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COVER PAGE

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The Sulfur-Iodine Cycle: Process Analysis and Design Using Comprehensive Phase Equilibrium Measurements and Modeling

Executive Summary

Of the 100+ thermochemical hydrogen cycles that have been proposed, the Sulfur-Iodine (S-I) Cycle is a primary target of international interest for the centralized production of hydrogen from nuclear power. However, the cycle involves complex and highly nonideal phase behavior at extreme conditions that is only beginning to be understood and modeled for process simulation. The consequence is that current designs and efficiency projections have large uncertainties, as they are based on incomplete data that must be extrapolated from property models. This situation prevents reliable assessment of the potential viability of the system and, even more, a basis for efficient process design.

The goal of this NERI award (05-006) was to generate phase-equilibrium data, property models, and comprehensive process simulations so that an accurate evaluation of the S-I Cycle could be made. Our focus was on Section III of the Cycle, where the hydrogen is produced by decomposition of hydroiodic acid (HI) in the presence of water and iodine (I_2) in a reactive distillation (RD) column. The results of this project were to be transferred to the nuclear hydrogen community in the form of reliable flowsheet models for the S-I process.

Many of the project objectives were achieved. At Clemson University, a unique, tantalum-based, phase-equilibrium apparatus incorporating a view cell was designed and constructed for measuring fluid-phase equilibria for mixtures of iodine, HI, and water (known as HIx) at temperatures to 350 °C and pressures to 100 bar. Such measurements were of particular interest for developing a working understanding of the expected operation of the RD column in Section III. The view cell allowed for the IR observation and discernment of vapor-liquid (VL), liquid-liquid, and liquid-liquid-vapor (LLVE) equilibria for HIx systems. For the I_2-H_2O system, liquid-liquid equilibrium (LLE) was discovered to exist at temperatures up to 310-315 °C, in contrast to the models and predictions of earlier workers. For the I_2-HI-H_2O ternary, LLE and LLVE were all observed for the first time at temperatures of 160 and 200 °C. Three LLE tie-lines were measured at 160 °C, and preliminary indications are that the underlying phase behavior could result in further improvements in the performance of the S-I Cycle. Unfortunately, these new results were obtained too late in the project to be incorporated into the modeling and simulation work described below.

At the University of Virginia, a uniquely complete and reliable model was developed for the thermodynamic properties of HIx, covering the range of conditions expected for the separation of product hydrogen and recycled iodine in the RD column located in Section III. The model was validated with all available property spectroscopy data. The results provide major advances over prior understanding of the chemical speciation involved. The model was implemented in process simulation studies of the S-I Cycle, which showed improvement in energy efficiency to 42%, as well as significantly smaller capital requirements due to lower pressure operation and much smaller equipment sizes. The result is that the S-I Cycle may be much more economically feasible than was previously thought. If both the experimental and modeling work described above were to be continued to ultimate process optimization, both the American public and the global community would benefit from this alternative energy source that does not produce carbon emissions.

Comparison of Actual Accomplishments with Goals and Objectives

Comparisons can be done with the Milestone Status Table listing as follows:

Milestone Status Table:

