Evaluation of Bunsen Reaction and Phase Separation in Continuous Reactor

By

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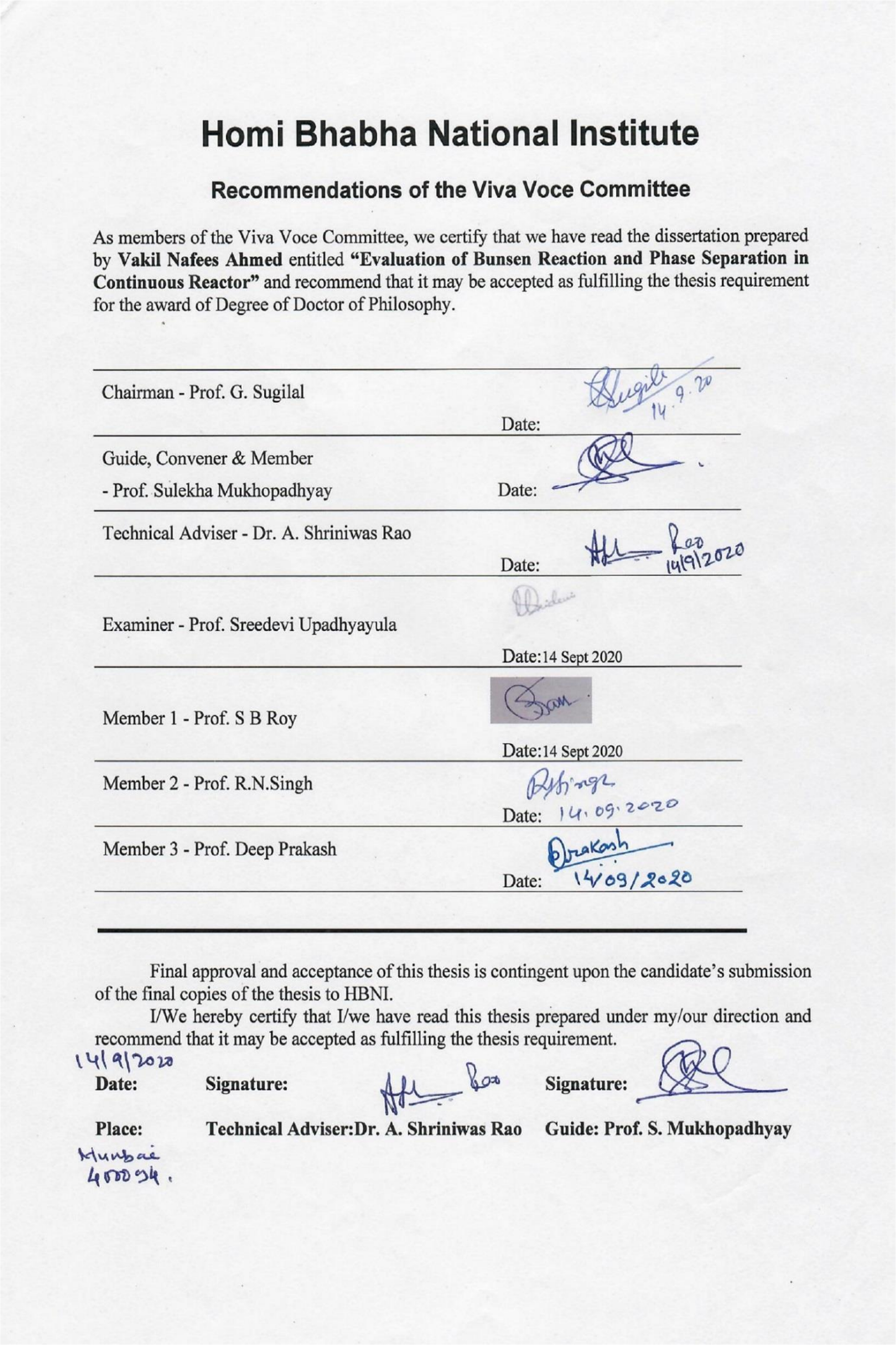

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DECLARATION

I, hereby declare that the investigation presented in the thesis has been carried out by me. The work is original and has not been submitted earlier as a whole or in part for a degree/diploma at this or any other Institution / University.

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LIST OF PUBLICATIONS

International Journal papers

1. “Role of operating conditions on cross contamination of products of the Bunsen reaction in iodine-sulfur process for production of hydrogen”, V Nafees Ahmed, A Shriniwas Rao, S Sujeesh, HZ Fani, A Sanyal, S Mukhopadhyay, International Journal of Hydrogen Energy, 2017, Volume 42, Issue 49, 29101-29106
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Conference Proceedings

1. “Iodine-Sulfur (I-S) Thermochemical process for Hydrogen Production”. V Nafees Ahmed, Poster presentation in “Chemfest-2014”, 28th Feb-03rd Mar 2014. TSH, Anushaktinagar, Mumbai.
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DEDICATED

TO MY

BELOVED PARENTS

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CONTENTS

SUMMARY

The Emission of Carbon dioxide gas is accountable for global warming. So, a non-polluting fuel is the need of the hour. Hydrogen is an environmentally favourable transportation fuel that can have the capability to dislodge fossil fuels.

The thermochemical cycles involve cyclic processes where hydrogen and oxygen are formed by splitting water through chemical reactions with the recycle of intermediates. Iodine-Sulfur (I-S) process is a thermochemical process consisting of three chemical reaction steps. The first step is the Bunsen reaction, which produces hydriodic and sulfuric acid from sulfur dioxide, water, and iodine as reactants. Then, the produced HI_x and H_2SO_4 phases are separated and sent to the concentration/decomposition sections for conversion to H_2 and O_2 respectively.

