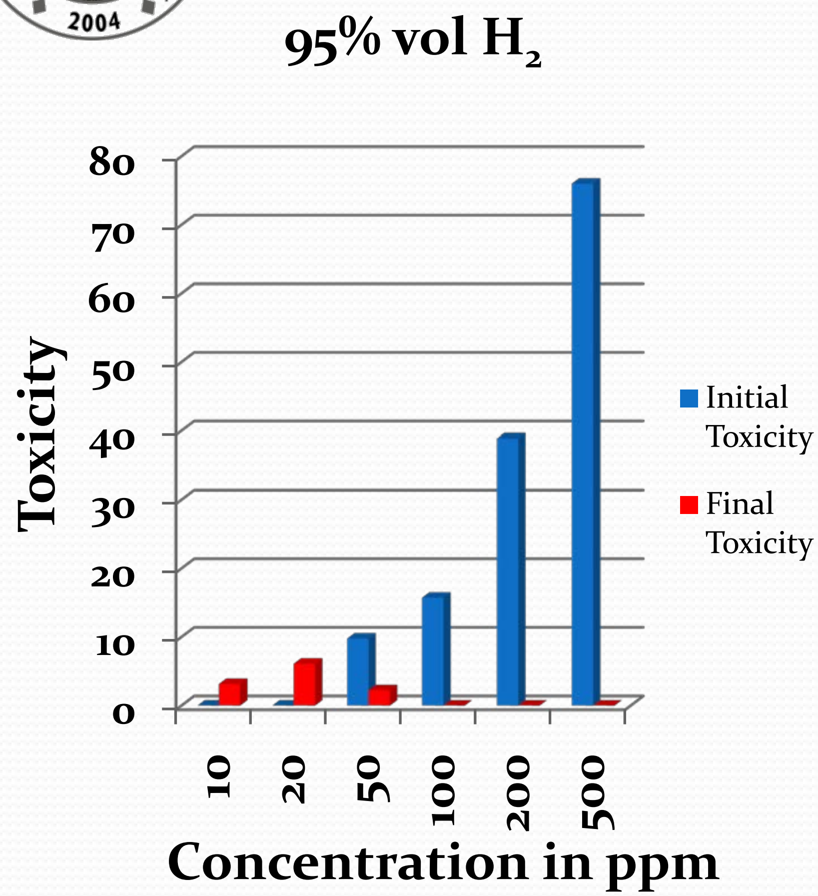
Conversion against Concentration for the 1% Rh/Al_2O_3 catalyst

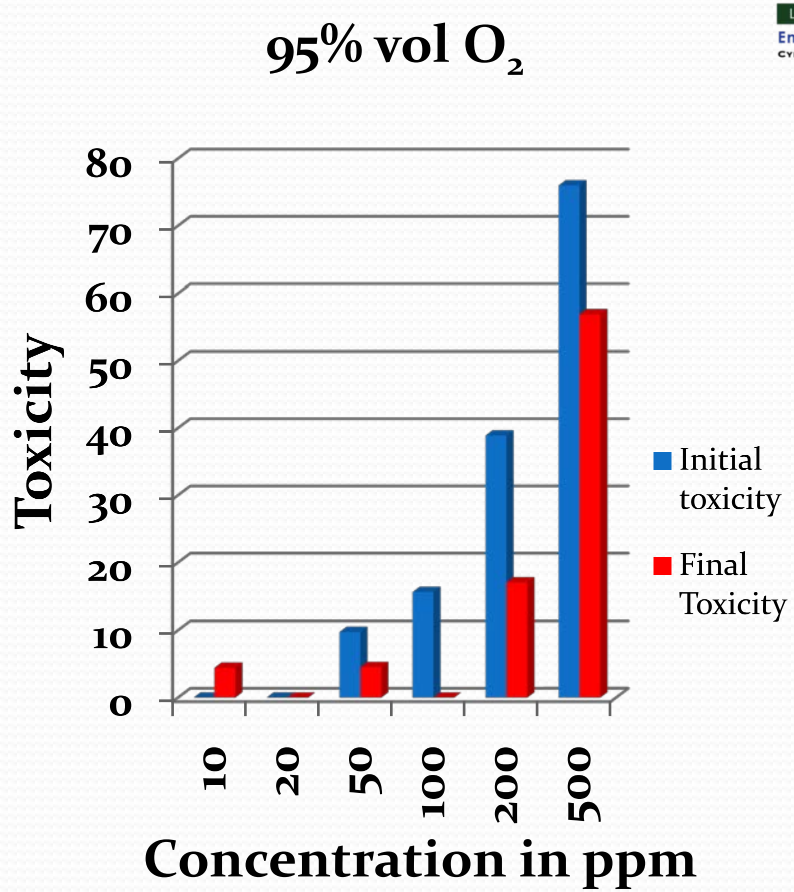


- For 95% O_2, the conversion decreases with concentration
- For 95% vol H_2, the conversion is almost 100% for all concentrations

