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आयोडीन-सल्फर ऊष्मा-रासायनिक प्रक्रिया का प्रौद्योगिकी विकास

Technology Development of Iodine-Sulfur Thermochemical Process

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सारांश

हाइड्रोजन एक आशाजनक स्वच्छ ऊर्जा वाहक के रूप में उभरा है जो पर्यावरणीय प्रभाव को कम करते हुए बढ़ती ऊर्जा मांगों को पूरा करने में सक्षम है। विभिन्न उत्पादन विधियों में, स्वच्छ ऊर्जा स्रोतों द्वारा संचालित ताप रासायनिक जल विभाजन को बड़े पैमाने पर हाइड्रोजन उत्पादन के लिए सबसे दीर्घकालिक दृष्टिकोणों में से एक माना जाता है। इस प्रक्रिया में, पुनःचक्रण योग्य मध्यवर्ती यौगिकों से जुड़ी रासायनिक अभिक्रियाओं के एक क्रम के माध्यम से पानी को हाइड्रोजन और ऑक्सीजन में अपघटित किया जाता है। जाँच किए गए कई तापरासायनिक चक्रों में, आयोडीन-सल्फर (आई-एस) चक्र ने अपनी उच्च दक्षता और उच्च तापमान ऊष्मा स्रोतों के साथ संगतता के कारण विशेष रूप से ध्यान आकर्षित किया है। आई-एस चक्र में तीन प्रमुख अभिक्रिया चरण शामिल हैं : बंसेन अभिक्रिया, सल्फ्यूरिक एसिड अपघटन और हाइड्रोजन आयोडाइड (एचआई) अपघटन। यह लेख इनमें से प्रत्येक चरण में प्रौद्योगिकीय प्रगति की समीक्षा करता है और एक पूरी तरह से एकीकृत, बंद-लूप आई-एस ताप-रासायनिक चक्र विकसित करने की दिशा में प्रगति पर प्रकाश डालता है। ये विकास बड़े पैमाने पर हाइड्रोजन उत्पादन के लिए एक स्थायी मार्ग के रूप में आई-एस प्रक्रिया की क्षमता को प्रदर्शित करते हैं।

ABSTRACT

There is an urgent need for an alternative energy carrier that can meet growing energy demands without posing a threat to the environment. Among the various clean energy options, hydrogen has emerged as one of the most promising and environmentally benign energy carrier. The most sustainable and attractive route for hydrogen production is the splitting of water using clean energy sources. Thermochemical water-splitting processes offer significant potential for large-scale hydrogen production. In these processes, water is decomposed into hydrogen and oxygen through a series of chemical reactions involving intermediate compounds that are continuously recycled within the cycle. Among the numerous thermochemical cycles investigated worldwide, the iodine-sulfur (I-S) thermochemical cycle is one of the most extensively researched due to its high efficiency and suitability for integration with high-temperature heat sources. The I-S process consists of three major reaction steps: the Bunsen reaction, sulfuric acid decomposition, and hydrogen iodide (HI) decomposition. This article discusses the technological developments achieved in each of these reaction sections and highlights the progress made toward the realization of a fully integrated closed-loop I-S thermochemical cycle for sustainable hydrogen production.

KEYWORDS: Iodine-Sulphur Process, Thermochemical, Hydrogen Energy



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HI decomposition setup

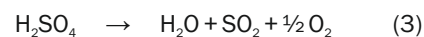
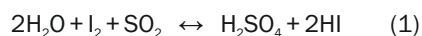
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Introduction

Fossil fuels are limited in supply and their use leads to greenhouse gas emissions. Hence there is a need to replace/limit the usage of fossil fuels with a clean fuel. Further the energy produced at the clean fuel source needs to be transported to the various end users. Apart from electricity, Hydrogen is seen as a clean energy carrier, if produced from water using non carbon based primary energy source [1]. There are many ways to produce hydrogen by splitting water, thermochemical methods are one such process. The thermochemical cycles are processes where water is decomposed into hydrogen and oxygen via chemical reactions using intermediate elements which are recycled. The sum of all the reactions is equivalent to the dissociation of the water molecule into hydrogen and oxygen. Thermochemical processes produce hydrogen by splitting water at far less temperatures in comparison to direct thermolysis of water. A number of thermochemical processes are studied to generate hydrogen from water, of this Iodine–Sulfur (I-S) process has been widely studied because of its high efficiency, scalability, all fluid process etc [1]. I-S process broadly consists of three steps (as shown in reaction 1, 2, and 3).