Under the current study, Bunsen reaction is studied to categorize the role of various operating conditions on yield and purity of Bunsen reaction product phases. Bunsen reaction is performed only up to 2 bar(g), which shows better yield and product purity, but beyond 2 bar(g) data in the literature is not available, hence to fill that gap it is planned to carry out the reaction at high pressures i.e up to 6 bar (g).

The present study is also focused on finding the contamination level in two product phases of the Bunsen reaction. Bunsen reaction is studied in a co-current reactor and continuous mode in the range of 50-75 ^{o}C, 2-6 bar (g) at different HIx (a mixture of hydroiodic acid, water, and iodine) and SO_2 flow rates. At 4 bar (g), 70 ^{o}C, purity of H_2SO_4 phase is maximum i.e. 99.85-mole percent. At 4 bar (g), 60^{o}C with HIx, purity in HIx phase is maximum i.e. 99.66-mole percent.

Further, experiments are performed for Bunsen reaction up to temperatures of 80 ^{o}C, 2-6 bar (g) pressure range. Higher pressure operation has enriched the Bunsen reaction products. The highest mole fraction of H_2SO_4 in the sulfuric acid phase i.e. 0.15 and highest mole fraction of HI in HIx phase i.e 0.165 is obtained at higher pressure operation.

Experiments have been performed in a stirred glass reactor to determine kinetic rate data for Bunsen reaction. Initial experiments have been performed to obtain the mass transfer coefficient in the H_2O-SO_2 system. Stirring speed has been varied from 0-360 rpm to obtain a regime where the mass transfer process dominates. Mass transfer coefficients evaluated varies between $8.7X10^{-6}$ m/s to $1.5X10^{-5}$ m/s and are compared with published literature. The Bunsen reaction kinetic rate constant is obtained as 1.8 second^{-1}. Hatta number and Infinite enhancement factors are calculated as 3.6 and 18 respectively. From the calculated values of Hatta number and Infinite enhancement factors, the regime of the chemical reaction is found to be in the fast-pseudo first-order reaction regime.

Experiments have also been performed to obtain the regime in which side reactions occur. The role of temperatures, excess I_2 and H_2O content on the side reaction occurrences have been investigated. To obtain an understanding of the phase separation characteristics, Bunsen reaction product phase experiments have been performed.

The thesis has given new insights into the regime of the operation of the Bunsen reaction. These studies will help during the design and scale-up of higher capacity setup. The major findings of the study are, increase in pressure leads to an increase in both HI and H_2SO_4 mole fractions in respective phases. It is recommended to operate the Bunsen reactor at 4 bar (g) pressure, in the temperature range of 60 ^{o}C-70 ^{o}C, to achieve improved phase purity levels. The thesis is concluded as; the purity of Bunsen reaction product phases can be enhanced up to 99.85 % H_2SO_4 by operating at higher pressure. A methodology has been developed for the evaluation of kinetic parameters for Bunsen reaction. The studies have brought out limiting temperature, pressure & feed composition under which maximum concentration & purity of phases is achieved with adequate I_2 consumption. The limiting conditions of operating parameters to avoid side reaction of Bunsen reaction product phases are identified. Recommendations are made for the future scope of the study that can be carried out.

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ABBREVIATIONS AND NOTATIONS

VOC	Volatile organic compounds
GHG	Greenhouse gas
LFL	Lower flammability limit
UFL	Upper flammability limit
LPG	Liquefied petroleum gas
LHV	Lower heating value, kJ/mol
HHV	Higher heating value, kJ/mol
CNG	Compressed natural gas
AFC	Alkaline fuel cell
DMFC	Direct methanol fuel cell
MCFC	Molten carbonate fuel cell
PAFC	Phosphoric acid fuel cell
PEMFC	Proton exchange membrane fuel cell
SOFC	Solid oxide fuel cell
Gtoe	Gigatons of oil equivalent
gge	Gallon of gasoline equivalent
ICE	Internal combustion engine
IEA	International Energy Agency
NG	Natural gas
SMR	Steam methane reforming
POx	Partial oxidation
ATR	Auto thermal reforming
PSA	Pressure-swing adsorption
WGS	Water-gas shift

DSU	Desulfurization unit
LT-WGS	Low temperature water gas shift
HT-WGS	High temperature water gas shift
HROs	Heavy residual oils
ASU	Air separation unit
CPO	Catalytic POx
GWP	Global warming potential
AWE	Alkaline-water electrolysis
PTFE	Polytetrafluoroethylene
PEM	Proton exchange membrane
PEWE	Polymer electrolyte water electrolysis
HTE	High-temperature electrolysis
YSZ	Yttria-Stabilised Zirconia
LSM–YSZ	Sr-doped $LaMnO_3$ and Yttria stabilized zirconia
JRC	The Joint Research Centre
RWTH	Rheinisch-Westfälische Technische Hochschule
GA	General Atomics
NERI	Nuclear Energy Research Initiative
SNL	Sandia National Laboratories
CEA	Commissariat à l'Énergie Atomique
NHI	Nuclear Hydrogen Initiative
SRNL	Savannah River National Laboratory
ANL	Argonne National Laboratory
SA	Sulfuric acid phase
HIx	Hydriodic acid

ppm	Parts per million
LLE	Liquid-liquid equilibrium
UNIQUAC	Universal quasi chemical
I-S process	Iodine-Sulfur process
PFA	PerFluoroAlkoxy
AO	Analog output
PLC	Programmable logic controller
CPU	Central processing unit
AI	Analog input
PI	Pressure indicator
PT	Pressure Transmitter
TI	Temperature indicator
FE	Flow element
PRV	Pressure reducing valve
MFC	Mass flow controller
TC	Thermocouple
RPM	Rotations per minute