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
1	Design and order Ta view cell for CFA; begin analytical methods dev. (AMD)	7/05	10/05	
2	Assemble CFA with new components; T and P calibration	10/05	6/06	Reproduced benzene-H_2O binary at 200-250 °C
3	Test CFA with dilute I_2-H_2O system; complete AMD; pass safety review	1/06	6/06	
4	LLE data for I_2-H_2O to 300 °C; selected HI-H_2O VLE data; (deliverables)	4/06	6/08	I_2-H_2O LLE observed up to 300C&100bar; deleted HI-H_2O work per modeling team rec.
5.1	Begin ternary VLE or LLE measurements (per modeling team recommendations)	7/06	8/08	Ternary LLE/LLVE began 8/08
5.2	Install *in situ* spectrometer; complete first ternary diagram (deliverable)	10/06	--	Insufficient resources to build spectrometer
5.3	Generate one ternary/3mo (at T, P, z per modeling team recommendations)	4/08	9/09	Ternaries for HIx at 160 and 200 °C.
6	Publish experimental data; write final report (deliverables)	4/08	12/09	1st paper publ. in *Int. J. Hydrogen Energy*; 2nd paper 3/10; M.S. Thesis of S. E. Mena 5/10.
7.1	Complete literature survey	6/05	6/05	
7.2	Complete initial recommendations for VLE, VLLE experiments	8/05	7/05	Earlier I_2-H_2O measure. Recommended
7.3	Develop full initial Aspen Plus™ properties model for Bunsen reaction	9/05	--	Initial study showed insuff. data to complete this model
7.4	Develop full initial Aspen Plus™ properties model for HI decomposition	12/05	12/08	
7.5	Publish "best estimate" properties models (deliverable)	4/06	--	Only final model was published (in *Fluid Phase Equilibria* (*FPE*)
8.1	Complete final recommendations for VLE, VLLE experiments	7/07	12/08	
8.2	Develop full final Aspen Plus™ properties models	10/07	6/09	Descr. in PhD Thesis of J. E. Murphy (UVa)
8.3	Publish final properties models (deliverable)	4/08	12/09	Publ. in *FPE*
9.1	Set initial flowsheet requirements for phys. props. to help guide exptl. measurements	7/05	7/05	Earlier I_2-H_2O measure. rec.; LL phase envelope for low-HI ternary rec.
9.2	Develop initial Aspen Plus™ models for Bunsen reaction section	11/05	1/06	Published in DOE report

ID Number	Task / Milestone Description	Planned Completion	Actual Completion	Comments
9.3	Develop initial Aspen Plus™ models for HI decomposition section	2/06	1/06	
9.4	Develop initial Aspen Plus™ flowsheet models for S-I cycle	7/06	--	Insufficient resources to complete full process model
9.5	Publish "best estimate" flowsheet models (deliverable)	10/06	6/07	
10.1	Set final flowsheet operating ranges for phys. props., experimental measurements	6/07	3/09	
10.2	Develop final Aspen Plus™ process unit models	12/07	3/09	
10.3	Develop final Aspen Plus™ flowsheet models for S-I cycle	2/08	--	Process model not possible w/o Prop. Models
10.4	Publish final flowsheet models (deliverable)	4/08	Expected 6/10	Descr. in PhD Thesis of J. E. Murphy

Comparisons can also be made from proposed goals and corresponding accomplishments:

Focus Area 1. Experimental.

Proposal: We propose that a windowed, continuous-flow apparatus be used to measure temperatures, pressures, and equilibrium-phase compositions for the HI-I_2-H_2O system. Corrosion studies carried out by General Atomics (GA) for the HI-I_2-H_2O system make it clear that many parts of our existing flow apparatus will need re-designing or replacing.
Accomplishments: A continuous-flow apparatus, with wetted parts fabricated from tantalum-tungsten alloys, was designed and constructed for the highly corrosive conditions of this work. A central feature of the apparatus is the equilibrium view cell, which allows for the observation and discernment of vapor-liquid, liquid-liquid, and liquid-liquid-vapor equilibria for HIx systems.

Proposal: LLE measurements for the two binaries with water will also be made as necessary…
Accomplishments: For the I_2-H_2O system, LLE was observed at temperatures and pressures to 300 °C and 104 bar. For the HI-H_2O system, the project team decided that such measurements were less relevant to Section III.

Proposal: We propose to take the first-ever comprehensive phase equilibrium (VLE and LLE) measurements for the HI-I_2-H_2O system at conditions relevant to the S-I cycle, and to directly detect the presence of I_x species.
Accomplishments: For the I_2-HI-H_2O ternary, VLE, LLE, and LLVE were all observed at 160 and 200 °C; the phase-boundary location for the water-rich side of the LLE region was determined; and three equilibrium tie-line compositions on the LLE phase envelope were measured at 160 °C. Resources were insufficient for the design and construction of a high-temperature, high-pressure spectroscopic device for the *in-situ* detection of I_x species.

Focus Areas 2 and 3. Properties and Process (Flowsheet) Modeling.

Proposal: We propose to develop the capability to fully explore process flowsheets for the synthesis and analysis of optimal S-I cycles.

Accomplishments: The capability to create and implement property and process models for the S-I Cycle was developed.