So, the reaction with 95% vol H_2 is efficient even at high concentrations

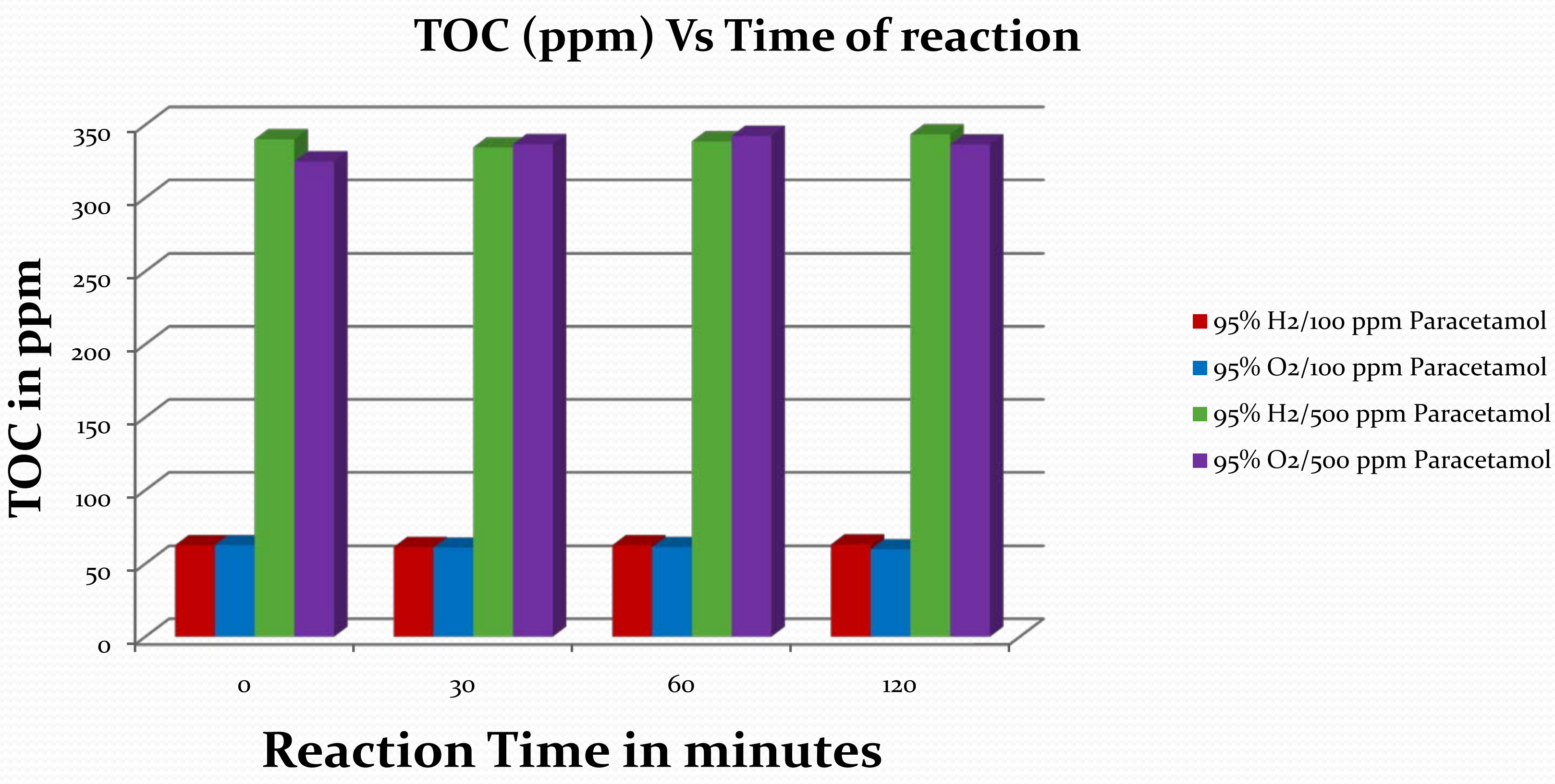
Toxicity versus Concentration for both conditions





- For 95% vol H_2 , toxicity is 0 or negligible, even at high concentrations
- For 95% vol O_2, toxicity still exists at concentrations greater than 100 ppm

TOC versus Time for 100 ppm and 500 ppm Paracetamol and 95% H_2 and 95% O_2



The TOC does not change for either concentrations and air streams. This indicates that Paracetamol is converted to other organic compounds, which however have lower toxicity.