Notations:

ΔG	Change in Gibbs free energy, kJ/kg
ΔH	Change in Enthalpy, kJ/kg
ΔS	Change in Entropy, kJ/kg.K
T	Temperature, K
T_d	Thermolysis temperature for water decomposition, K
F	Faradays constant, Charge/mol
n	Number of electrons transferred

E	Cell potential, V
R	universal gas constant, J/mol.K
a_{H2}	Activity of hydrogen
a_{O2}	Activity of oxygen
a_{H2O}	Activity of water
C_p	Heat capacity, kJ/kg K
x	Excess moles of iodine, moles
$(y+z)$	Excess moles of water, moles
N_{AL}^{*}	Flux entering the liquid phase, moles/m^2.s
E_A	Enhancement factor
k_{AL}	Mass transfer coefficient, m^2/s
C_{AL}^{*}	Concentration of A at liquid interface, moles/m^3
C_{AL}^{b}	Concentration of A in bulk liquid, moles/m^3
A	Gas reactant
B	Liquid reactant
C	Liquid product
E_∞	Infinite enhancement factor
Ha	Hatta number
k_2	Intrinsic rate constant, m^3/mole.s
D_{AL}	Diffusion coefficient of A in liquid, m^2/s
D_{BL}	Diffusion coefficient of B in liquid, m^2/s
b	stoichiometric coefficient
H	Henrys constant, m^3 atm/mole
k`	Overall reaction rate constant, 1/s
V_G	Gas phase volume, m^3

A`	Gas liquid interfacial area, m^2
$p_{i,o}$	Initial pressure, bar
p_i	Final pressure, bar
t	Time interval, s
p_A	Partial pressure of A, bar
Sh	Sherwood number
Re	Reynolds number
Sc	Schmidt number
η_{WS}	Thermal efficiency
δ	Stagnant liquid/gas layer of thickness, m
φ	Equivalence ratio

1 INTRODUCTION

1.1 Preamble

The world population is increasing; with this, the energy demand is projected to increase considerably in the future. Energy development [1, 2] is focused primarily on harnessing adequate primary energy sources [3] and identifying secondary energy forms [4, 5]. Production of conventional and renewable energy sources and recovery of waste energy are the various methods for the development of energy. Presently, maximum of the energy necessity in the world for transportation and heating (67 % of the primary energy demand) is obtained from natural gas and petroleum [6]. The two fuels are easy to transport in liquid or gaseous form. But hydrocarbon fuels contribute more than 50% of the greenhouse gas discharges and a significant amount of air pollutant discharges through the combustion process [7]. Typically, a coal-based power plant generates billions of kilowatt-hours per year [8]. Emissions resulting from such power station with fossil fuel as a primary source include carbon dioxide, sulfur dioxide, small particulates, nitrogen oxides, smog with high levels of ozone, carbon monoxide (CO), hydrocarbons, volatile organic compounds (VOC), mercury, arsenic, lead, cadmium, and other heavy metals. Various studies have been carried out on the impact of these gases on the environment in the literature [9-14]. All these gases account for nearly 86% of the surge in annual mean radiative forcing since 1750. Further, considered as the primary cause for increased average global temperature over the last century [15].

Hence, today’s world is urgently required to develop alternative fuels. Along with other sustainable energy sources, nuclear power is a low carbon power generation method with low emissions of greenhouse gas emissions per unit of energy generated [16].

Amongst numerous alternatives, hydrogen as a fuel has the greatest benefits in terms of expanded supply and reduction in emission of pollutants and less or no greenhouse gases releases. The major criteria for an ideal fuel are inexhaustibility concerning the availability of raw materials, clean to the surroundings, convenient to use, and no dependency from overseas interventions. Hydrogen has all these properties and is being assessed and endorsed worldwide as an ecologically competitive alternative for gasoline, natural gas, heating oil, and supplementary fuels in both transportation and non-transportation sectors [17].

Hydrogen can be generated using a diversity of resources, and from renewable and non-renewable sources, by numerous diverse process paths. With the start of the hydrogen economy, the main attention of hydrogen technology has diverted to the benign and reasonable consumption of hydrogen as an alternate fuel based on the continuous combination of production, supply, and storage know-hows [18, 19].

Thermo-chemical processes produce hydrogen by splitting water at very less temperatures, e.g. iodine-sulfur process, highest temperature requirement is 850 ^{o}C in comparison to thermolysis of water which occurs at around 4500 ^{o}C [20]. There are many thermo-chemical processes such as the Copper-chlorine process, Bromine cycles, Iron-chlorine cycles, etc..., one of the potential processes is the iodine-sulfur process (I-S), which is first proposed by General Atomics (G.A.) [21]. The iodine-sulfur (I-S) cycle is a thermochemical process that uses the heat energy from a heat source at high temperature to yield hydrogen (H_2) by splitting water and this is discussed in detail in subsequent chapters. In the I-S process all the chemicals are in a fluid state, there is no solid handling. It is having the highest predicted thermal efficiency among all the other thermochemical water-splitting cycles.

1.2 Hydrogen- As an energy carrier

The hydrogen economy is a system for delivering energy using hydrogen. The term hydrogen economy is devised by John Bockris during a talk he gave in 1970 at General Motors (GM) Technical Centre [17].

Hydrogen is a high-grade energy carrier like electricity. Hydrogen can be utilized with high efficacy and zero or low emissions at the application point. Demonstrations have carried out that hydrogen can be used for power generation, heating, transportation, and could substitute existing fuels [22-25].

