FLORIDA SOLAR ENERGY CENTER
A Research Institute of the University of Central Florida

Hydrogen Production via Photolytic Oxidation of Aqueous Sodium Sulfite Solutions

Cunping Huang, Clovis A. Linkous, Olawale Adebiyi & Ali T-Raissi

Hydrogen 2008 – Materials Innovations in an Emerging Hydrogen Economy

Cocoa Beach, Florida, USA
February 27, 2008

Background

- SO_2 is a criteria air pollutant that can cause respiratory & other problems as an acid gas
- SO_2 emissions occur both naturally (20%) & anthropogenically (80%)
- Natural sources include: geothermal (e.g. volcanic), oceanic, vegetative & land emissions.

Anthropogenic Sources of SO_2 Emissions

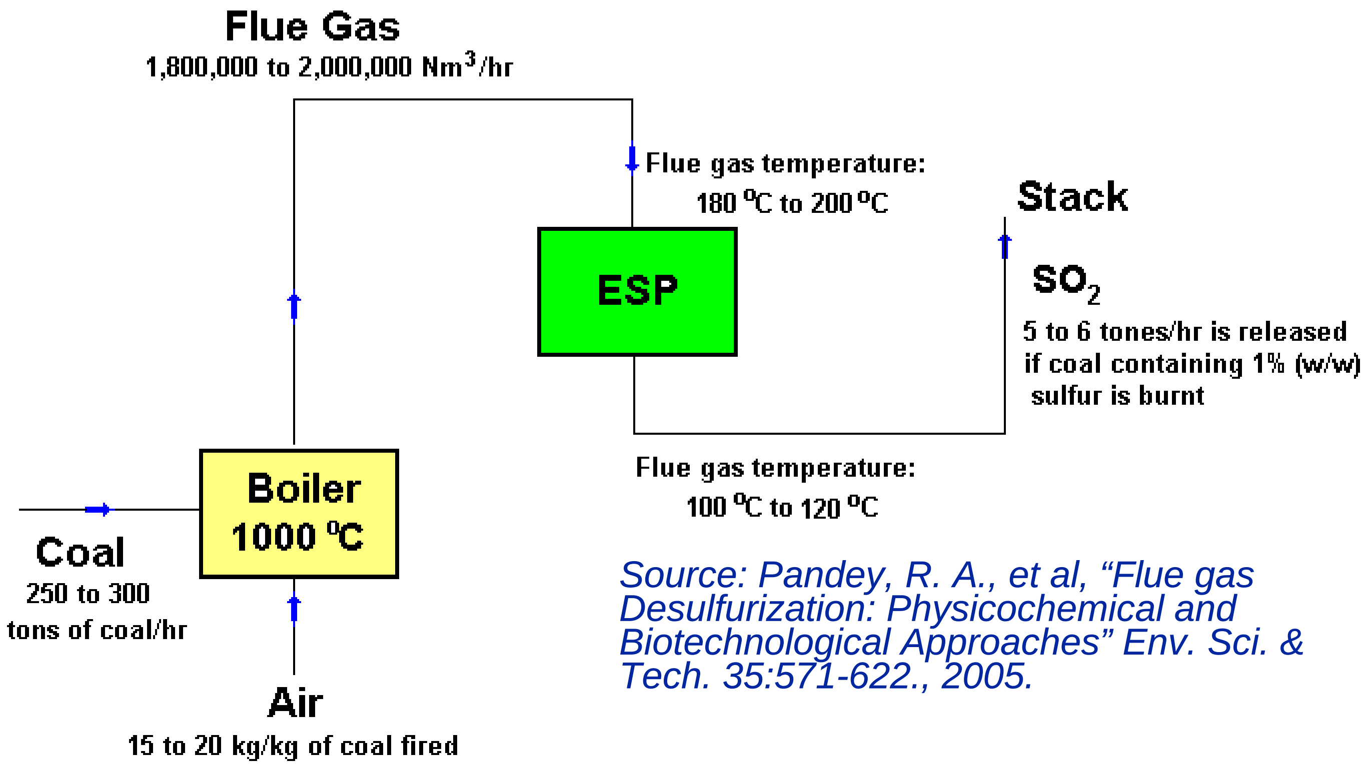
- Combustion of high-sulfur-containing fossil fuels
- Sulfuric acid & ammonium sulfate plants
- Power plants using coal, crude oil & crude oil-based fuel oil.

Major Global Anthropogenic Sources of SO_2 Emissions

Emission Source	Emission (%)
Electric utility	69.7
Industrial fuel combustion	13.6
Metal processing	3.8
Transportation	3.5
Others	9.4

Source: Schnelle, K.B., and Brown, C.A., Control of So$_x$, In Air Pollution Control Technology Handbook, ed. Kreith, F., CRC Press, Boca Raton, FL, 257, 2002

SO_2 is both a Pollutant & a Resource



Source: Pandey, R. A., et al, “Flue gas Desulfurization: Physicochemical and Biotechnological Approaches” Env. Sci. & Tech. 35:571-622., 2005.