Thermochemical process consisting of three chemical reaction steps [2] which are shown below.



Reaction (1), called Bunsen reaction, produces two acids (hydriodic and sulfuric acid) via reaction with water, iodine and sulfur dioxide exothermically. Afterwards, produced HI_x and H_2SO_4 phases are separated and sent to the respective sections for production of H_2 and O_2 by reactions (2) and (3), respectively. I-S process involves highly corrosive chemicals [3], hence it becomes necessary to have corrosion resistance materials. As an important step toward the demonstration of the I-S process, Bhabha Atomic Research Centre (BARC) Mumbai, initiated extensive research and development activities on the process. Initially, a closed-loop I-S system was established using glass and quartz equipment operating at atmospheric pressure and prototypical temperature conditions. Since the process involves highly corrosive chemicals and severe operating environments, extensive corrosion studies were carried out successfully under representative process conditions.

Subsequently, individual reaction sections of the I-S process were studied using engineering materials to evaluate their long-term feasibility and material compatibility. Building upon these developments, a demonstration facility employing engineering materials has been established to realize and validate the closed-loop operation of the I-S thermochemical process for sustainable hydrogen production.

I-S Process in Glass/Quartz Setup

The initial development of a laboratory-scale closed-loop I-S thermochemical system to demonstrate continuous hydrogen production through water splitting is focused. The

overall process flow sheet was designed for a hydrogen production basis of 150 Nlph.

The closed-loop experimental setup was fabricated using glass, quartz based equipment and consisted of reactors, separators, purifiers, heat exchangers, and associated auxiliary components.

The development programme was carried out in a phased manner. Initially, individual equipment units were tested independently to evaluate their performance and operational stability. Subsequently, section-wise integrated experiments were conducted to study the interaction between interconnected equipment and to establish stable continuous operation of the process.

Based on the experience gained from equipment-level and section-wise experimentation, the fully integrated closed-loop glass system was operated successfully in continuous mode for 20 hours, achieving a hydrogen production rate of 30 Nlph. With this successful demonstration, India became the fifth country in the world—after the United States, Japan, South Korea, and China—to demonstrate continuous closed-loop operation of the I-S thermochemical cycle for hydrogen production. Fig.1 gives the integrated facility of I-S Process in glass/quartz setup. Fig.2 shows the temperature profile of various unit operations and processes during stable closed loop operation. Hydrogen is sampled periodically and analyzed using gas chromatograph and flow rate was analyzed using water displacement method periodically.

Material Testing Studies

Material identification issues are crucial for successful deployment of I-S process on large scale [3]. materials research areas relate to development of construction materials, and catalysts. Efforts are on to find solutions, which render the I-S process efficient and economical.

I-S Process involves highly corrosive and hazardous media. Identification of compatible material of construction would be a breakthrough in realization of technology. In order to identify compatible material of construction, corrosion test study has been done with special metals, ceramic, PTFE and



Fig.1: Closed loop glass/quartz I-S facility.



