

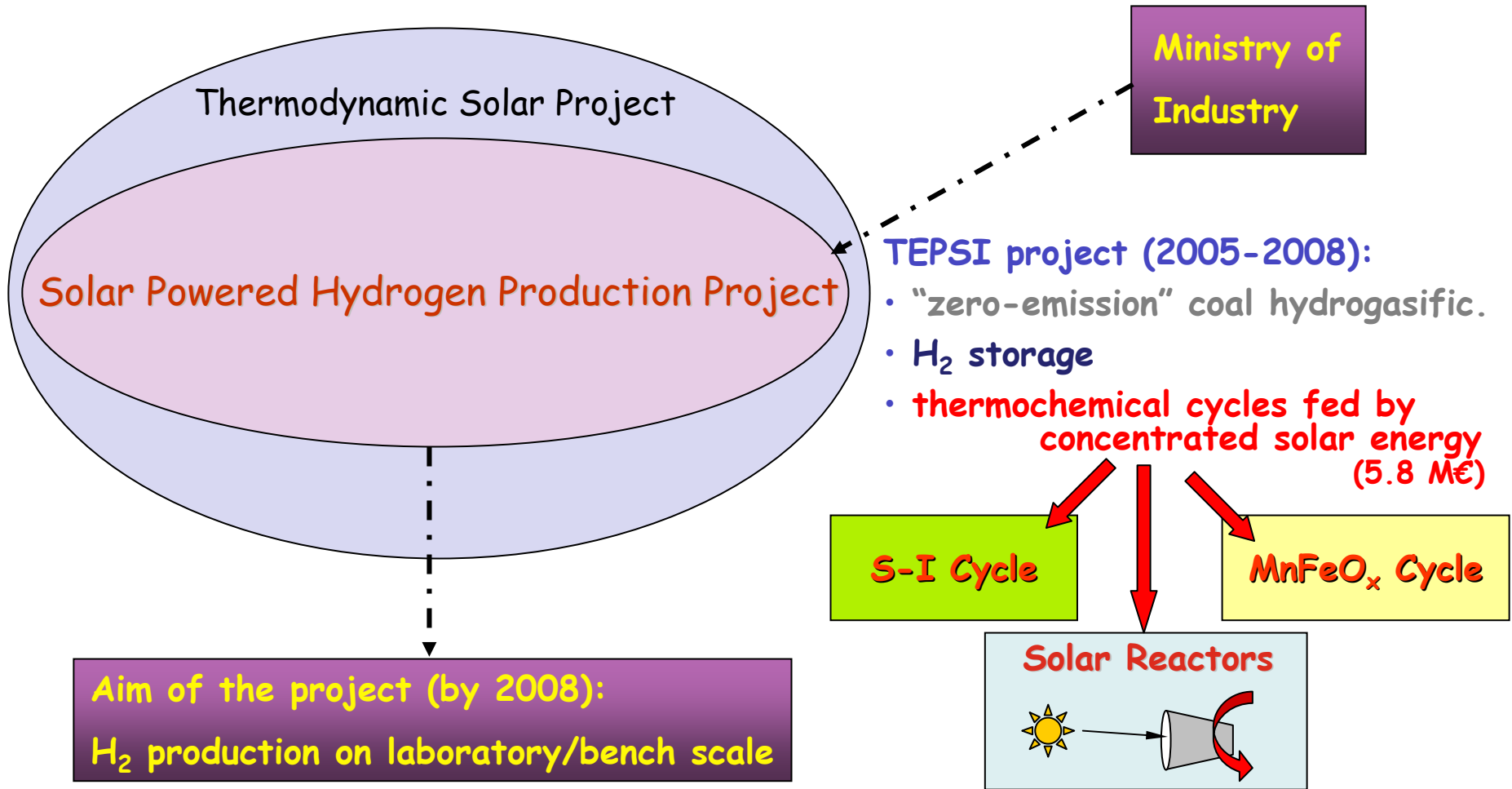
Experimental Study of the Bunsen Reaction for the S-I Thermochemical Cycle

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ENEA = Italian National Agency for New Technologies, Energy and the Environment



Research Context

TEPSI Project (2005-2008) *scientific feasibility demonstration*

targets	→ Production at laboratory scale	0.001 ÷ 0.01 m³ / h
	→ Bench production	0.05 ÷ 0.1 m³ / h

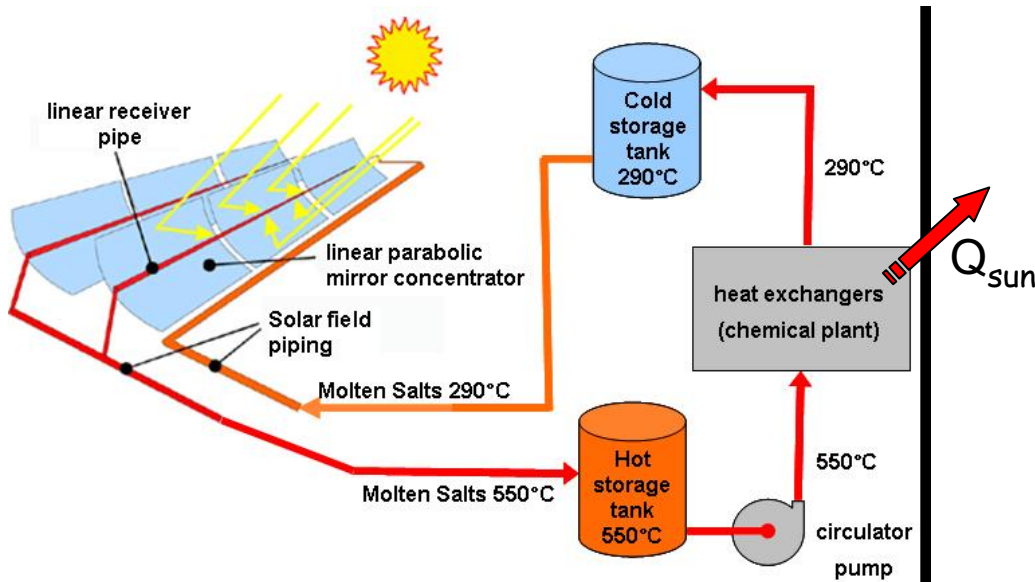
(demonstration of the complete process chemistry in an integrated laboratory scale flow loop)

future (2008-) *technological feasibility demonstration*

Pre pilot production	30 ÷ 90 m³ / h
(Design, fabrication and operation of an engineering demonstration loop)	
Pilot production	400 ÷ 800 m³ / h
(Design, fabrication and operation of a small hydrogen production demonstration plant)	