The contention of the proposal for hydrogen production and application is on the basis that the fuel cell is demonstrated technology. Hydrogen is in plentiful supply on Earth, but the issue is, maximum of the hydrogen on the planet Earth is found to as H_2O, which gives no fuel value, and there is no hydrogen is not a naturally available.

Currently, the production of hydrogen is an important industry [26]. Today's hydrogen is mainly produced (>90%) from fossil sources [23]. The present worldwide hydrogen production is 48% from methane, 30% from petroleum, 18% from coal, and 4% from electrolysis [24].

Hydrogen is mainly utilized in two non-fuel uses: (a) about 60% to produce ammonia through the Haber process for later use in fertilizers [28] and (b) approximately 40% in the refinery, petrochemical, and chemicals sectors. Hydrogen production could be increased by 5 to 10 times through other non-conventional resources, such as nuclear, solar, wind power [24]. All these methods lead to carbon emissions. Thus, the production of hydrogen through non-carbon emission methods is of great importance. This is where the role of the I-S process becomes important.

Figure 1.1 illustrates several application ranges of hydrogen energy [29].

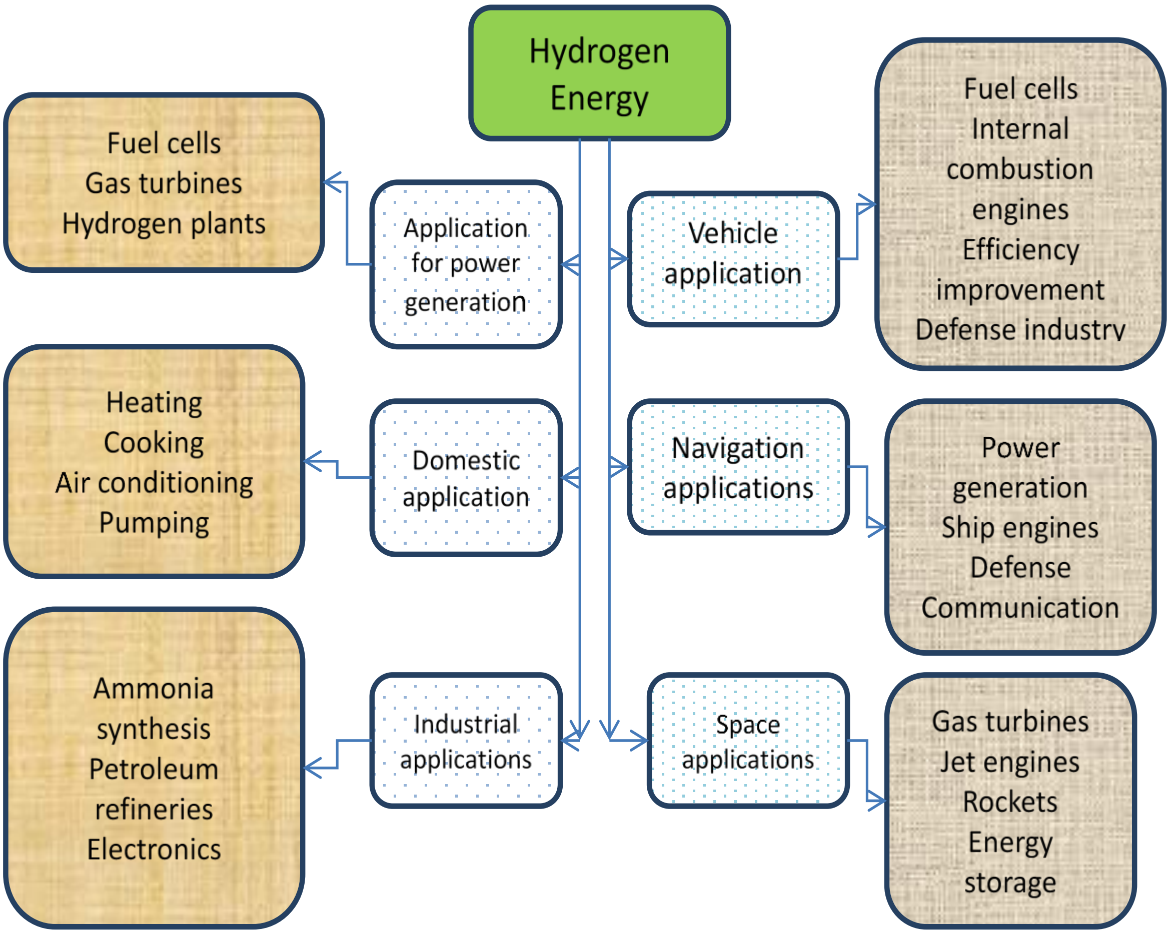


Fig. 1-1 Application areas of Hydrogen Energy

At normal temperatures, hydrogen is relatively nonreactive lest it has been activated [30]. Hydrogen is considered as a fuel; hence its fuel properties should be competitive enough with existing fuels. Hydrogen is highly flammable in a varied range of temperatures and concentrations. Hydrogen has both resemblances and variances when associated with existing fuels which are gasoline, natural gas, liquefied petroleum gases (LPG) and other fuels used in transportation sector. The important challenges mainly related to technical and economics are of implementing a hydrogen economy requires a resolution to the important issue of production of renewable energy [26 & 31]. Hydrogen can be used directly in internal combustion engines [32].

Hydrogen has the highest energy content per unit mass, 141.8 kJ/g any fuel. The higher heating value (HHV) of hydrogen is highest among all the other fuels [33]. It also requires the highest air to fuel ratio. It has a wide combustion range. One of the major differences in the properties among other fuel is hydrogen requires the least amount of ignition energy.