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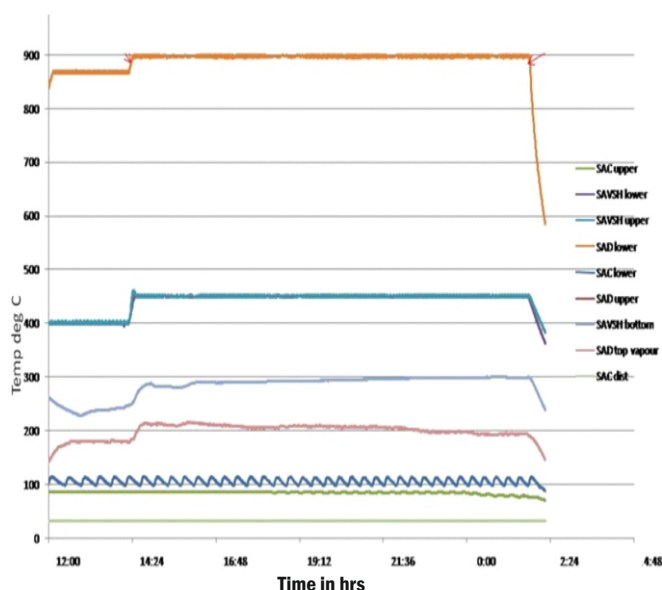


Fig.2: Temperature profiles during period of closed loop operation.

noble metals in actual chemical reaction environment in flowing streams for the development of I-S thermochemical process in metallic system.

Test coupons studied in the process are Incoloy 800H, Incoloy 800, Tantalum, Hastelloy-C276, Alloy 33, Molybdenum, Titanium, Niobium, Niobium-1% Zirconium, PTFE, Silicon Carbide, Platinum, Silver and Gold.

Bunsen Section

Metallic Bunsen system

Bunsen reaction constitutes one of the three main reaction steps of I-S [4].

Bunsen reaction is a multiphase, reversible and exothermic in nature as given in Fig.3 [5]. Reactor selection and design procedure should reckon this and exothermicity of the reaction in addition to the product quality and side reactions [4, 5].

Materials have been identified for individual sections of I-S Process after corrosion studies.

An experimental facility to study Bunsen reaction and phase separation is designed and installed. Elaborate

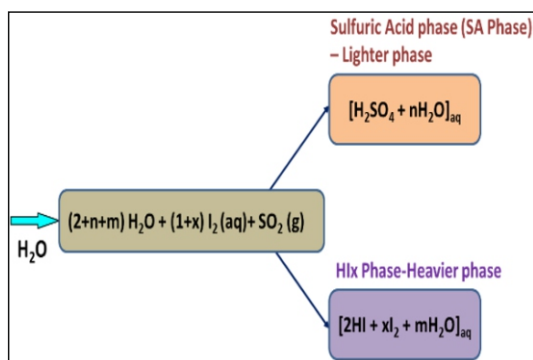


Fig.3: Bunsen reaction scheme with excess I_2 and H_2O .

Table 1: Typical summary of compatible material of construction in various equipments.

Equipment & temperature	Test Coupons							
	Incoloy 800H	Ta	Alloy C276	Ti	SiC	Pt	Ag	Au
SO_3 Decomposer & 900 °C	✓				✓	✓		✓
H_2SO_4 Decomposer & 500 °C	✓				✓	✓	✓	-
HI_x solution & 127-180 °C		✓			✓	-	-	-
HI decomposer & 500 °C		✓	✓	✓	✓	✓		✓
50 wt % H_2SO_4 & 122 °C	✓	✓	✓		✓	-	-	-
70 wt % H_2SO_4 & 167 °C	✓	✓	✓		✓	-	-	-
90 wt % H_2SO_4 & 260 °C		✓	✓		✓	-	-	-
HI vaporizer & 127 °C	✓	✓	✓	✓	✓	-	-	-

experimentation are carried out in the facility. The schematic of the setup is shown in Fig.4. The feed and reaction system are shown in Fig.5 & 6 respectively.

Operating conditions like temperature, composition etc. have to be optimally selected to achieve high purity of product phases, conversion [5].

Sulfuric Acid Decomposition Section

Thermal decomposition of sulfuric acid is, where high temperature heat input is required for endothermic reaction [6,7]. Decomposition involves three steps; Equation (4) represents sulphuric acid vaporisation or phase change step, takes place near 337 °C at atmospheric pressure condition.