Research Context: the Thermodynamic Solar Project

- Solar collection technology: **parabolic trough**
- Energy Vector: **Molten Salts ($\text{NaNO}_3/\text{KNO}_3$ 60/40 w%)**
- Heat Storage: **1 kWh for 5 liters of molten salts (550-290°C)**
- Receiver pipe: **ENEA patent*** for coating
- Pilot plant: **located at ENEA Casaccia Research Center**



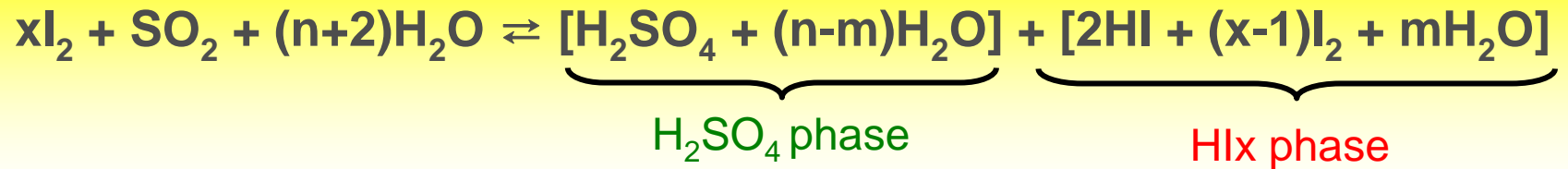
Casaccia Research Centre

* Rubbia C., Antonaia A., Esposito S. (ENEA) Surface Coating of the Collector Tube of a Linear Parabolic Solar Concentrator. Patent n° DE60202142D (2005)

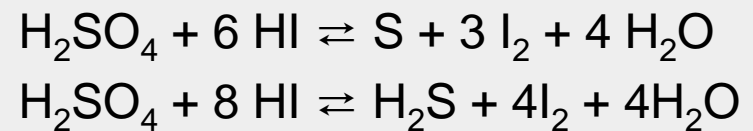
Content

- ✓ (Research Context (ENEA program))
- ✓ Work Schedule for the Bunsen Section Development
- ✓ Study of liq-liq phase behavior for $I_2/HI/H_2O/H_2SO_4$ mixtures:
 - Experimental set up, analytical techniques and procedures
 - Effect of I_2 content
 - Effect of water content
 - Effect of temperature
 - Conclusions & future steps

Bunsen Reaction - General Remarks



high I_2 excess needed to {
 enhance liq-liq phase separation
 avoid side reactions