Generation of SO_2 in 500 MW coal fired power plants can produce huge amounts of SO_2 that can be used for the production of H_2 as well as fertilizers.

Objectives

- Develop an innovative process for utilizing SO_2 in flue gas for the production of hydrogen
- Explore chemistry & chemical engineering aspects of SO_2 utilization
- Investigate effects of reaction conditions on the hydrogen production rate.

Flue Gas Treatment and H_2 Production

Conventional process:

Absorption: $SO_2 + NaOH = Na_2SO_3$

Oxidation: $Na_2SO_3 + O_2 = Na_2SO_4 + H_2O$

FSEC Approach:

Absorption: $SO_2 + NaOH = Na_2SO_3$

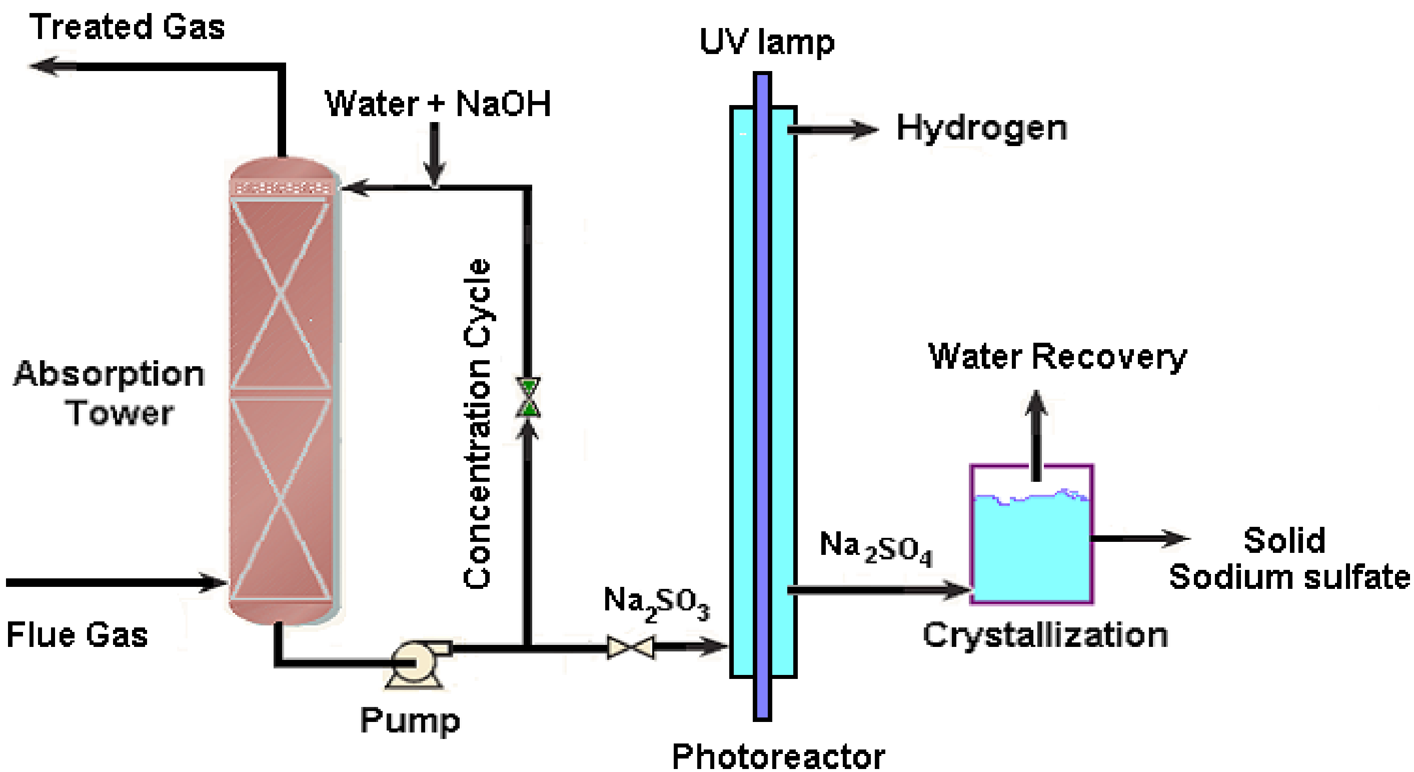
$SO_2 + (NH_4OH) = (NH_4)_2SO_3$

Photooxidation:

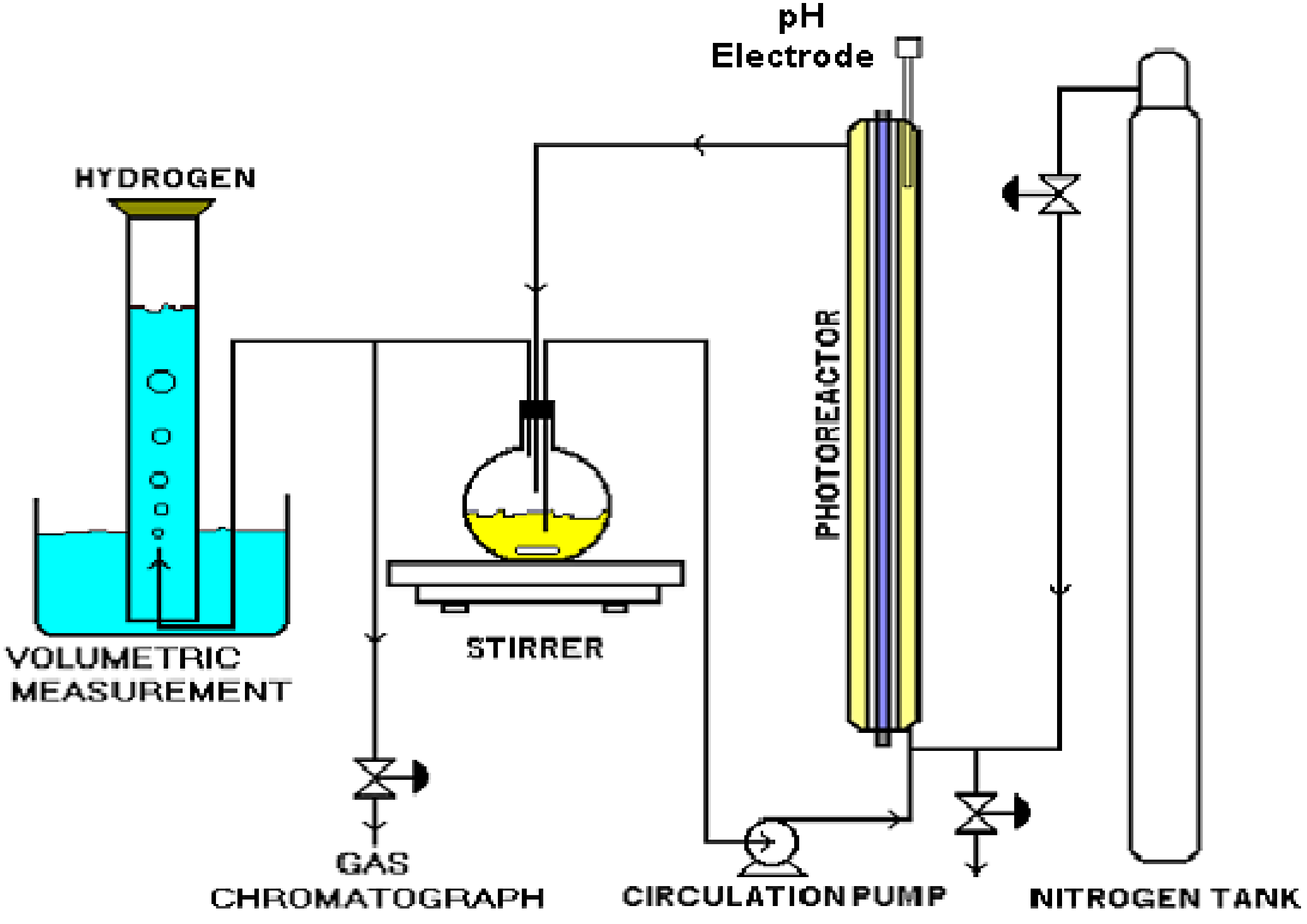
$Na_2SO_3 + H_2O + \text{UV light (or } \Delta E) = Na_2SO_4 + H_2$