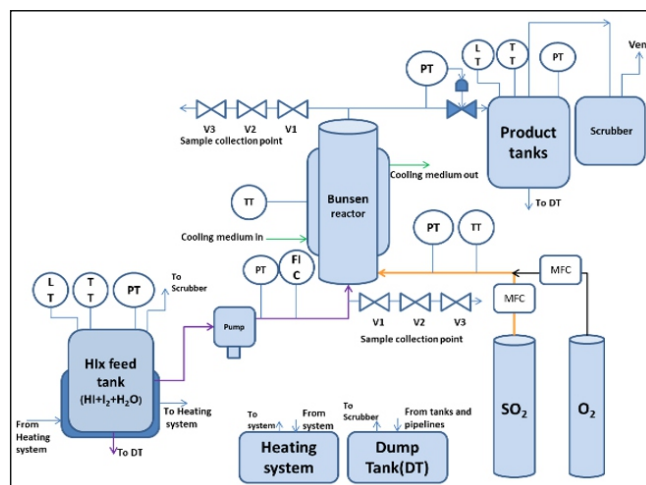


Fig.4: Schematic of Metallic Bunsen setup.

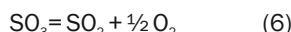
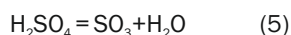


Fig.5: Feed system of Metallic Bunsen setup.



Fig.6: Bunsen reactor in Metallic Bunsen setup.

Eq (5) and (6) represent acid decomposition, at temperature up to 550 °C and sulfur trioxide decomposition, at 900 °C, respectively. Sulfur trioxide decomposition is the heterogeneous catalytic reaction step [7]. The schematic is shown in Fig.7



Chromium doped iron oxide catalyst, is found to be promising, active and stable mixed oxide catalyst for trioxide decomposition, a better alternate for Pt catalyst [6].

Activation energy and frequency factor of this catalyst are obtained during intrinsic reaction kinetic study with powder catalyst. Catalyst is found to be stable and hence considered for further studies [7].

HI Decomposition Section

HI decomposition is one of the important reaction step in I-S Process [2]. It is an endothermic catalytic reaction. Problems of HI section are azeotrope formation by HI_x mixture, lack of appropriate thermodynamic data and difficulty in decomposing HI. To break azeotrope H_3PO_4 was used by GA, USA. JAEA, Japan is focused on using EED (Electro-electro dialysis) combined with a H_2 permselective membrane reactor.

The HI_x solution, which is produced in the Bunsen process reactor, is nearly quasi-azeotropic. Application of the conventional distillation to separating HI from the solution is viable solution but energy intensive. Alternative distillation methods including the extractive distillation using phosphoric acid and the reactive distillation in pressurized condition have been investigated in literature [3]. In addition, application of membrane technologies has also been considered such as the pervaporation and the electro-membrane process called electro-electrodialysis (EED).

HI decomposition studies are carried out using conventional packed bed reactor. The setup is shown in Fig. 8.



Metallic Closed Loop I-S Process

BARC has been involved in technical demonstration of IS process. To achieve this target, a bench scale facility is set up in BARC, Mumbai.

The objective of the project is demonstration of a metallic closed loop I-S process system involving three sections at prototypical process conditions for hydrogen production at 150 Nlph at atmospheric pressure by using electrical heat and compatible materials of construction for various equipments. The schematic of the process is shown in Fig.9 and the facility in Fig.10.

Various issues cropped up which have been overcome during demonstration. The facility is commissioned and successfully demonstrated H_2 production at 150 Nlph capacity.

After successfully demonstrating I-S process in engineering materials, the process is scaled up to 3 m^3/h (3000 Nlph) hydrogen production capacity. This setup is coming up at HWB(M) facility and being worked out in collaboration with HWB. Modified I-S process is envisaged to decrease the highest temperature requirement of the I-S process from 850 °C to ~500 °C by eliminating sulphuric acid decomposition step. The SO_2 required in the Bunsen reaction can be provided from industries where it is generated or by combustion of sulphur itself.