Fuel cells translate the energy in chemical form of hydrogen into thermal and electrical energies [34]. Automobiles highly suited to be powered using Proton exchange membrane fuel cell, mainly because of relatively low operating temperatures (appx. 80°C), large power density, fast change in on demand power, and rapid start up [35].

The global energy utilization is in different sectors such as in electricity ~38 %, in heating and industries ~44 %, and in transport ~18%, excluding electric vehicles. Around 10% is the loss because of transmission and distribution, which denotes around 4% loss in the entire primary energy [36]. Considering the growth rate of oil consumption and the rate of a surge of known oil reserves, it can be deduced that, the end of the petroleum supply will possibly take place around 2050 [36]. The hydrogen-based energy source can be expected to meet the additional demand. The cost of generating hydrogen fluctuates considerably by the category of process technology and delivery network selected [28].

The important features in initiating hydrogen economy is transport and on-vehicle loading of hydrogen [37-45]. Hydrogen fuel deployment includes storing hydrogen from production to its final use.

The storage tank to maintain temperature essentially be insulated, and needs to be strengthened to withstand high-pressure storage [46].

The permeability, buoyancy, and flammability of hydrogen are the challenges for its benign usage which are dissimilar from, but not excessively problematic than those of other energy carriers. Also, an important aspect of public approval of hydrogen is the improvement of safety standards and practices that are common and regularly used [47].

1.3 The Iodine-Sulfur (I-S) cycle

The closed-loop Iodine-Sulfur process is consists of three chemical reactions, as presented in figure 1. 2. Primary, the Bunsen reaction at lowest temperature of all (Section I) is performed to generate two products as two phases from reactants of sulfur dioxide (SO_2), iodine (I_2), and water (H_2O). The reaction is exothermic and heat of reaction is -93 kJ/mole. Under certain conditions, the two product phases convert into immiscible in nature and can be separated readily. The lighter phase is sulfuric acid (H_2SO_4) also referred as top phase, and the lower phase is a denser aqueous complex of HI, H_2O, and I_2 (HIx). After phase separation, the two immiscible liquid phases are passed to the subsequent sections for decomposition from section 1. H_2SO_4 decomposition is section 2 where sulfuric acid is concentrated followed by decomposing into SO_2, O_2, and H_2O at high temperature. The decomposition is endothermic and heat of reaction is +198 kJ/mole. The decomposed products are recycled to Section 1 for the continuous I-S cycle. HI decomposition is section 3 where HI is distilled from HIx followed by decomposing into H_2 and I_2 at intermediate temperature. The decomposition is endothermic and heat of reaction is +10 kJ/mole H_2 is separated from Iodine and unreacted HI. Iodine is recycled back to Section I to perform the Bunsen reaction. The key benefits of the I-S cycle are that it has no waste discharge and the components are transportable easily in gaseous or liquid form. All the chemicals utilized are recycled, and the process required only water and heat as an input. Heat sources that can deliver the heat for H_2SO_4 decomposition reaction which is a high-temperature reaction are met through high nuclear temperature reactor or solar tower, and coal- and natural gas-burning plant.

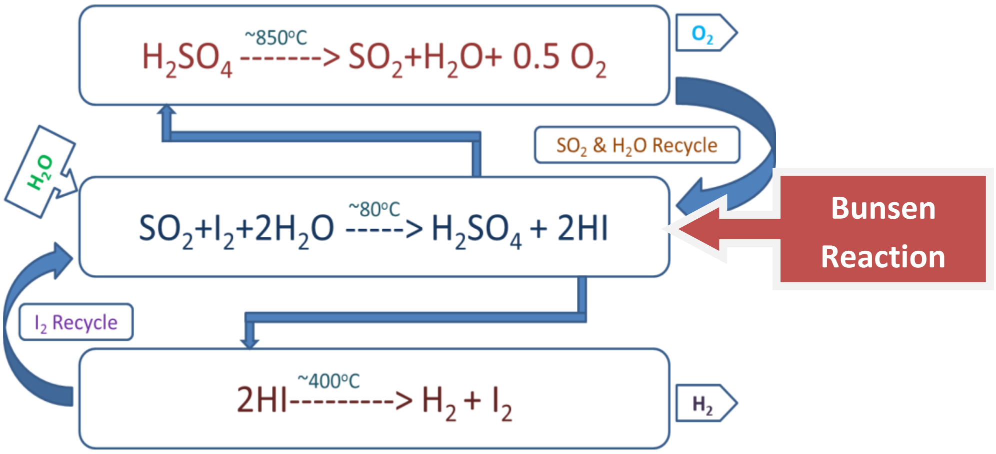


Fig. 1-2 Three steps of I-S process

The I-S cycle can achieve an efficiency of 50% [115], because of this reason, it one of the highest efficient cycles amongst all water-splitting processes. Also, the advantages of I-S cycle include suitability for large scale production of H_2 i.e scalability is very good. This is very important attribute with respect to delivering large quantities of low-cost hydrogen.

1.3.1 I-S Process Flow Sheet

An enormous amount of flow sheet effort has been achieved to describe the reaction environments and process flow details within the I-S cycle, through which determining the material's performance can be obtained [48-50]. Developments in materials know-how can redefine the already existing flow sheets, as improved materials will drive the reactions to be performed more resourcefully and extend equipment lifetime. Because of this there will be an rise in the total cycle efficiency and further this will also decrease the cost of H_2 produced. Energy details for various processes are discussed in [51].