Proposal: The proposed work on these [H_2SO_4 and Bunsen] sections will initially (1) examine how well existing models describe any new data and (2) do sensitivity analyses (i.e., study responses of the results to small variations in parameters and conditions) to find which aspects of the models and code most strongly impact computational efficiency and transferability to alternative process configurations.

Accomplishments: There were no new published data to challenge the accuracy of the existing models. An analysis of the H_2SO_4 and Bunsen sections was published in a report to DOE in Dec. 2007. There was insufficient time to complete the sensitivity analyses for these sections.

Proposal: We will do sensitivity studies to learn the responses of properties to changes in parameters, species (in particular, the differences when Ix species are included) and conditions, especially of the VLE and LLE behavior, of the HI-I_2-H_2O system. Also, any new models needed for simulating process alternatives below will be developed. . . . When new data become available, reformulation and parameter redetermination will lead to optimal properties models.

Accomplishments: Although data from our team did not appear until late in the project, other laboratories published new VLE results, which allowed development of the required new models. This allowed sensitivity studies relative to experiment with these models.

Proposal: The proposed work is intended to eliminate this ambiguity with comprehensive data and better modeling. For process modeling, we have developed new techniques for more robust simulation convergence that will be implemented and evaluated. Upon their completion and validation, all computational improvements will be disseminated to the nuclear hydrogen process development community. To demonstrate transferability to alternative processes, we will simulate a version of the GA flowsheet with reactive distillation of HI; a GA version with reactive distillation replaced with phosphoric acid extraction; and the Japan Atomic Energy Research Institute (JAERI) process, which uses an electroelectrodialysis cell and a membrane reactor.

Accomplishments: A fully convergent and robust simulation program was completed and is in the process of being disseminated. There was insufficient time to complete simulation modeling of the alternative phosphoric acid and JAERI processes. It is believed that the optimal reactive distillation process of the current work is considerably more efficient than these alternatives.

Summary of Project Activities

Original hypothesis: The S-I cycle is a primary target of international interest for the centralized production of hydrogen from nuclear power. Of the 100+ thermochemical hydrogen cycles that have been proposed, the S-I cycle, originated by General Atomics (GA), is expected to become a major source of centralized hydrogen production from nuclear power. However, the S-I cycle, and its many proposed variations, all involve complex, highly nonideal phase behavior and reactions, and none have ever been operated at design temperatures and pressures. Many of the performance projections use semi-empirical property models, often based on extrapolation of uncertain and incomplete data. Thus, thermodynamic measurements and physical property models for this system have been identified as a basic research need for the Hydrogen Economy. Only with reliable data, along with carefully constructed property and process models that correctly describe the process, will the true potential of the S-I cycle be unlocked.

Approaches Used: The proposed approach was to take the first-ever comprehensive phase equilibrium (VLE and LLE) measurements for the HI-I_2-H_2O system at conditions relevant to the S-I cycle. Binary LLE measurements were also planned as necessary to ensure the accuracy of ternary measurements and modeling. Operating conditions for the experimental measurements were to be selected in concert with input from properties and process (i.e., flowsheet) modeling in order to maximize project efficiency. Then, as new experimental results were obtained, re-evaluation of the property models was to be carried out. The revised models were then to be provided for process modeling of S-I process alternatives. Finally, the results of process modeling were to be fed back to the experimental and modeling efforts, where any necessary adjustments to the research effort would be made.

Experimental. From an experimental standpoint, by the end of this project a unique, reliably operating, continuous-flow apparatus incorporating a view cell had been successfully designed and constructed for measuring the fluid-phase equilibria of interest [Publ 1]. However, first significant technical obstacles had to be overcome. Primary among these was the development of in-house expertise for the design and fabrication of equipment and components made from tantalum and its tungsten alloys (e.g., a view cell, a molten I_2 syringe pump (assisted by GA), valves, and fittings), as such expertise was either not available or exorbitantly expensive. Nevertheless, in the end we did follow the originally proposed approach. Thus, binary LLE measurements for the I_2-H_2O system were made at temperatures and pressures up to 300 °C and 100 bar, conditions meeting or even exceeding those that would exist in the RD column of Section III. Based on recommendations from our properties/process modeling team, binary measurements for HI-H_2O were deleted from consideration, and experimental efforts focused on the ternary HI-I_2-H_2O system, in the low-HI region where LLE and LLVE could exist. Unfortunately, because of the technical obstacles described above, the desired LLE measurements were not initiated until the final year of the project. Thus, at the time that project funds had been expended, experimental runs had not yet exceeded 225 °C, and only a few LLE compositions had been measured. However, even these few LLE results revealed new, unexpected phase behavior that could have a significant positive impact on RD column operation [Publ 4]. Unfortunately, no time was left in the project to incorporate these results into the properties model and simulation work, which is described below.