$(NH_4)_2SO_3 + H_2O + \text{UV light (or } \Delta E) = (NH_4)_2SO_4 + H_2$

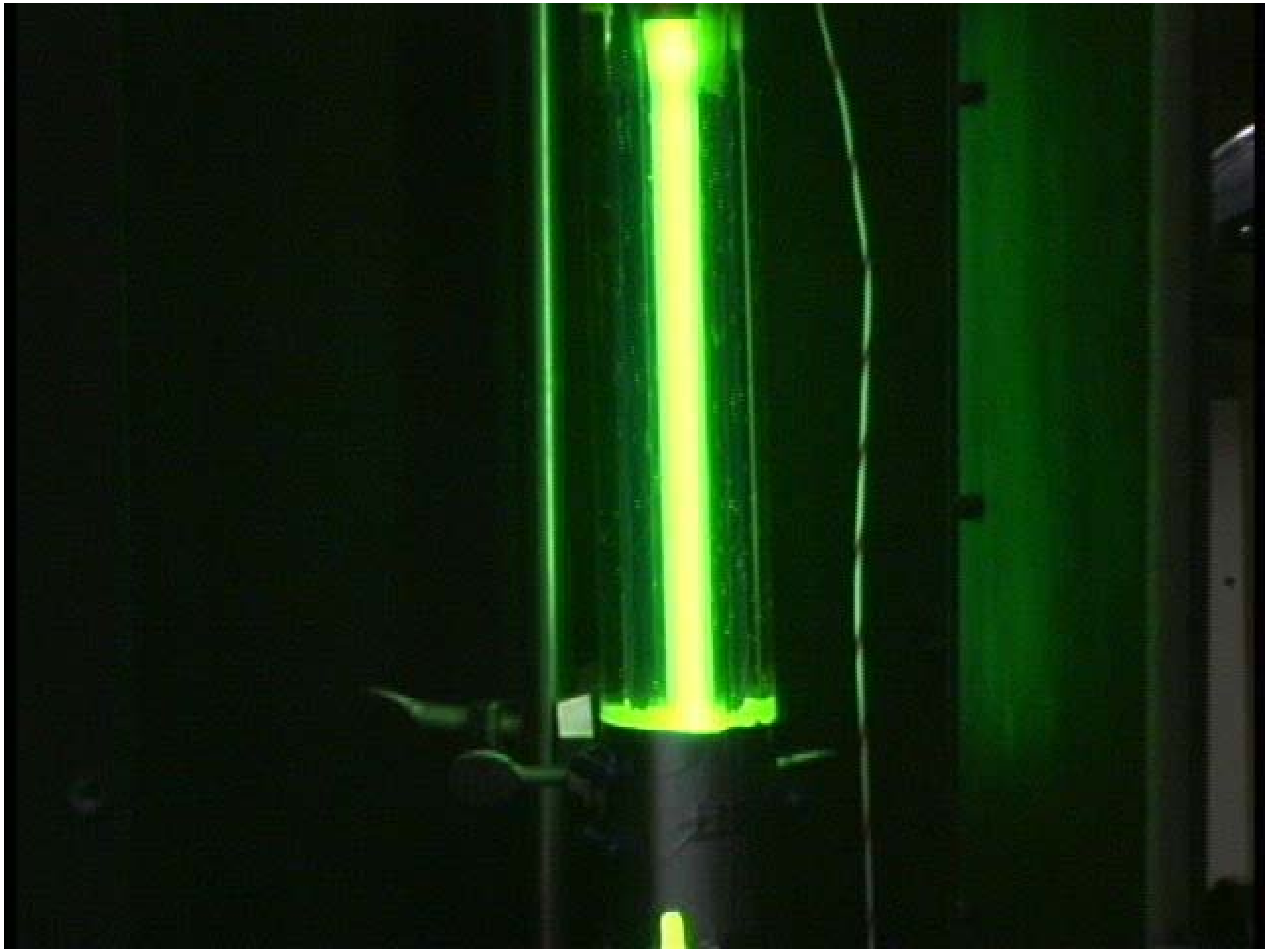
Experimental Setup for SO_2 Treatment



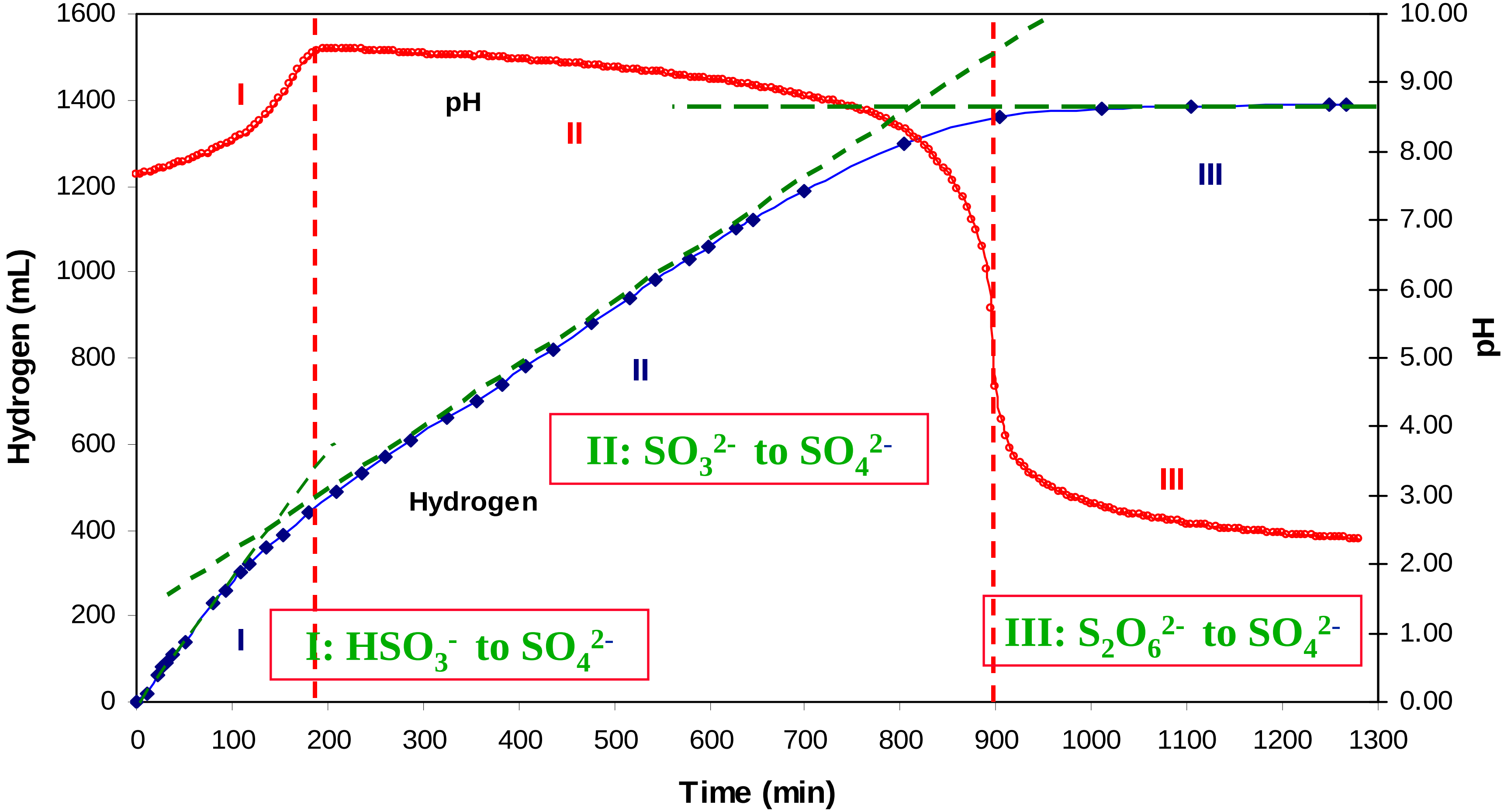