Work Schedule for Bunsen Section

1. Preliminary study of product liq-liq mixtures (H_2SO_4/HI_x) phase behavior

2. Product (H_2SO_4 & HI) purification:

- I_2 and HI removal from H_2SO_4 phase
- H_2SO_4 removal from HI_x phase

3. Study of the effect of SO_2 pressure and excess on the Bunsen reaction

4. Fluid dynamics characterization of the HI_x phase for continuous flow operations

5. Design and set up of suitable methods for on-line analysis

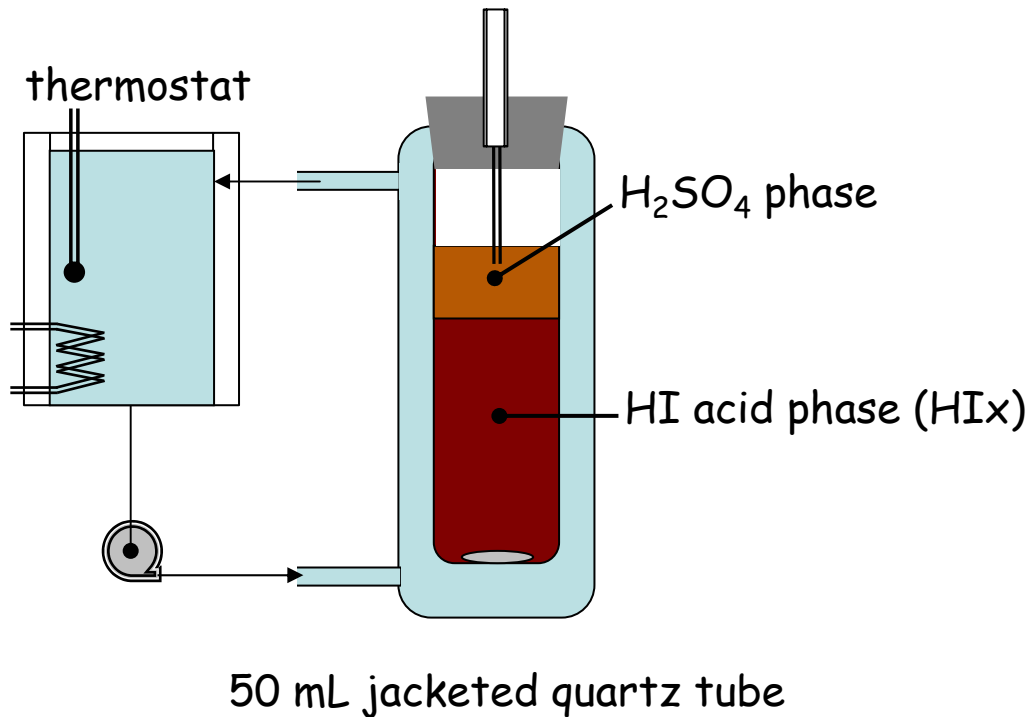
6. Continuous reactor design

7. Continuous-flow operation study

8. Coupling with the H_2SO_4 decomposer (integrated 2/3 S-I loop)

9. Study of viable options for the Bunsen reaction (electrochemical, solvent utilization)

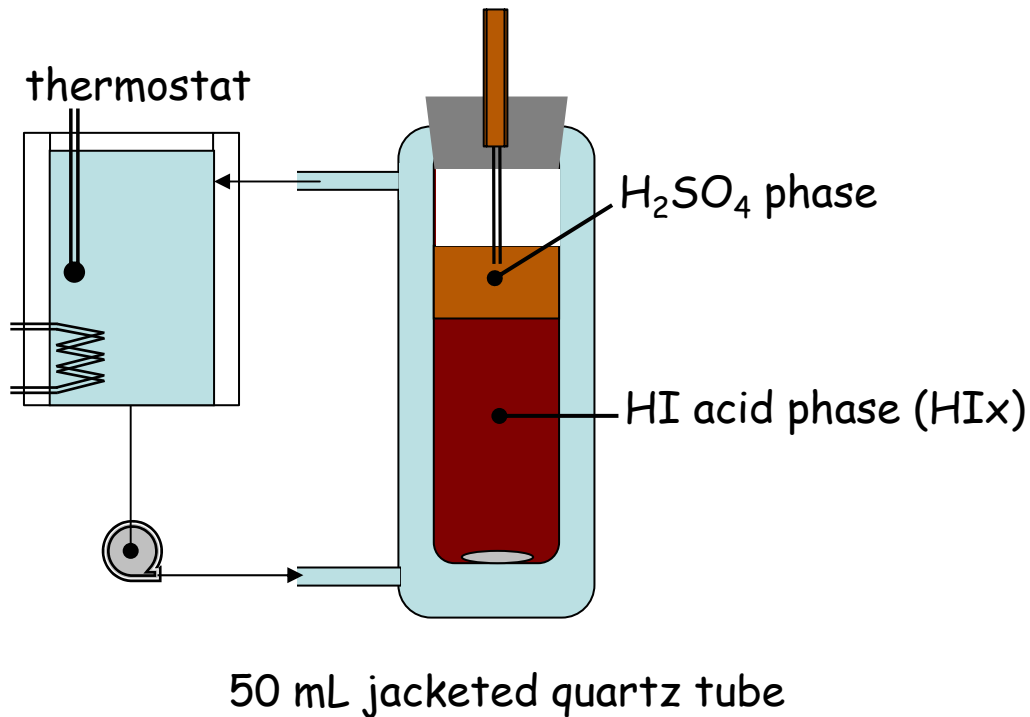
liq-liq phase behavior of $I_2/HI/H_2O/H_2SO_4$ mixtures: experimental set up



Procedure:

- 1) HI (57 wt.%) + I_2 addition;
- 2) Heating up to high enough T (I_2 dissolution);
- 3) H_2SO_4 & H_2O addition;
- 4) Intense mixing;
- 5) Rest (ca. 1 h);
- 6) Upper phase samplings and analyses:
 - a) Density det.;
 - b) I_2 det. by titration;
 - c) H_2SO_4 & HI det. by ionic chromatography;
- 7) Upper phase removal and lower phase density det.;
- 8) Sulfur formation determination.

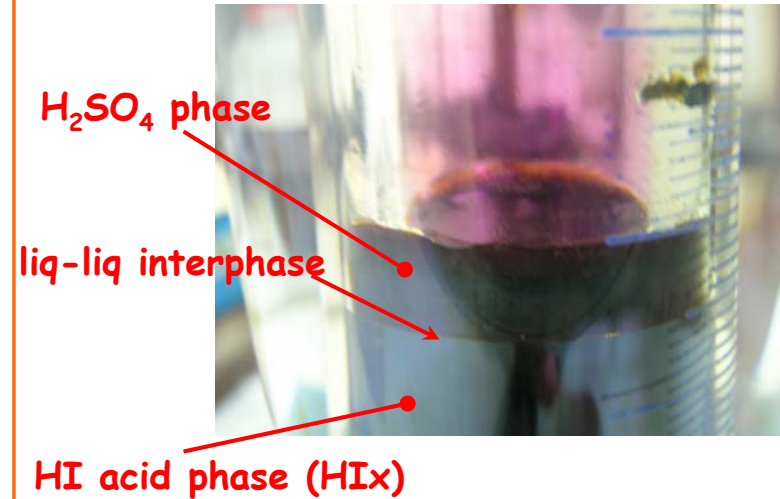
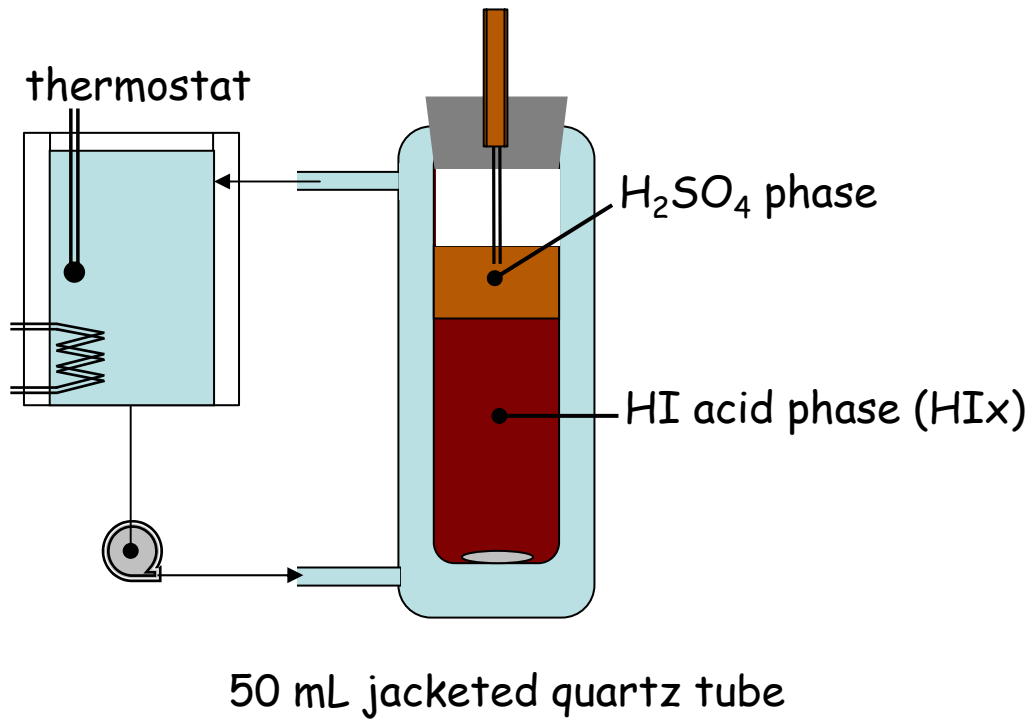
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liq-liq phase behavior of $I_2/HI/H_2O/H_2SO_4$ mixtures: experimental set up

