AC 2008-2665: NUCLEAR HYDROGEN -CHEMICAL AND NUCLEAR ENGINEERS' DREAM

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Nuclear Hydrogen -Chemical and Nuclear Engineers' Dream

Abstract

Nuclear energy is one of the practical energy sources to produce CO2 free hydrogen. This nuclear hydrogen technology requires both Nuclear and Chemical Engineers. At an undergraduate level this concept of bringing chemical engineers and nuclear engineers to work together in future energy technology is exciting and has created interest in chemical engineering undergraduate students to participate in research activities in Nuclear Engineering discipline. An account of projects on nuclear hydrogen area carried out by chemical engineering undergraduates in nuclear engineering school is presented. The projects were on thermochemical water splitting, sodium borohydride hydrolysis, and fuel cell modeling. The paper highlights the experience in handling the undergraduate students for research participation and presents students' experience working in nuclear engineering program. The undergraduate participation in research provided unique opportunity in recruiting students in the nuclear engineering program for graduate program.

Introduction

Since the beginning of the nuclear industry, early 1960s, chemical engineering has been a significant discipline within the U. S. nuclear industry[1]. Traditionally the chemical engineers have made and now continue to make significant contribution in the areas of fuel fabrication, isotope separation, fuel reprocessing, and waste management. Chemical engineers monitor the chemistry of the coolant and cleanup systems in an operating nuclear plant. Thus since 1970s Nuclear Chemical Engineering has emerged as an important area that links chemical engineering processes in nuclear industry.

Very recently new technologies are being considered where the nuclear power can be used to produce hydrogen without much CO_2 emission to the environment[2]. The hydrogen is considered as a clean and efficient energy carrier and has flexibility in terms of production by number of primary sources. There are number of thermochemical or thermoelectrochemical processes available for splitting water in to hydrogen and oxygen.

In nuclear industry currently there is great interest in new reactor design specifically operating at high temperature in the range of 500-1000C. The high temperature reactor have high thermal efficiency and have other beneficial features such as fuel proliferation resistance and application in hydrogen generation with thermo-chemical and thermo-electrochemical processes. The high temperature gas cooled reactors are one of the few new generation reactor designs[3, 4].

The new reactor design and new technology of thermochemical processes to generate hydrogen bring chemical and nuclear engineers in novel setting. It is expected that the undergraduates will be excited to learn and to participate in research and development activities in this new area. A research initiative was launched to attract undergraduate students to participate in the nuclear chemical hydrogen generation and related areas. This paper highlights some of the projects that were carried out by the chemical engineering and nuclear engineering undergraduate students in the nuclear engineering school. It tries to capture studnets' experience and possible outcome from such research activity at undergraduate level.

Tradition Nuclear Chemical Engineering

The reactor fuel cycle involves several chemical engineering processes. Individual operations in the nuclear fuel cycle for light-water power reactors are shown in Figure 1.

The first step in the fuel cycle is mining of uranium ore. Due to small fraction of uranium in the ore (typically contains only a few kilograms of uranium per ton), it is first concentrated in a uranium mill, which is located near the mine. The concentration processes typically include leaching, precipitation, solvent extraction, and ion exchange. The product of the uranium concentrate is commercially known as "yellow cake," because the sodium diuranate or ammonium diuranate commonly produced by uranium mills is a bright yellow solid.

The concentrate is shipped from the uranium mill to a uranium refinery or conversion plant. The uranium is further purified by removing chemical impurities and is then converted into the uranium hexafluoride which is in gaseous state as feed to the next step in the fuel cycle, the fuel enrichment. The uranium hexafluoride is then subjected to enrichment of the fissile isotope either through a gaseous diffusion process or a centrifuge. The enriched uranium hexafluoride is then converted to uranium dioxide (UO_2) or other chemical form used in reactor fuel such as uranium metal, uranium nitride, or uranium carbide.