1.3.1.1 Bunsen Reaction

Section 1 obtains the sulfurdioxide gas from Section 2 i.e decomposition of sulfuric acid, and liquid iodine from Section 3. They are mixed with excess water to carry out a Bunsen reaction. Addition of excess iodine promotes the reaction products to form two immiscible liquid phases that can be divided into two streams through gravity separation. The lighter phase is H_2SO_4 and the denser phase is an HIx (mixture of HI, H_2O, and I_2).

1.3.1.2 Sulfuric Acid Decomposition

Sulfuric acid section obtains diluted sulfuric acid from Section 1 and catalytically decomposes it into O_2, SO_2, and H_2O at highest temperature of the cycle [52]. The product gases from this reaction are then recycled to Section 1 and SO_2 is consumed in the Bunsen reaction. First, the incoming acid is concentrated from 57 to 86 wt%. The sulfuric acid is initially given heat to raise the temperature up to 475°C for vaporization. At about 500°C, H_2SO_4 gas starts decomposing into H_2O and SO_3 [53]. In next step decomposition of SO_3 into SO_2 and O_2 is achieved by using a catalytic driven reaction at a temperature of 850°C [54-58].

1.3.1.3 HI Decomposition

HI section obtains HIx from Section 1 to produce hydrogen by decomposition of HI. Hydrogen iodide (HI) in the HIx feed stream is initially concentrated and decomposed into H_2 and I_2 [59] and to achieve this reaction two possibilities are: *extractive distillation* or *reactive distillation* [28]. These two processes involve different reaction conditions and also the chemicals used are different. Membrane separation of hydrogen is also a good option found in the literature [60-62].

1.3.1.4 Extractive Distillation

Extractive distillation uses phosphoric acid to extract HI and H_2O from HIx, as they, unlike I_2, are soluble in H_3PO_4. Also, H_3PO_4 breakdowns the azeotrope of HI and H_2O, hence letting the distillation of HI from the acid complex followed by decomposition. This process has 4 steps: (a) iodine removal, (b) HI distillation, (c) concentration of phosphoric acid, and (d) HI decomposition. In the step (a), phosphoric acid is mixed with the HIx from Bunsen section and this results in the creation of a liquid mixture of I_2 and HI + H_2O + H_3PO_4 as two separate phases. The iodine is removed by gravity and recycled to Bunsen section. The lighter HI-H_3PO_4 acid compound is sent to the distillation column for performing HI distillation as shown in figure 1.3. HI gas is removed from the mixture of HI + H_2O + H_3PO_4 and is flowed on to the decomposition reactor for HI decomposition in the existence of a catalyst to produce iodine and hydrogen. The phosphoric acid which is diluted with water in the distillation column is concentrated to 96 wt% from 87 wt % through the usage of boilers by vacuum recompression. The concentrated phosphoric acid is mixed to the inward HIx feed to afresh the extraction process.