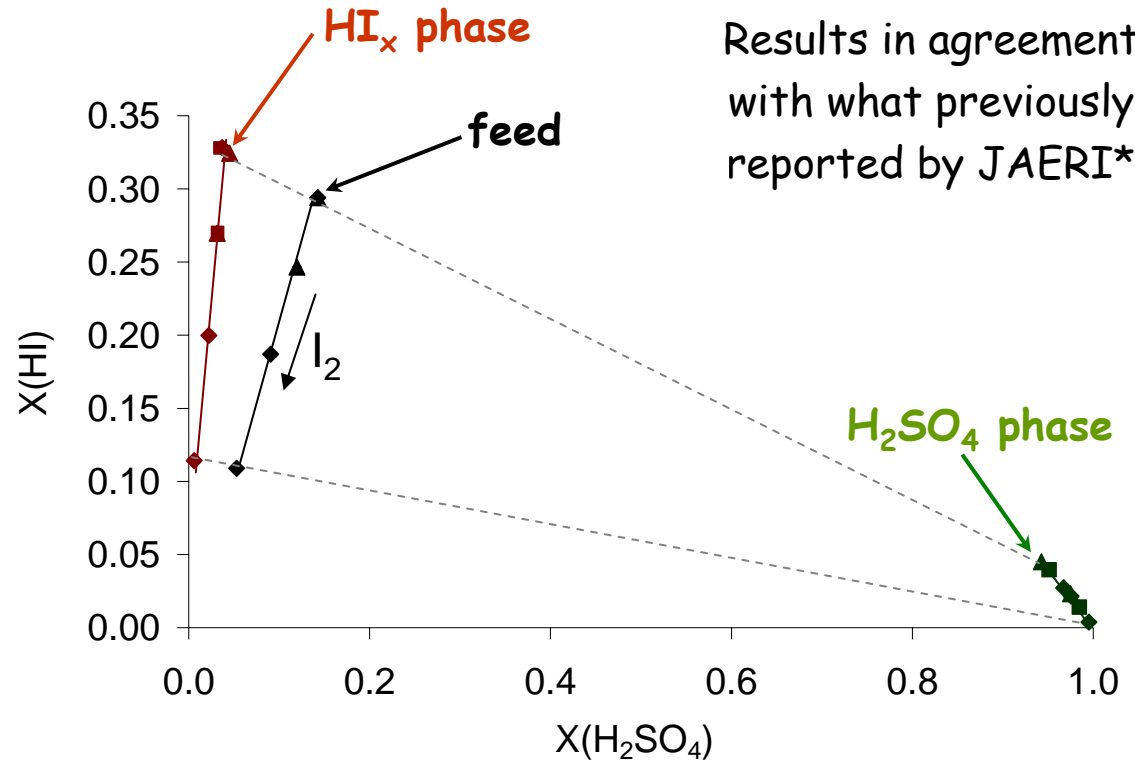


liq-liq phase behavior of $I_2/HI/H_2O/H_2SO_4$ mixtures

Results: effect of I_2 content

FEED ($HI/H_2SO_4 = 2/1$)

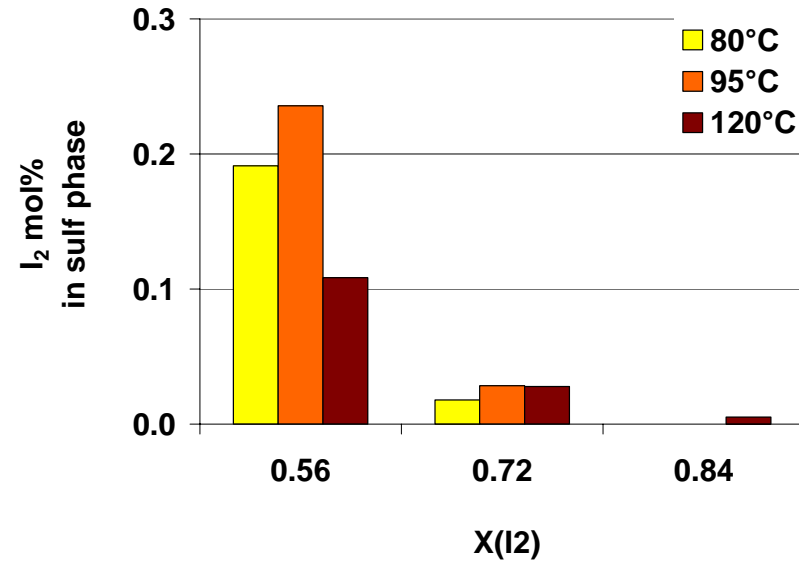
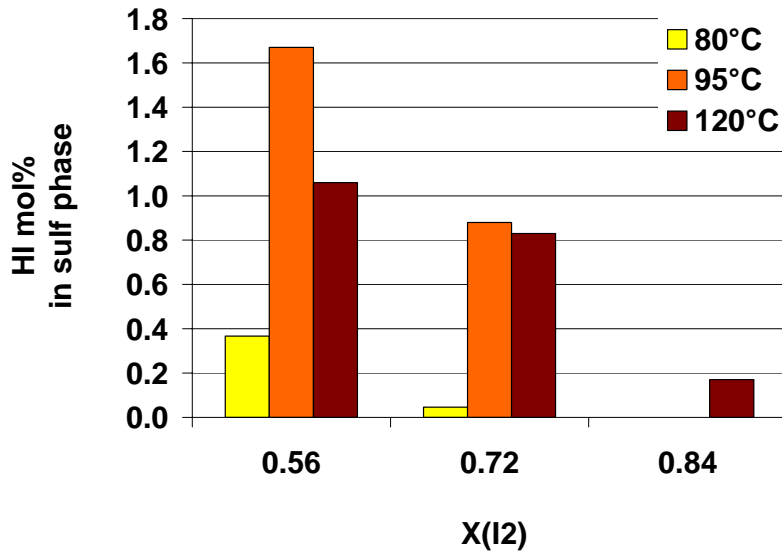
T (°C)	HI	H ₂ O	I ₂	H ₂ SO ₄
80 ■	0.09	0.69	0.17	0.04
	0.11	0.57	0.27	0.05
95 ▲	0.09	0.69	0.17	0.04
	0.11	0.57	0.27	0.05
120 ◆	0.11	0.61	0.22	0.05
	0.09	0.50	0.36	0.05
	0.07	0.37	0.53	0.03