Exp. Setup for H_2 Production from Aqueous Na_2SO_3 Solution



Hydrogen Production



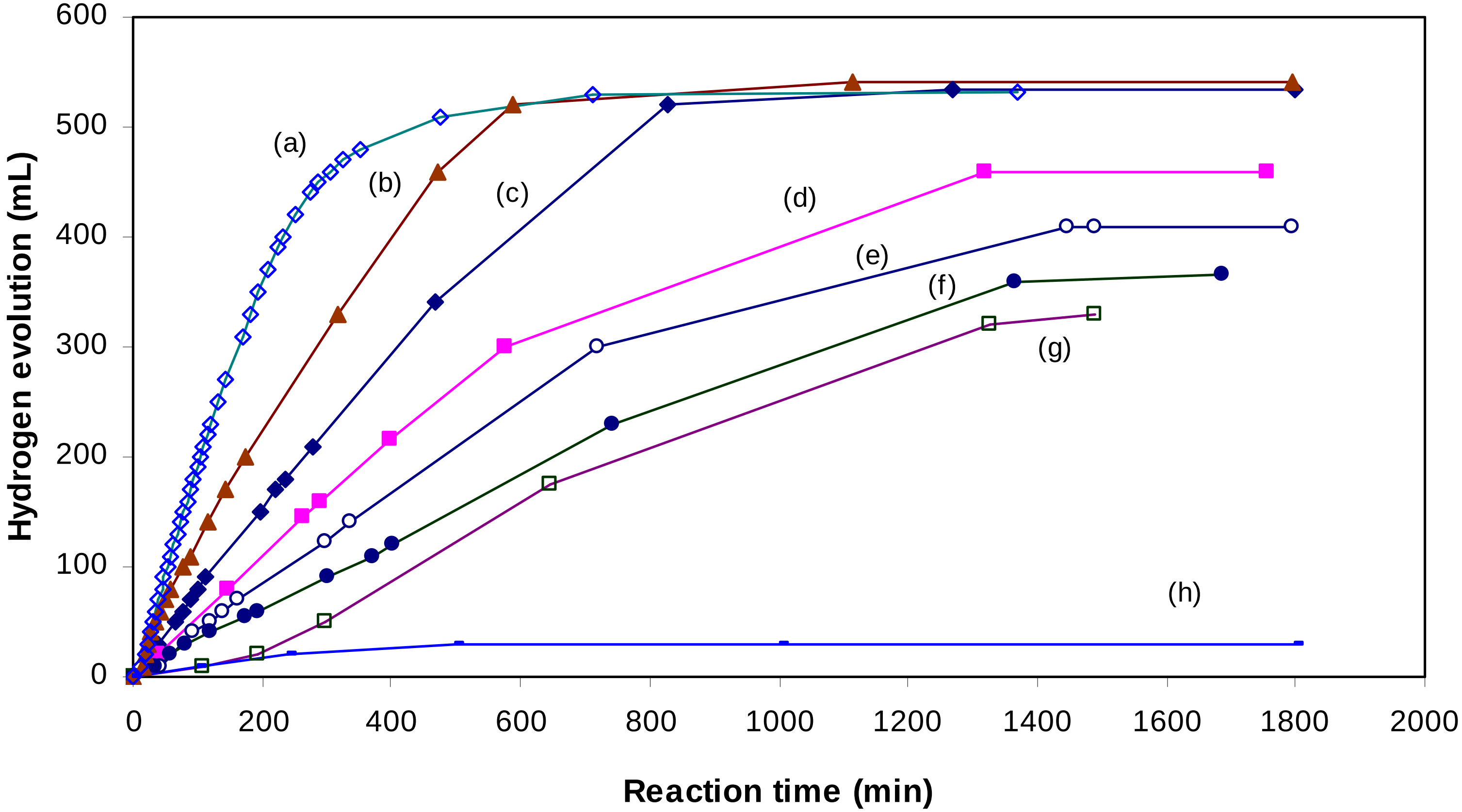
Kinetics of H_2 Production via Photo-oxidation of Na_2SO_3