For light-water reactors the UO_2 is pressed into cylindrical pellets, which are sintered, ground to size (about 1 cm diameter), and loaded into zircaloy tubing filled with inert helium gas. This is called a fuel rod. Several fuel rods are assembled into fuel bundles for use in reactor core. The spent fuel from the reactor contains substantial amounts of fissile and fertile material, which are valuable enough to offset part or all of the cost of reclamation. In the fuel reprocessing plant, fuel cladding is removed chemically or mechanically, the fuel material is dissolved in acid, and fissile and fertile materials are separated from fission products and from each other. The remaining radioactive fission product is held at the reprocessing site for additional decay, and then it is converted in to solid form, packaged, and shipped to storage vaults.

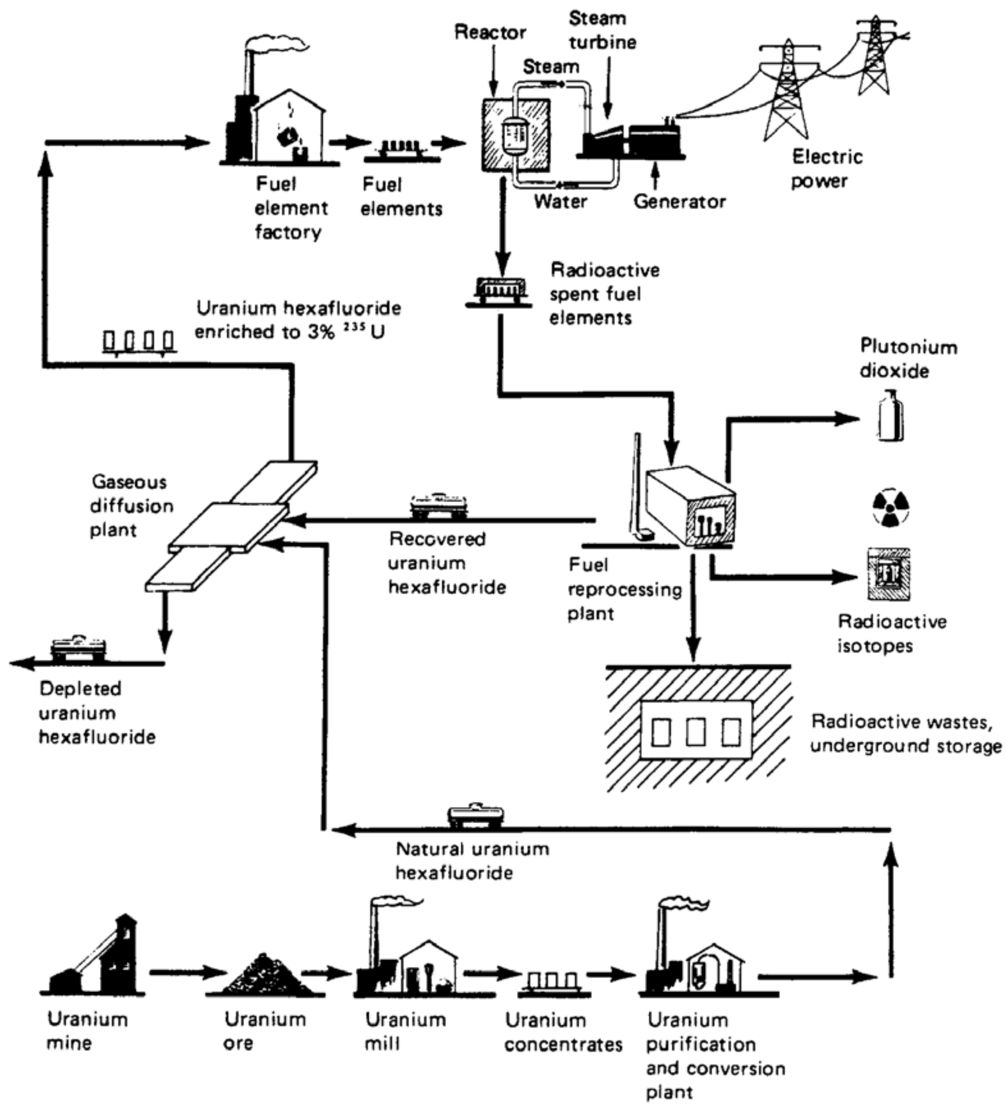

Figure 1. Uranium Fuel cycle and associated chemical processes[5]