* Sakurai M. et al. *Int. J. Hydrogen Energy*, 2000, 25, 605

liq-liq phase behavior of $I_2/HI/H_2O/H_2SO_4$ mixtures

Results: effect of I_2 content



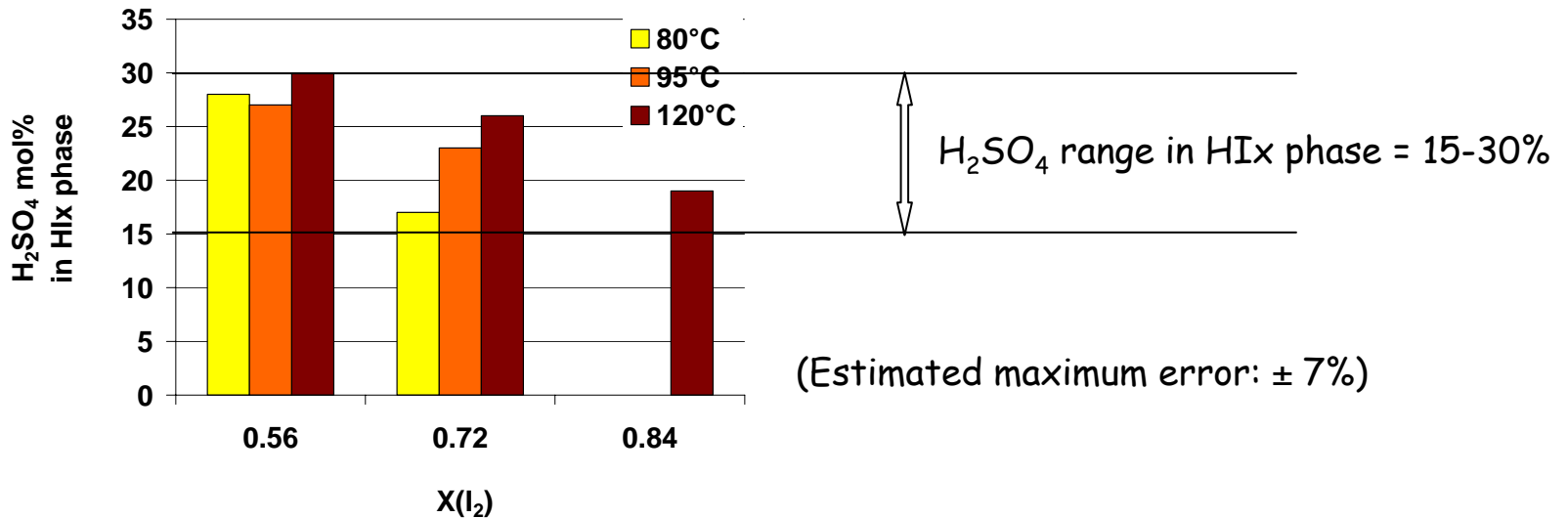
25-50%
increase I_2



- HI in Sulf. phase reduced from 5 to 0.4 mol_{HI/molH₂SO₄}%
(i.e. **ca. 1.7 to < 0.1 %HI_{tot}**)
- I₂ in Sulf. phase reduced from 1.3 to 0.1 mol_{I₂/molH₂SO₄}%
(i.e. **ca. 0.2 to < 0.02 %I_{2tot}**)