It is proposed to utilize the high temperature heat from high temperature gas cooled reactor (HTGCR) which is being developed for demonstrating production of clean hydrogen using modified I-S process. Modified versions of the process wherein highest temperature step of the process can be avoided are being worked out with private vendors through Atal Incubation Center, Mumbai.

Summary

The realization of the hydrogen as an energy carrier for future energy relies on a practical method of producing hydrogen in large scale with no emission of greenhouse gases. In order to realize an industrial scale process, materials play a vital role. I-S process involves highly corrosive atmosphere.

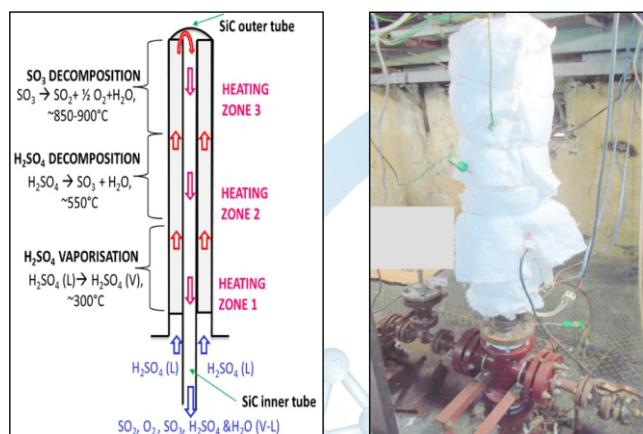


Fig. 7: Sulfuric acid decomposition scheme and experimental setup.



Fig. 8: HI decomposition setup.

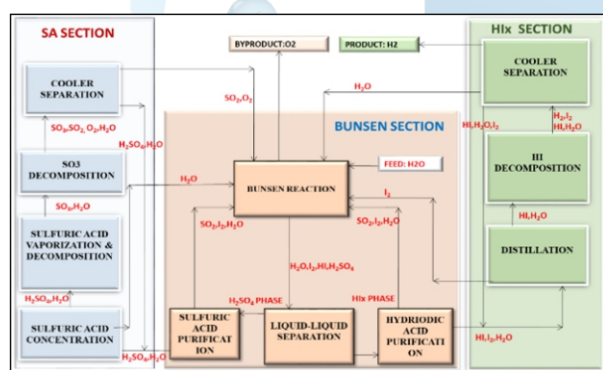


Fig. 9: Schematic of I-S process.

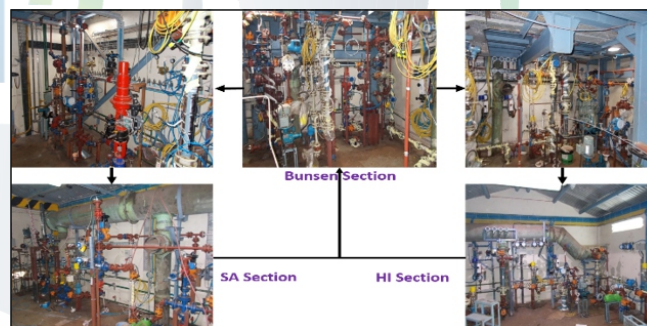


Fig. 10: Metallic closed loop I-S Process facility.

Subsequently, various process equipment and subsystems were fabricated, integrated, and tested under prototypical operating conditions, culminating in the successful demonstration of the complete I-S process in a closed-loop configuration. Based on the experience gained and performance demonstrated, a higher-scale I-S process facility is currently being established to advance the technology towards larger-scale operation. Further, modified configurations of the I-S process are envisaged for integration with HTGCR and, subsequently, for industrial deployment. These efforts will provide a systematic pathway for scaling up the technology and enable the eventual realization of the I-S process at an industrial scale for large-scale hydrogen production.

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