Properties and Process Modeling. From a properties and process (flowsheet) modeling standpoint, the approach used was to (1) gather all available, relevant data from the literature; (2) attempt to create a computer process flowsheet for Section I, which had not yet been achieved; (3) carry out a fundamental thermodynamic analysis of the efficiency limits, as well as the effects of irreversibilities on the S-I Cycle; (4) propose new chemical speciation reactions for Section III, where hydrogen is recovered by reactive distillation of the HIx feed, with recycle to Section I; (5) develop a thermodynamic properties model for integration into a new process flowsheet; (6) manually optimize the conditions of Section III; and (7) develop collaborations that would lead to full optimization.

In the properties/process modeling approach, the expectation was that new data for the HIx system would become available from the experimental members of the project (see above) in a timely manner. However, this was not realized. Fortunately, other laboratories (notably in France) published some VLE data that could be used to validate the proposed model speciation with only some delay, but none of the more difficult to model LLE data was available. In the end, LLE data measured by our project team (see above) not available in the literature did assist us in completing the model validation for liquid-liquid immiscibility conditions in the RD column of Section III.

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Conclusions. The ternary LLE compositions obtained at the end of this project are given as Figure 1 below, where comparison with our model is also made. Clearly, the three tie lines obtained are in significant disagreement to model predictions, with the slopes of the tie lines (and thus selectivities and distribution coefficients) being dramatically different. But recall that the model was developed using only VLE data, as our LLE data was at that time unavailable. The chemical species present in a H_2O-rich liquid (vs an I_2-rich one) could be quite different and/or present in dramatically different quantities, so a different set of parameters may be needed to model LLE vs VLE. In addition, because of the surprising nature of the LLE results below, they need to be validated. Several additional LLE experiments have been run, and the slopes of the tie lines have not changed from what is presented here, but we would still recommend that an alternative method other than mass balance be developed in order to determine the compositions of the I_2-rich liquid phase.

Now that we have a reliably operating experimental apparatus and an excellent start to a useful model for Section III of the S-I Cycle, an accurate and reliable assessment of the S-I Cycle would be virtually assured with a 2-3 year follow-up project. Unfortunately, with the shutdown of U.S. DOE research on the S-I Cycle, such funds will be difficult to obtain in this country. Thus, continuation of this work is being pursued by collaboration with Nuclear Energy agencies who continue to do research in this area, including those in Italy, France, and Korea.
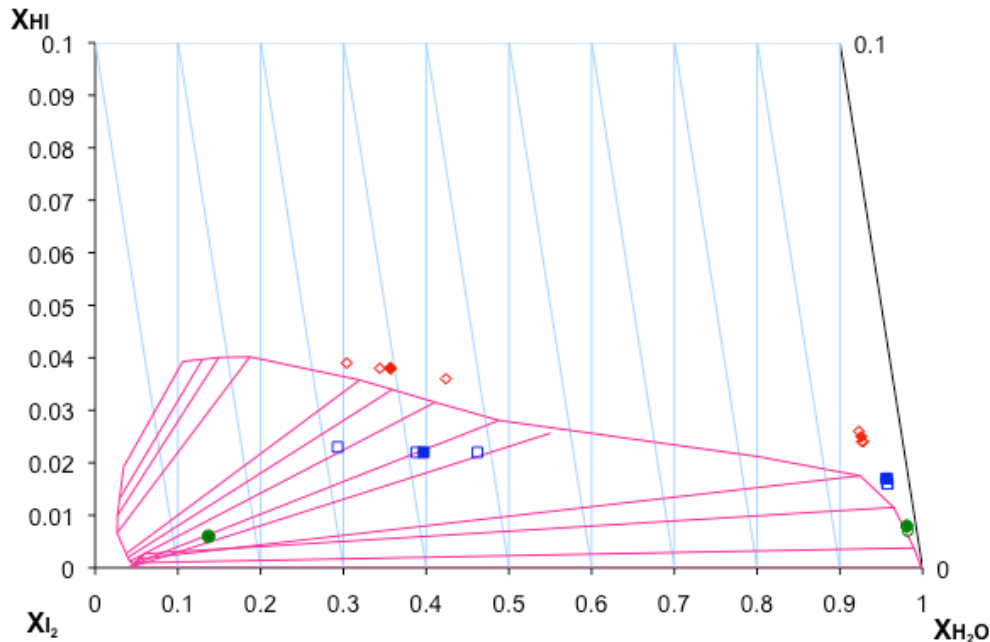