liq-liq phase behavior of $I_2/HI/H_2O/H_2SO_4$ mixtures

Results: effect of I_2 content



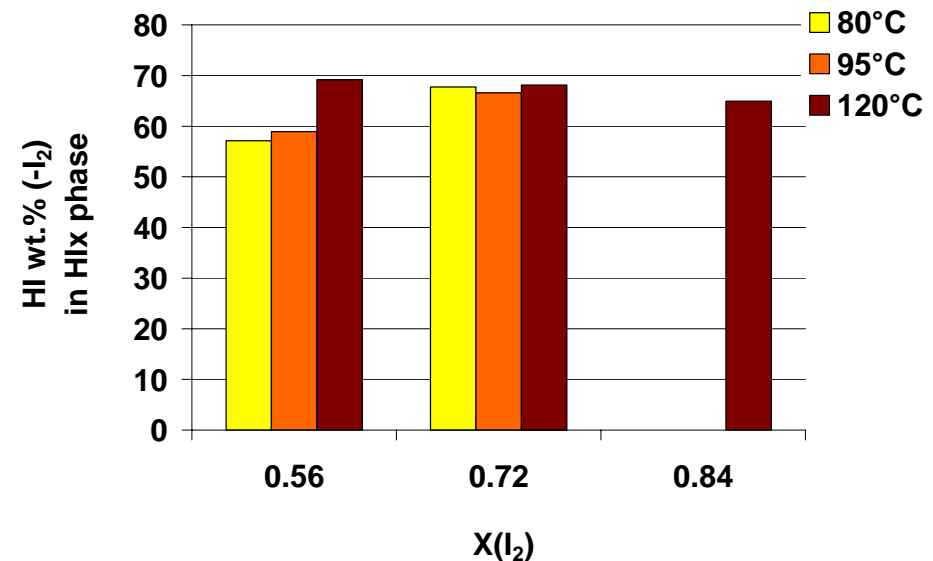
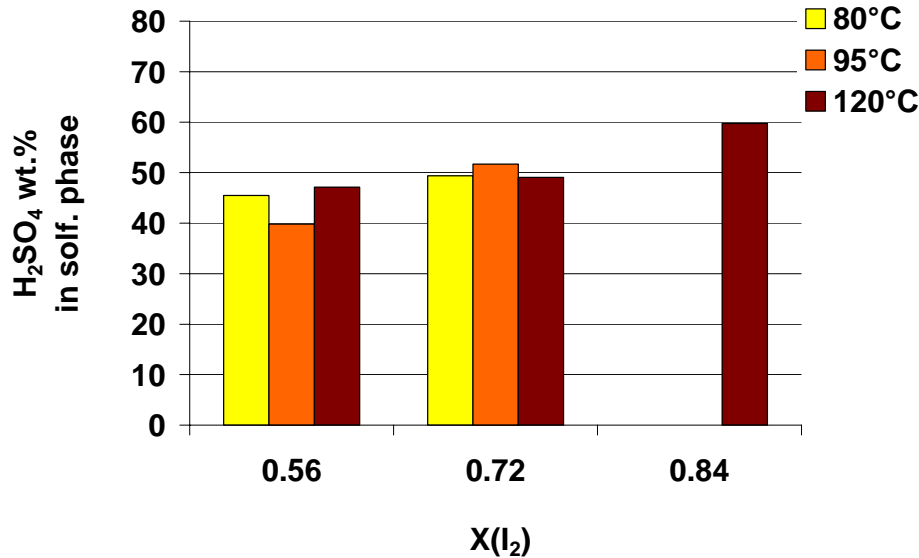
25-50%
increase I_2



- H_2SO_4 in HIx phase is in the 10-25 mol $_{H_2SO_4/molHI}$ % range (i.e. 15-30 % H_2SO_{4+tot}) with a very slight decrease
- H_2SO_4 in HIx phase reduces down to ca. 5 mol $_{H_2SO_4/molHI}$ % (i.e. < 20 % H_2SO_{4+tot}) only at the highest I_2 conc.

liq-liq phase behavior of $I_2/HI/H_2O/H_2SO_4$ mixtures

Results: effect of I_2 content



25-50%
increase I_2

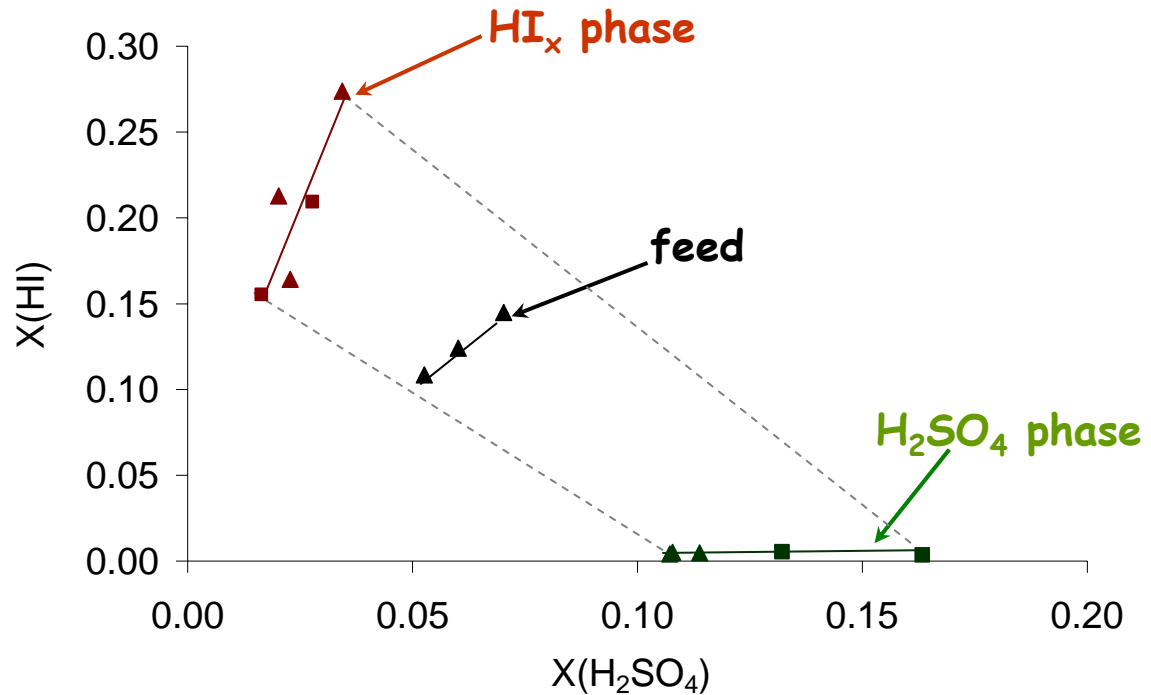


- H_2SO_4 conc. in Sulf. phase slightly increases
from 40 ca. to 60 wt%, density = 1.2-1.3 g/mL
- HI conc. in HIx phase is in the 57-69 wt% range
(relative to H_2O), density = 2.9-3.6 g/mL