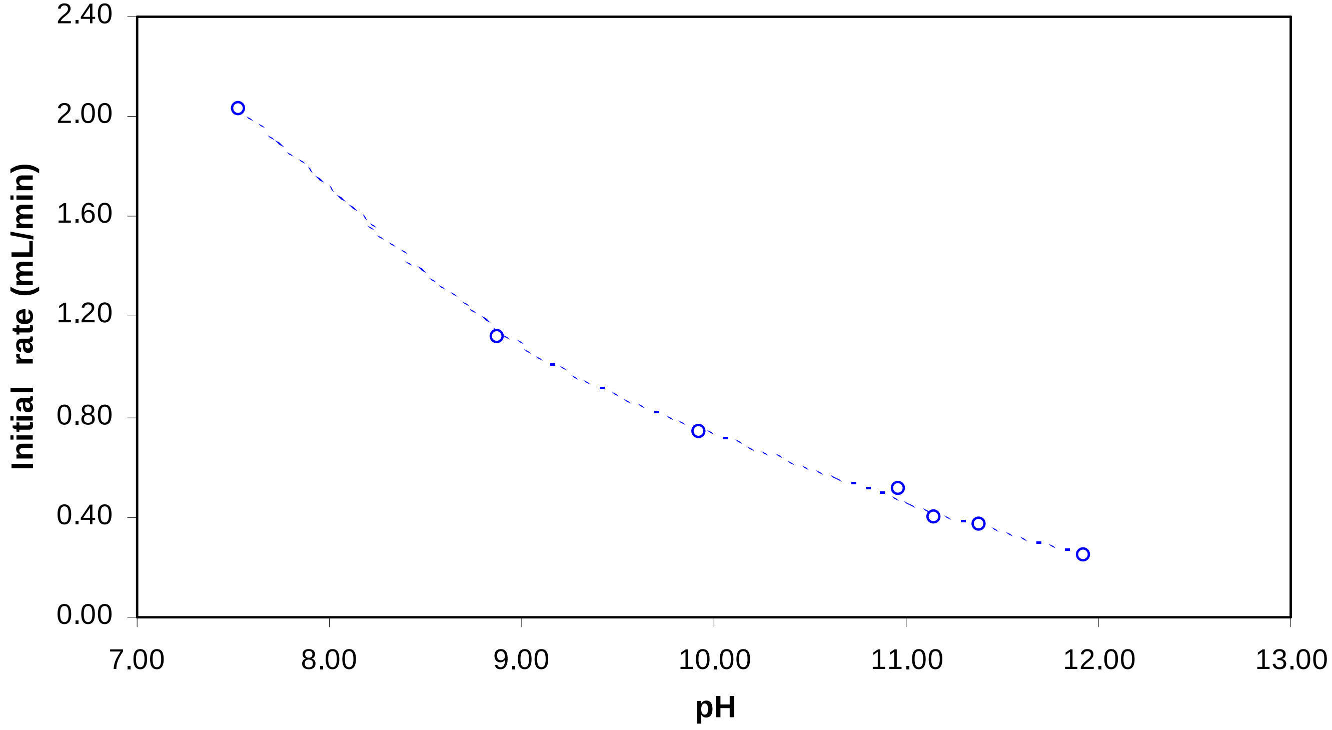
Material Balance

Ionic Species	Initial (mmol)	Final (mmol)	Diff. (mmol)
SO_3^{2-}	63.41	0.00	63.41
SO_4^{2-}	2.40	63.59	61.19
Gas Produced	**Theoretical (mL)**	**Exp. (mL)**	**Diff. (mL)**
H_2	1550	1390	160