Figure 1. LLE for the system I_2-HI-H_2O at 160 °C and 35 bar. Pink solid (——) lines are the LLE phase boundaries and equilibrium tie-lines predicted by our model [Publ 3]. Open symbols ($\circ$,$\square$,$\diamond$) denote individual samples for both the top, H_2O-rich phase (RHS) and the bottom, I_2-rich phase (LHS), while solid symbols ($\bullet$,$\blacksquare$,$\blacklozenge$) denote average values. H_2O-rich compositions (RHS) are by titration and are accurate to better than 5% deviation. I_2-rich compositions are by mass balance, giving large scatter in the values for the minor component water.

Refereed, Archival Publications

1. "Phase Equilibrium Measurements for the I_2-H_2O and I_2-HI-H_2O Systems of the Sulfur-Iodine Cycle using a Continuous-Flow Apparatus", SE Mena, EG Cervo, JM Crosthwaite, MC Thies. *Int. J. Hydrogen Energy*, submitted for publication, 2009.

2. "Process model-free analysis for thermodynamic efficiencies of sulfur–iodine processes for thermochemical water decomposition", JP O'Connell, P Narkprasert, MB Gorensek. *Int. J. Hydrogen Energy*, 34 (2009) 4033–4040.

3. "A Properties Model of the HI-I_2-H_2O-H_2 System in the Sulfur-Iodine Cycle for Hydrogen Manufacture", JE Murphy, JP O'Connell, *Fluid Phase Equilibr.* 288 (2010) 99–110.

4. "Liquid-Liquid Equilibrium Phase Compositions for the I_2-HI-H_2O System at 160 and 200 °C for the Sulfur-Iodine Cycle", SEMena, DABruce, MCThies. *Int. J. Hydrogen Energy,* submitted for publication, 2010.

5. "Computational Study of Speciation in HI-I_2-H_2O Systems: Contribution to a Thermodynamic Properties Model for the Sulfur-Iodine Process for Thermochemical Hydrogen Production", J.E. Murphy, C.O. Trindle, JP O'Connell, in preparation for submission to *J. Chem. Phys.*

6. "Properties Modeling and Process Synthesis of the Sulfur-Iodine Cycle for Thermochemical Water Decomposition to Hydrogen", in preparation for submission to *Int. J. Hydrogen Energy.*

Conference Proceedings, Presentations, Theses, and Reports

i.   "Experimental Studies of the Iodine-Water System for the Sulfur-Iodine Thermochemical Cycle", Crosthwaite, J.M.; Thies, M. C. *AIChE 2006 Spring National Meetin*g, Orlando, FL, April 2006, paper 182b.

ii. "Investigation of the Reactive Distillation Separation for HI-I_2-H_2 in the S-I Process for Thermochemical Hydrogen Production", O'Connell, J. P.; Bellezza, K. P.; Murphy, J. E.; Gorensek, M. B.; Mathias, P. M.; Thies, M. C.; Crosthwaite, J. M. *AIChE 2006 Annual Meetin*g, San Francisco, CA, Nov 2006, paper 126e.

iii. "Liquid–Liquid Equilibrium Measurements for the Sulfur–Iodine Cycle: the Iodine–Water System", Crosthwaite, J. M.; Edling, M. A.; Thies, M. C. *AIChE 2006 Annual Meetin*g, San Francisco, CA, Nov 2006, paper 207e.