Effect of Metal Precursor on % Conversion of Paracetamol

- 7 catalysts were prepared and tested using the gas feed stream composition of 95% vol. H_2/5% vol. Air

Catalyst	% Conversion of Paracetamol
1 % wt. in Pt/Al_2O_3	41,3%
1 % wt. in Pd/Al_2O_3	13,4%
1 % wt. in Rh/Al_2O_3	96,8%
1 % wt. in Ni/Al_2O_3	1,4%
1 % wt. in Mo/Al_2O_3	0%
1 % wt. in Cu/Al_2O_3	23,4%
1 % wt. in Fe/Al_2O_3	0%

The catalyst with the highest % paracetamol conversion is 1% wt. in Rh/Al_2O_3

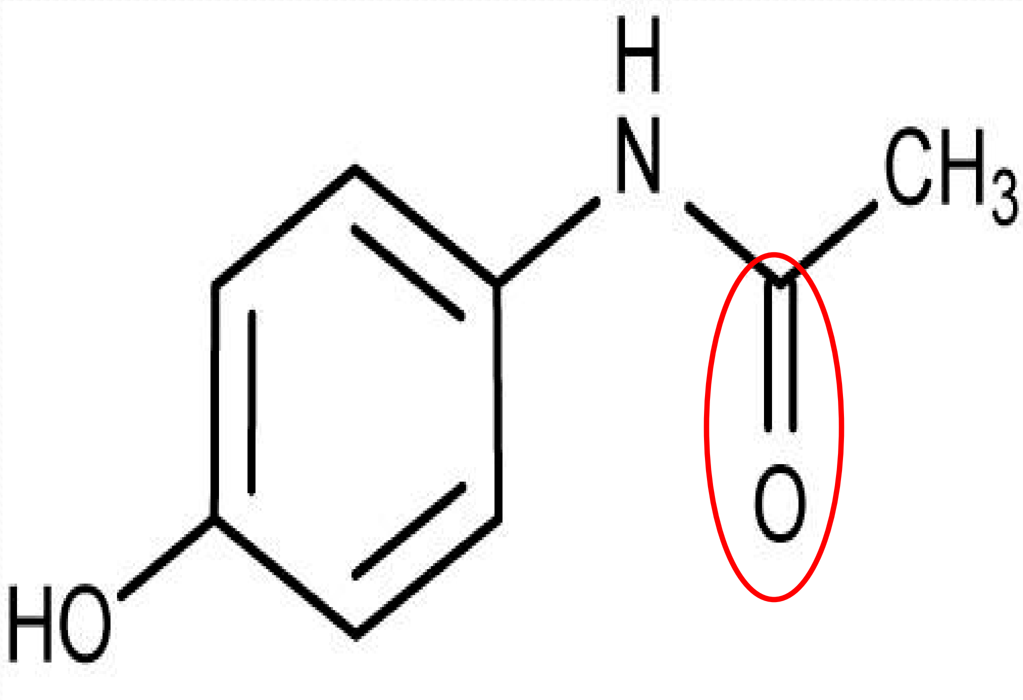
% Conversion of Different Pharmaceutical Substances

- 5 different pharmaceutical substances were used under a gas feed stream of 95% vol. H_2/5% vol. of Air to test the applicability of the method

Pharmaceutical Substances	% Conversion
Paracetamol	96.8 %
Ibuprofen	8.9 %
Diclofenac Sodium	85.6 %
Tetracycline HCl	61.5 %
Amoxicillin Trihydrate	57%

All the above pharmaceutical substances showed satisfactory % conversion except for Ibuprofen that had only a 9 % conversion

Hydrogenation of Paracetamol



Possible hydrogenation site for Paracetamol is the double oxygen bond of the ketone. Benzyl ring probably can not be hydrogenated at these temperature and pressure conditions. Further investigations are being done.

Conclusions

- 1% Pd/Al_2O_3 and 1% Rh/Al_2O_3 are suitable catalysts for the Catalytic Wet Oxidation of Paracetamol using 95% O_2/5% H_2. 70% of Paracetamol is eliminated in 2 hours.

- 1% Rh/Al_2O_3 is the most suitable catalyst for the catalytic reaction of Paracetamol using Hydrogen. Almost 90% elimination of Paracetamol was achieved in just 30 minutes of reaction. Applies to concentrated samples and toxicity is eliminated even at high conc.

- The reaction using 95% vol. H_2/5% vol. O_2 is effective with other pharmaceutical substances too with % Conversion of Paracetamol above 55%.

- **Both catalytic methods are extremely promising**

Future Plans

- More catalysts are going to be examined with the effect on % loading and support.

- Study of the mechanisms of the reactions involved.

Thank you!