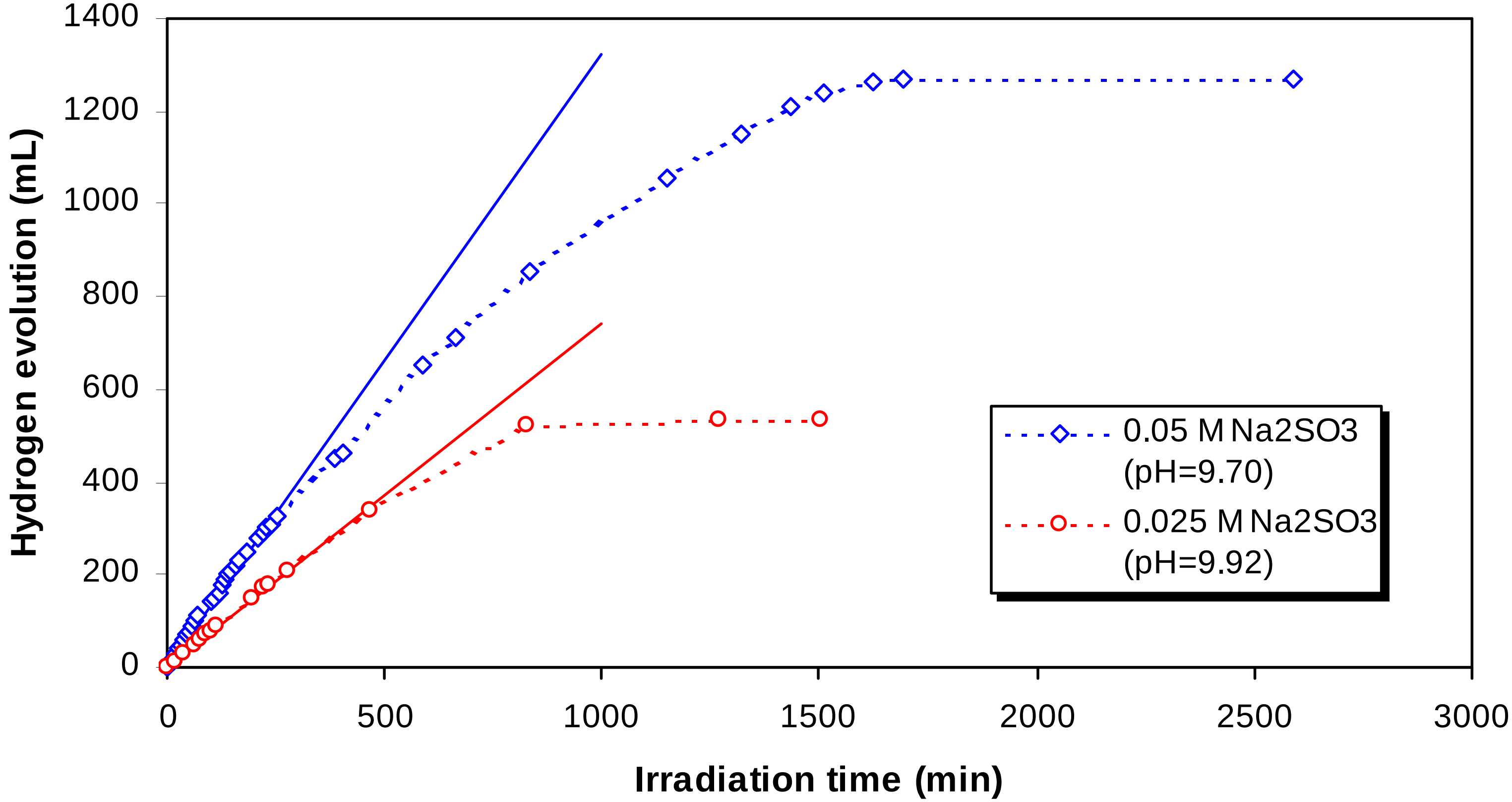
Effect of Solution pH on H_2 Production



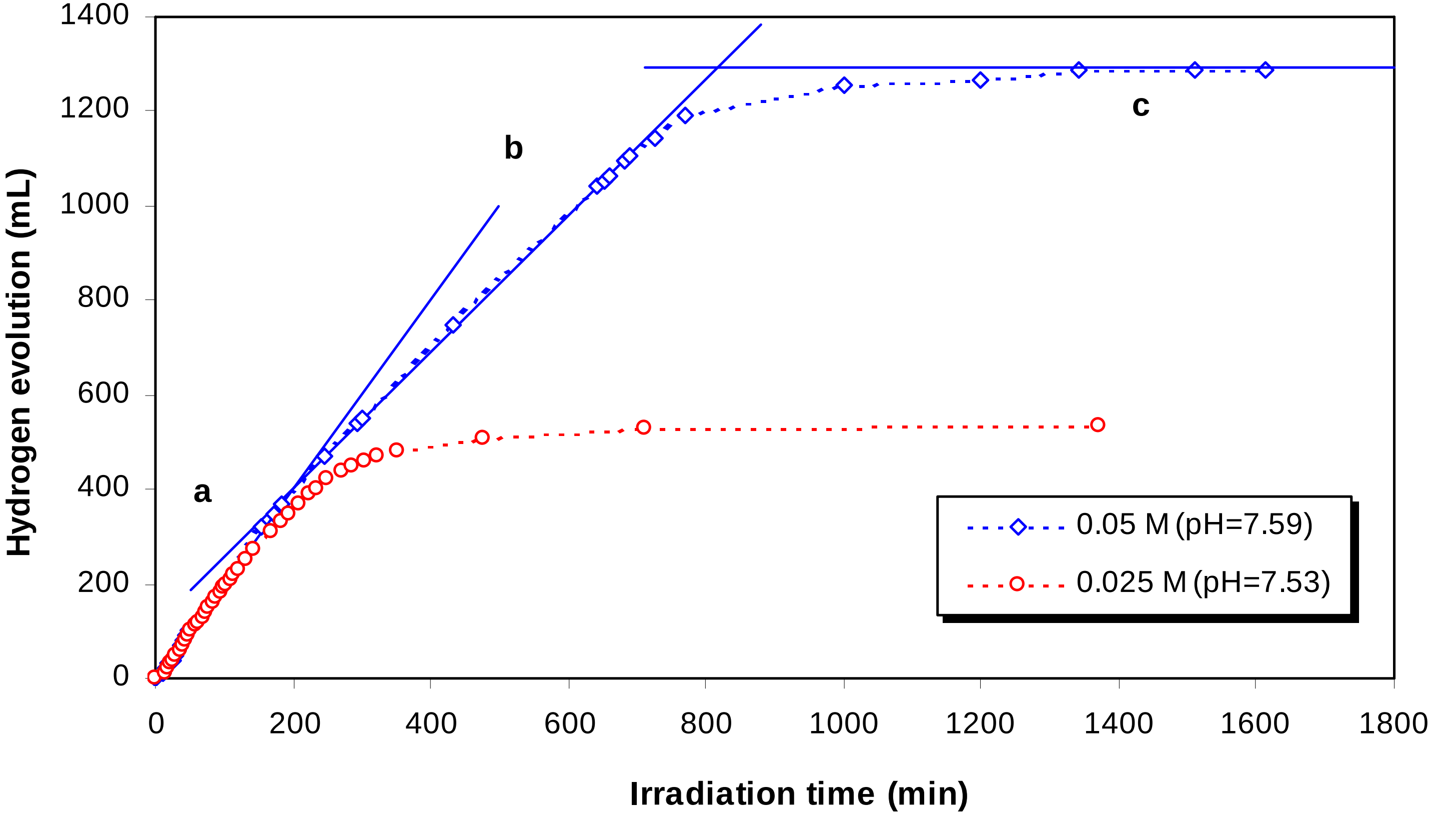
Effect of Solution pH on H_2 Production *(cont'd)*



Concentration Effect on H_2 Production Rate (at pH = 9.70)



Concentration Effect on H_2 Production Rate (at pH = 7.55)



Summary

Solution	Conc. 0.025 M	pH 9.92	Conc. 0.05 M	pH 9.70	Conc. 0.025 M	pH 7.53	Conc. 0.05 M	pH 7.59
H_2 prod rate	0.74 mL/min		1.40 mL/min		1.91 mL/min		1.91 mL/min	

At pH = 9.95, H_2 production rate increases with an increase in the concentration of the sulfite.
At pH = 7.55, H_2 production rate is independent of the sulfite concentration.

Conclusions

- A novel approach for utilizing SO_2 in flue gas for hydrogen production has been developed
- Photolytic H_2 production from aqueous Na_2SO_3 solutions is a clean and efficient process
- Experimental data indicate that SO_3^{2-} can be fully converted into SO_4^{2-}
- FSEC process requires no catalysts, reducing the process capital & operating costs.

Future Work

- Investigate effects of other flue gases (*e.g.* NO_x, CO_2) on the photolytic production of hydrogen
- Investigate effects of metal catalysts in enhancing the photolytic hydrogen production from SO_2
- Photoreactor design considerations
- Process design & optimization.

Acknowledgment

- National Aeronautics and Space Administration (NASA) - Glenn Research Center (GRC) under contract No. NAG3-2751.