Undergraduate Research in Chemical Nuclear Projects

Undergraduate research program provides unique opportunity to encourage undergraduate students to continue for graduate programs and also exposes students to new technology. Recently several research programs in nuclear hydrogen have been sponsored by the Department of Energy under Nuclear Hydrogen Initiative (NHI). With existing university interdisciplinary and undergraduate research programs students specifically from chemistry and chemical engineering background were sought to participate in the nuclear hydrogen research program. The motivations for this were: (i) to make use of the scholarship/fellowship support from university to bring the students with multidisciplinary background, (ii) to recruit students in advanced energy research, (iii) to encourage students to continue for graduate programs and (iv) to establish stronger contacts between nuclear engineering, chemistry and chemical engineering programs. University summer undergraduate research fellowship and academic year research intern programs supported the student selection and facilitated their research work. Through these program students from other university were able to work as undergraduate researchers during summer period.

Summary of Key Projects

1. *Investigation of metal-boride catalyzed hydrolysis of alkaline sodium borohydride for fuel cell hydrogen production*

Using Ru and Co_3B catalysts made with a reduction method, the catalyzed hydrolysis of NaOH-stabilized $NaBH_4$ was investigated under varying operating conditions of temperature (273 K to 351 K) and $NaBH_4$ concentration (1 wt. % to 50 wt. %) by monitoring the hydrogen generation rate. From the temperature data for 1 wt. % $NaBH_4$, the activation energies of the reaction for the two catalysts were determined to be 34.14 kJ mol^{-1} and 25.71 kJ mol^{-1} for the Ru and Co_3B respectively. The application of Ru catalyst on a nickel foam support was also studied to determine reusability characteristics. A progressive degradation in the foam-supported catalyst was observed as the hydrogen generation rate drops from 27 ml min^{-1} to 5.4 ml min^{-1} over a cumulative usage period of 6.4 hours.

2. *Simulation of Sulfur Iodine Process Based Thermochemical Generation of Hydrogen*

The sulfur/iodine thermochemical process was looked at as an efficient and cost effective way to generate hydrogen. However, the entire SI process flowsheet has not been fully simulated. There are three sections in this process described by three reactions. Each Section was simulated using ASPEN PLUS. Section I is the Bunsen reaction, reacting iodine (I_2), sulfur dioxide (SO_2), and water (H_2O) to from hydriodic acid (HI in water) and sulfuric acid (H_2SO_4). The following two sections are devoted to acid decomposition. Section II decomposes H_2SO_4 and produces oxygen, sulfur dioxide, and water. In Section III HI is decomposed into hydrogen and iodine. The oxygen and hydrogen exit the process while the water, sulfur dioxide, and iodine are recycled to Section I. Section III is the slowest reaction, therefore is the rate determining step. Sections I and III currently have convergence issues. Section II was able to converge by modeling the individual components first. Once each converged, the components were combined until the entire Section II converged. The same approach was applied to Section III.

3. *Controlled Hydrolysis of Sodium Borohydride for use in Proton Exchange Membrane Fuel Cells*

Because of its stability and high energy density, sodium borohydride is a possible choice in transporting large quantities of hydrogen for use in fuel cells. Unfortunately, the hydrolysis of sodium borohydride in an aqueous solution is a slow process. Our goal was to find the highest rate of hydrogen production by adjusting temperature, pressure, concentrations of borohydride, concentrations of catalysts, the delivery of catalysts to the solution, the age of the catalyst, the preparation of the catalyst, and type of catalyst. Current data indicates that the activation energies of Ru-B and CoB catalysts (34.14 kJ/mol and 25.71 kJ/mol respectively) are significantly lower than other literature suggests. In tests to determine the reusability of the Ru-B catalyst, it was determined that the catalyst action decreases quickly, dropping from a rate of .45 ml/s to .09 ml/s in about 6 hours.