liq-liq phase behavior of $I_2/HI/H_2O/H_2SO_4$ mixtures

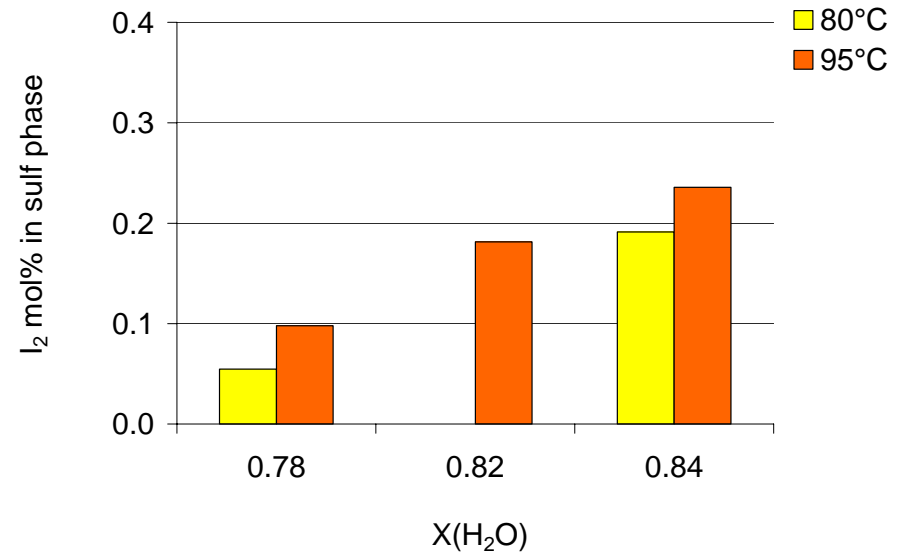
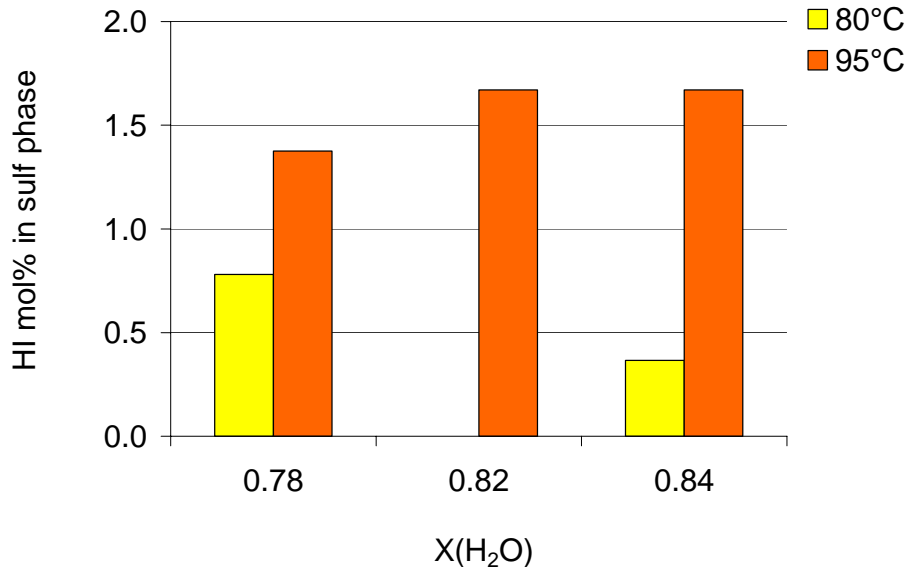
Results: effect of water content

FEED ($HI/H_2SO_4 = 2/1$)				
T (°C)	HI	H ₂ O	I ₂	H ₂ SO ₄
80 ■	0.11	0.61	0.22	0.05
	0.09	0.69	0.17	0.04
95 ▲	0.11	0.61	0.22	0.05
	0.10	0.66	0.19	0.05
	0.09	0.69	0.17	0.04



liq-liq phase behavior of $I_2/HI/H_2O/H_2SO_4$ mixtures

Results: effect of water content



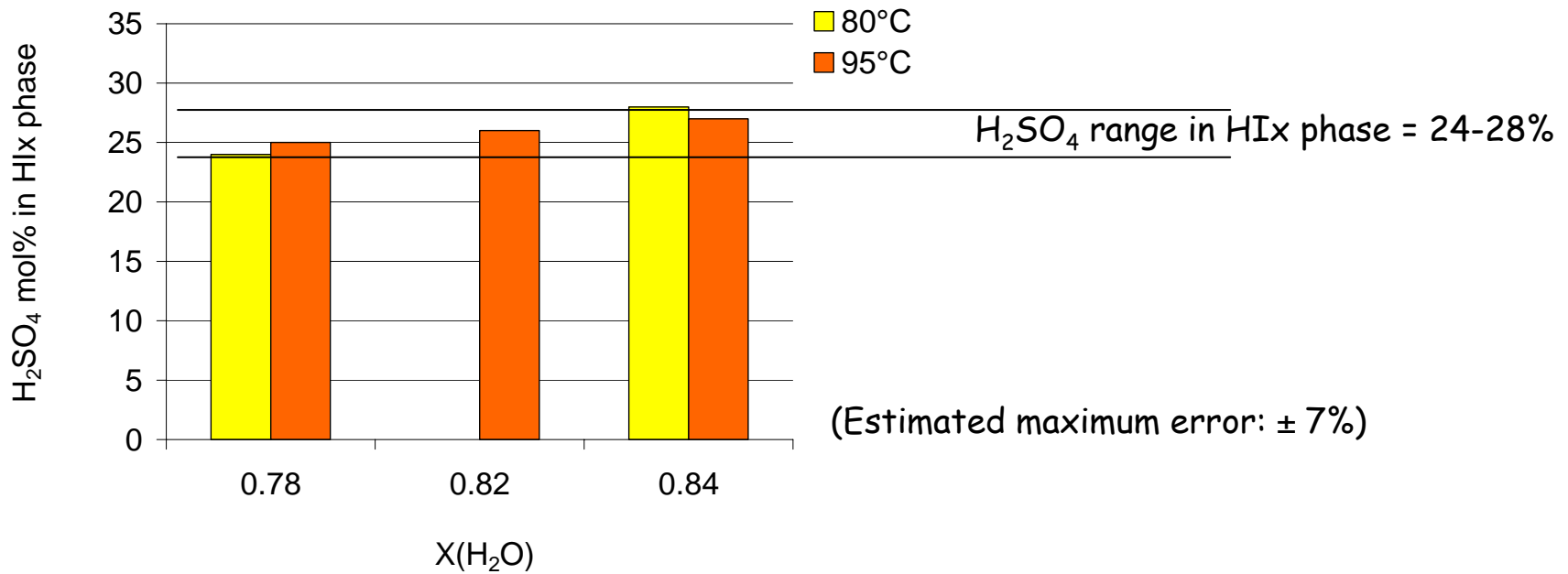
increasing
 H_2O conc.