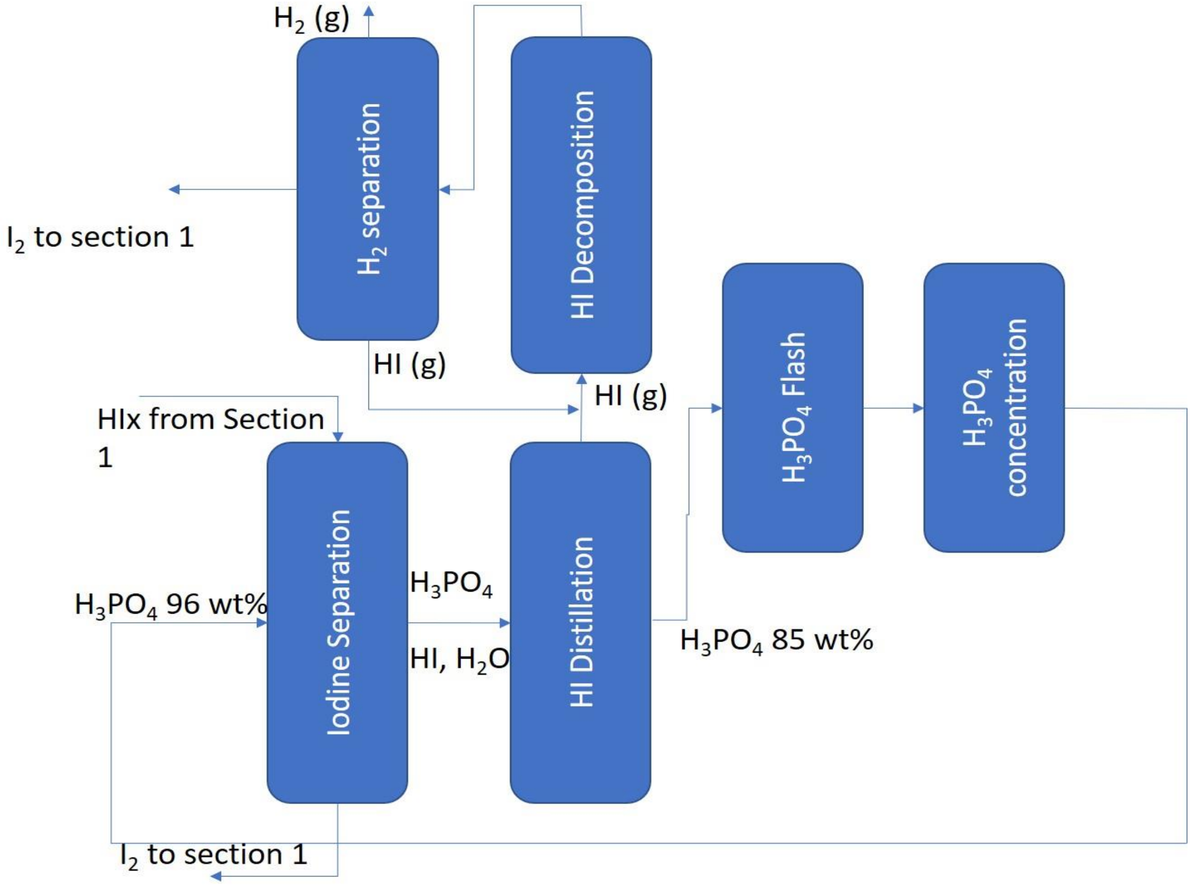


Fig. 1-3 Extractive Distillation flow sheet

1.3.1.5 Reactive Distillation

Reactive distillation is a simpler process than extractive distillation in theory, but the process to be experimentally performed. There are two important differences amongst extractive and reactive distillation. Initially, not like the extractive process, the HIx azeotrope is not overcome, this results in the same composition in liquid and vapor phases. Next, pressure is requied for reactive process. In this process, distillation of azeotropic mixture of HIx is done under pressurized column and the HI decomposition within the HIx vapor stream is achieved catalytically, giving the gas mixture of HI, I_2, H_2, and H_2O. At the reboiler section of the column, the HIx is heated to around 310°C. The distilled HIx (HI, I_2, and H_2O) vapor flows over a catalyst bed at the top of the reactive column as shown in figure 1.4, and HI inside the stream of vapor is converted into H_2 and I_2 gases at 300°C. A condenser at the top of the column condenses the unreacted HI, I_2, and H_2O and the liquid is reflux back to the column.

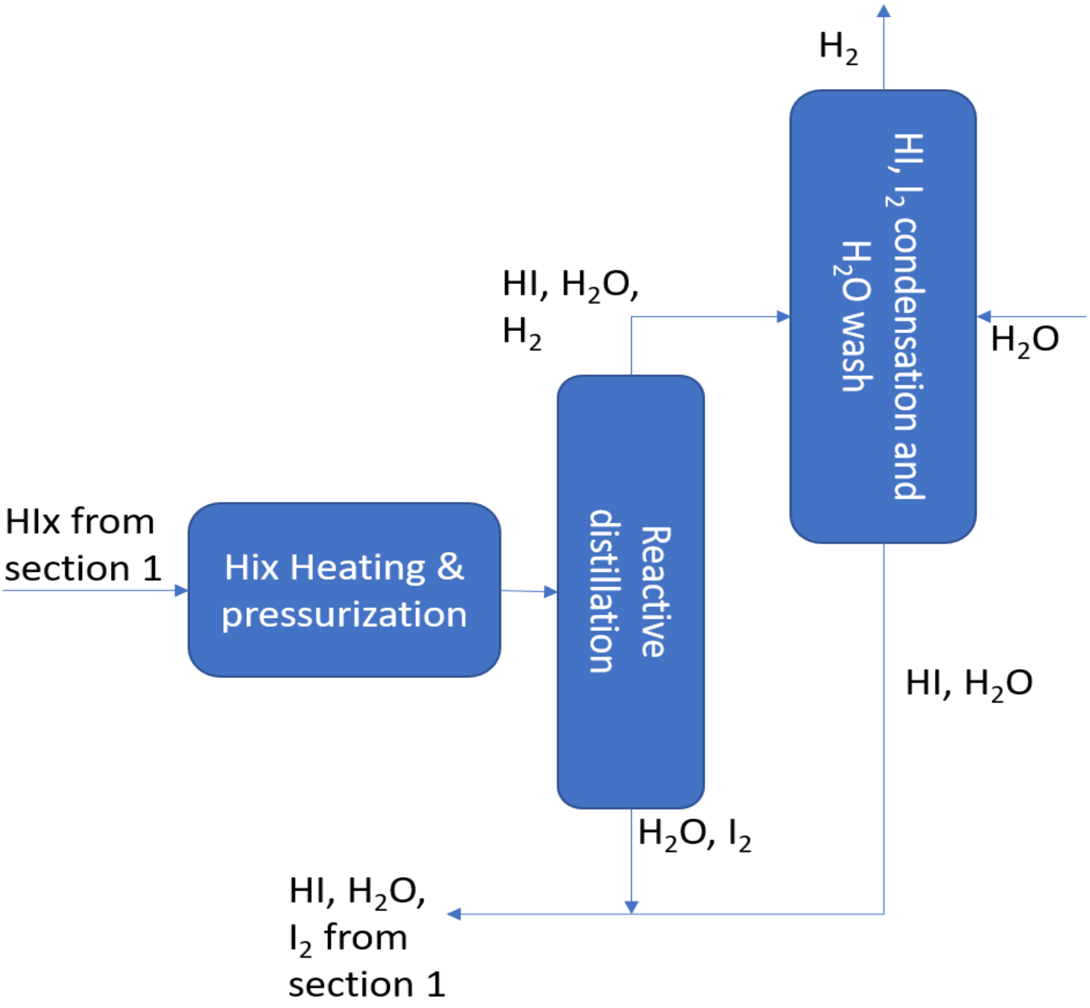


Fig. 1-4 Reactive Distillation Flowsheet

1.4 Objective of the study

Bunsen reaction constitutes one of the three main reaction steps of the I-S process and can be considered as the ‘key’ step as overall process feasibility, stability & efficiency are determined by the conditions of operation of this non-ideal reacting system. In this process step, water is reacted with iodine (I_2) and sulfur dioxide (SO_2) to obtain Hydriodic acid and sulphuric acid. Excess iodine and water are utilized to make the reaction feasible and to achieve product phase separation.