iv. "Thermodynamic Analysis and Properties Modeling of the S-I Process for Massive Hydrogen Production", JP O'Connell, JE Murphy*,* MB Gorensek, MC Thies, J Crosthwaite,*11th Triennial International Conference on Properties and Phase Equilibria for Product and Process Design* Hersonissos Crete, May 2007.

v.   "The Sulfur−Iodine Cycle: Process Analysis and Design Using Comprehensive Phase Equilibrium Measurements and Modeling", MC Thies, *FY07 NHI Semiannual Review Meeting,* Idaho Falls, ID, Oct. 2007.

vi. "Modeling the Solubility of Sulfur Dioxide in Sulfuric Acid Solutions", MB Gorensek, JP

O'Connell, PM Mathias *AIChE 2007 Annual Meetin*g, Salt Lake City, Nov. 2007.

vii.   "Dependence of S-I Thermochemical Decomposition Process Configuration and Efficiency on Property Models*",* JP O'Connell, P Narkprasert, MB Gorensek *AIChE 2007 Annual Meetin*g, Salt Lake City, November 2007.

viii.   "Massive Hydrogen Production via Thermochemical Water Decomposition" JE Murphy, *University of Virginia UVERS competition for graduate students in Engineering, and the UVa nanoSTAR Energy & the Environment*, April 2008.

ix.   "Thermochemical Water Decomposition to Hydrogen: Properties and Phase Behavior for Process Simulation of the Sulfur-Iodine Cycle", JE Murphy, MB Gorensek and JP O'Connell, *23rd European Seminar on Applied Thermodynamics*, Cannes, France, May 2008.

x.   "Thermodynamic Analysis and Properties Modeling of Thermochemical Processes for Massive H2 Production" by JP O'Connell, JE Murphy, MB Gorensek, MC Thies, *18th European Symposium on Computer-Aided Chemical Engineering*, Lyon, France, May 2008

xi.   "Process Simulations of Reactive Distillation for HI Decomposition in the Sulfur-Iodine Cycle", JE Murphy and JP O'Connell, *AIChE Annual Meeting*, Philadelphia PA, November, 2008.

xii.   "A Properties Model for HI-I2-H2O systems", JE Murphy and JP O'Connell, *AIChE Annual Meeting*, Philadelphia PA November, 2008.

xiii.   "Liquid–Liquid Equilibrium Measurements for the Sulfur–Iodine Cycle: the Iodine–HI–Water and the Iodine–Water Systems", SE Mena, EG Cervo, DA Bruce, MC Thies, *17th Symposium on Thermophysical Properties*, Boulder CO, June 2009

xiv.   "Process Simulations of Reactive Distillation for HI Decomposition in the Sulfur-Iodine Cycle", JE Murphy, JP O'Connell, *17th Symposium on Thermophysical Properties*, Boulder CO, June 2009

xv.   "Thermochemical Water Decomposition to Hydrogen: An Update on Properties and Process Simulation of the Sulfur-Iodine Cycle", JE Murphy, MB Gorensek, JP O'Connell, *24th European Symposium on Applied Thermodynamics*, Santiago de Compostela, Spain, June 2009.

xvi.   "The Sulfur-Iodine Cycle: Phase Equilibrium Data for the Ternary I_2-HI-H_2O and the Binary I_2-H_2O Systems", SE Mena, EG Cervo, DA Bruce, MCThies, *AIChE Annual Meeting*, Nashville, TN, November, 2009. (2009 NED Outstanding Student Paper Award)

xvii.   "INTEGRATED FLOWSHEET DEVELOPMENT FOR THE SULFUR-IODINE CYCLE", PM Mathias, JE Murphy, MB Gorensek, and JP O'Connell, Report to Department of Energy through Savannah River National Laboratory, Dec. 4, 2007.

xviii.   "Phase Equilibrium Measurements for the I_2-H_2O and I_2-HI-H_2O Systems of the Sulfur-Iodine Cycle using a Continuous-Flow Apparatus", SE Mena, M.S. Thesis, Clemson University, May 2010.

xix.   "Properties Modeling and Process Synthesis of the Sulfur-Iodine Cycle for Thermochemical Water Decomposition to Hydrogen", JE Murphy IV, Ph.D. Dissertation, University of Virginia, May 2009.