- HI in Sulf. phase ranges from 2 to 5 mol_{HI/molH₂SO₄}% (i.e. **ca. 0.4 to 1.7 %HI_{tot}**), increasing with T
- I_2 in Sulf. phase increases from 0.3 to 1.3 mol_{I₂/molH₂SO₄}% (i.e. **ca. 0.1 to > 0.2 %I_{2tot}**), increasing with T

liq-liq phase behavior of $I_2/HI/H_2O/H_2SO_4$ mixtures

Results: effect of water content



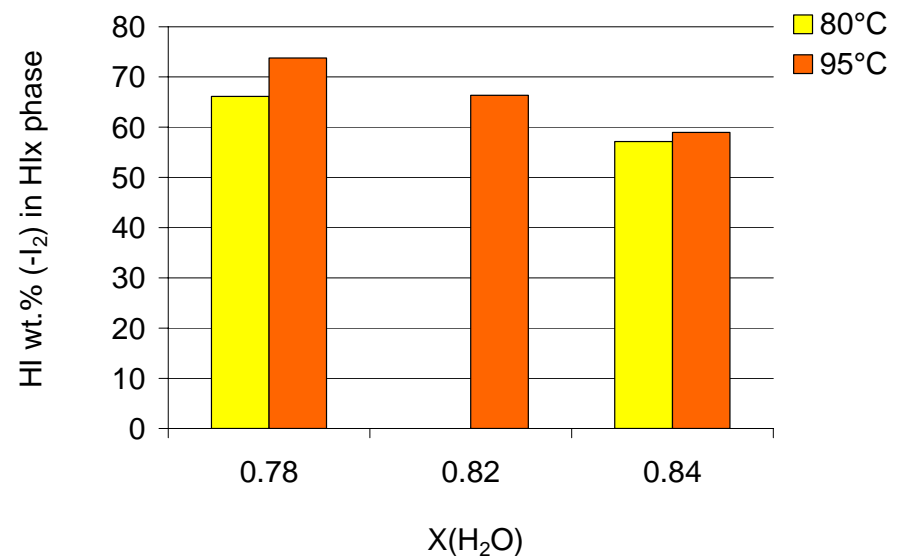
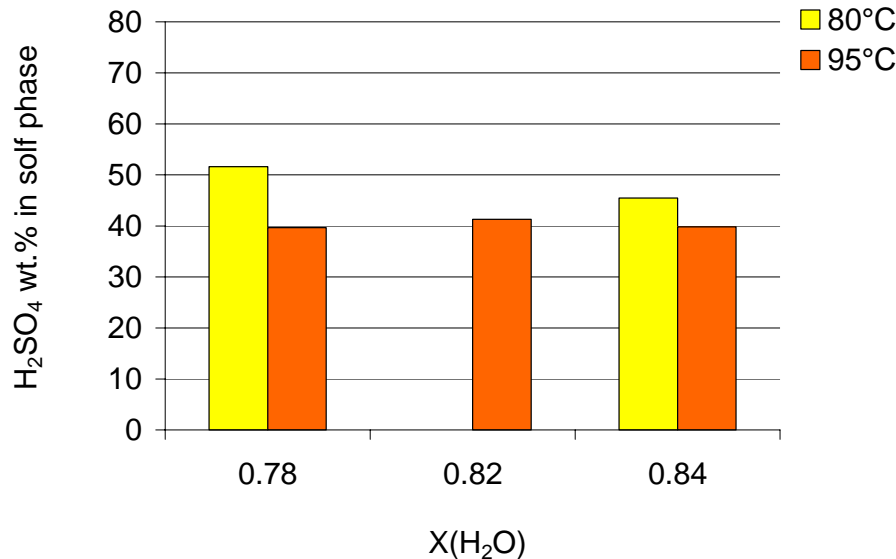
increasing
 H_2O conc.



• H_2SO_4 in HIx phase is in the 10-14 mol $_{H_2SO_4}$ /molHI% range (i.e. **24-28 % H_2SO_{4+tot}**) with a slight increase

liq-liq phase behavior of $I_2/HI/H_2O/H_2SO_4$ mixtures

Results: effect of water content



increasing
 H_2O conc. →

- H_2SO_4 conc. in Sulf. phase decreases
from 52 to 40 wt%, density = 1.2-1.4 g/mL
- HI conc. in HIx phase decreases from 74 to 57 wt%
(relative to H_2O), density = 2.9-3.2 g/mL

liq-liq phase behavior of $I_2/HI/H_2O/H_2SO_4$ mixtures

Results: effect of temperature and side reactions

- T has not a relevant effect, in the 80-120°C, on the concentration of both phases
- a slight increase of impurities (I_2 and HI) in sulf. phase observed by increasing T
- no side reaction occurrence (sulfur or H_2S formation) was observed provided that a proper H_2SO_4 addition procedure is followed

Conclusions

- **phase purity** is almost unaffected by I_2 content, T and water:
 I_2 and HI in sulfuric phase is always $< 2\%$, H_2SO_4 in HIx 15-30% of total
- **T and I_2 content have both little effect** on sulfuric and HIx phases concentration
- increasing water content **a dilution of both phases is observed** (as expected)
- T and I_2 content effect **in agreement with JAERI**
[Sakurai M. et al. *Int. J. Hydrogen Energy*, 2000, 25, 605]
- **secondary reactions were never observed** under the adopted conditions
- **best conditions:** $80^\circ C$, lowest water content (e.g. HI/ H_2O / I_2 / H_2SO_4 = 0.11/0.61/0.22/0.05)

Near Future Steps

- (More precise measurements in wider ranges of conditions to get reliable data for **process modeling**)
- Investigation of **phase purification options** for both products streams (sulfuric and HI acids)
- Study of the **effect of pressure** (SO_2 concentration)
- **Continuous-flow operation** for the Bunsen reactor
- **Continuous-flow operation** for the **Bunsen reactor integrated with the separation/concentration units and the sulfuric acid decomposer**

Thank You!