4. *Simulation of molten carbonate fuel cell for distributed generation*

Distributive energy systems are those that employ small-scale power generation technologies in close proximity to the load it serves. The use of high temperature molten carbonate fuel cell technology is an ideal candidate in the distributed power generation. A dynamic molten carbonate fuel cell model based on chemical and thermodynamic principles was developed for use in the simulation of fuel cell and turbine gas hybrid power system. For modeling purpose the fuel cell was split into two compartments. One compartment was used to model both the anode sides indirect internal reforming and direct internal reforming volume, while the other compartment represented the cathode volume. The model was a lumped parameter, zero-dimensional model with each volume representing a continuously stirred tank reactor. The balance equations for molar mass, energy and chemical reactions including the reformation-water shift reaction in the anode, cathode reactions and the combustor were developed. The gases were treated as ideal gases. The model was simulated in MATLAB Simulink. The steady state cell performance curves were compared with literature data and the agreement was good.

Tools for the Research

For experimental projects the following materials and training were given to the undergrad students

(1) Basic Lab Safety Principles and Procedures
(2) Material Safety Data Sheets (MSDS) for the various in the lab.
(3) Reading material including journal papers on the topic of the research
(4) Topical presentations by undergraduates to demonstrate understanding of raeding material as required
(5) Practice experimental runs
(6) Introduction to special techniques as required for the experiments such as X-Ray Diffraction (XRD), and Scanning Electron Microscopy (SEM)
(7) Laboratory note book entry
(8) Weekly written reports on progress

For analytical and code modeling research work the following training and materials were provided

(1) An computer account and access to the code usage
(2) Reading material and
(3) Topical presentations by undergraduates to demonstrate understanding of reading material
(4) Research note book entry
(5) Weekly reports on progress

Laboratory experimental faculties included

(1) Hydrolysis experimental facility that includes high pressure reactor chamber (15 MPa or 2000 psi max), precision balance, controlled heater, glass equipments and piping
(2) Small power (300 W) fuel cell testing facility that can used to test direct methanol fuel cell or PEM fuel cell.
(3) Access to XRD and SEM at the university materials laboratory

For the research projects the following commercial software were used

(1) ASPEN PLUS –chemical engineering process simulation software

(2) FLUENT – Computation Fluid Dynamics (CFD) software
(3) CFX - Computation Fluid Dynamics (CFD) software
(4) MATLAB-Simulink – Mathematical modeling and simulation software

Student Experience

A total of six chemical engineering and chemistry students participated in various chemical engineering related projects in the past three years along with eight nuclear engineering students. At conclusion of the research projects the students were asked to give feedback on their overall experience in nuclear engineering department and on the particular projects. Here some of student's feedbacks are summarized that reflect the need to integrate some of the chemistry, chemical engineering and nuclear engineering topics in undergraduate education

(1) The nuclear engineering undergraduates expressed strong interest in taking advanced chemistry courses in reaction kinetics as it helps them understand the chemical reactions and models. The current curriculum lacks higher chemistry courses for nuclear engineering undergraduates.
(2) The chemical engineers desired to take basic nuclear engineering course to understand reactor principles, operation and control. They also showed interest in radiation measurement, radiation safety and protection.
(3) Both nuclear and chemical engineering students expressed need to learn advanced thermodynamics courses as this has direct impact on understanding energetic involved various processes.
(4) Student that worked in experimental work felt more rewarding as they generated data or good results. The students who were working on code or modeling felt that they should have some hands-on work related to their research.
(5) Some chemical engineering students expressed interest in doing nuclear engineering minor in their degree program.

Bibliography

1. Axtmann, R. C. Nuclear chemical engineering, Nuclear Technology., v. 27, no. 1, pp. 78-83 1975
2. Brown LC, Besenbruch G E, Lentsch R D, Shultz K R, Funk J F, Pickard P S, Marshall A C, Showalter S K. High Efficiency Generation of Hydrogen Fuels Using Nuclear Power 2003, General Atomics, Final Technical report, GA- A24285 Rev. 1 for the period August 1, 1999 through September 30, 2002.
3. KosterA. , Matzner H. D. and Nicholsi D. R., PBMR design for the future, *Nuclear Engineering and Design*, *Volume 222, Issues 2-3*, *June 2003*, *Pages 231-245*