Bunsen reaction is a multiphase, reversible, and exothermic. Bunsen reaction involves a complex and highly non-ideal phase and chemical equilibrium [21]. It is challenging to understand the relative role of kinetics and mass transfer. Enhancement of purity of product phases, conversion & yield needs a close understanding of the role of operating conditions like temperature, compositions, etc. Phase and chemical equilibria of this highly non-ideal reacting system is another challenging task [63]. Contacting scheme, reactor type and size also have a severe bearing on reaction and product phase separation. Published literature on these aspects of the I-S process is not adequate. Bunsen reaction in continuous mode is carried out only up to 2 bar(g), which shows better yield and product purity, but beyond 2 bar(g) data is not available in the literature, hence to fill that gap it is planned to carry out the reaction at high pressures also in continuous mode. Thus, the objective of the research study is to understand the role of various operating conditions such as temperature, pressure, and feed composition purity and yield of product phases. Further, to develop a methodology to obtain the kinetic parameters for a heterogeneous reaction. To perform experiments to evaluate the mass transfer and kinetic parameters from the developed methodology. The objective includes identification studies on the side reaction occurrence regime so that such conditions are avoided during Bunsen reaction.

1.4.1 Scope of the study

The scope of the study is

1. To investigate the role of various operating parameters for the Bunsen reaction system which includes reactor temperature, reactor pressure, iodine to water ratio in the feed, and feed flow rates. Bunsen reaction will be carried out in a continuous & co-current mode.
2. During the phase separation, HI & I_2 are contaminants in the H_2SO_4 phase and H_2SO_4 is a contaminant in HI phase, to minimize/eliminate the cross-contamination; temperature, pressure, and feed composition need to be selected. Experiments will be carried out at different operating conditions to identify the impurity levels in each of the product phases.
3. Imprecise assessment of the kinetics of gas-liquid reactions may result in an inaccurate design of reaction apparatus as the precision of process modelling strongly depends on the quality of the model parameters. Modeling will be carried out to model the Bunsen reaction system and obtain the kinetic parameter which also includes mass transfer effects. In value, the mass transfer coefficients and the interfacial area has to be identified in these units and the consequence of the chemical reaction may be then parted from the diffusion mass transfer. Hence experiments will be carried out to determine the unknowns.
4. Undesired side products (reactions 1.2 & 1.3) such as hydrogen sulfide and sulfur are formed during the Bunsen reaction, to eliminate such undesired products and maximize the yield, Iodine content & temperature play a vital role that needs to be identified. Under lower amounts of excess I_2 there is a formation of side products, as I_2 presence makes a strong complex formation with HI and H_2O, in the case of lower I_2, HI easily reacts to form side products which are why I_2 concentration plays a major role in the inhibition of side reactions.

$$H_2SO_4 + 6\ HI \rightarrow 3I_2 + 4H_2O + S \qquad (1.2)$$

$$H_2SO_4 + 8\ HI \rightarrow 3I_2 + 4H_2O + H_2S \qquad (1.3)$$

Hence experiments will be conducted to identify the limiting conditions of operating parameters to avoid side reaction of Bunsen reaction product phases.

1.5 Layout of the thesis

The thesis is structured with an introduction to hydrogen as an energy carrier. A brief discussion on the properties of hydrogen, advantages, and challenges involved in the application of hydrogen is discussed and is presented in the first chapter.

The first chapter also presents the hydrogen production method by the iodine-sulfur process and its brief process flow sheet. The importance of the Bunsen reaction is presented. The scope of the study is discussed in this chapter.

In the second chapter, hydrogen production methods are discussed. Methods that are being used to produce hydrogen and other routes that are in the research stage are also discussed. This chapter presents an extensive literature survey on the Bunsen reaction of the iodine-sulfur process. The studies which have been carried out in Bunsen reaction, phase separation, side reactions are presented and discussed. Gap areas in the study and motivation of the study to fill the gap areas are discussed in this chapter.

In the third chapter experimental methodology is discussed. The experimental setup which has been developed for all the experiments are described in this chapter. Bunsen reactor and simplified process flow diagram are represented. All the features of the experimental facility including safety features are given in this chapter. The kinetics study apparatus for the Bunsen reaction study is also explained. Side reaction experimental setup and Bunsen reaction product phase settling setup are described. Sampling methodology under high-pressure conditions is described. Analysis of various samples and the method of analysis are described.

In the fourth chapter, all the experimental conditions are given. Initially schematic of the experimental setup is described. The methodology is given for the selection of experimental conditions for experiments involving cross-contamination of Bunsen reaction product phases. Similarly, an experimental schematic is described for the Bunsen reactor and experimental conditions are presented for carrying out Bunsen reaction in co-current continuous mode operation. The methodology to obtain the mass transfer coefficient and kinetic rate constant is presented. Various options to obtain these parameters are discussed. Justification for the selection of a stirred reactor to obtain mass transfer coefficient and kinetic rate constant is discussed in this section. The experimental schematic is described and the experimental conditions presented.

In the fifth chapter, results are discussed for cross-contamination in Bunsen reaction product phases. The role of different operating parameters such as temperature, pressure, SO_2 flow rate, HIx flow rate on the contamination levels of two product phases is discussed. In another section of chapter 5, the results of the Bunsen reaction in co-current continuous mode operation are presented. The effect of various operating conditions such as iodine to water ratio in the feed, temperature, pressure, feed flow rates on the concentrations of Bunsen reaction products are discussed. Results of experiments conducted to obtain mass transfer coefficient and kinetic rate constant are presented in this subsection. The rate of pressure variation with time at different operating conditions is presented. Finally, validation of the methodology adopted to obtain reaction parameters is verified from the results. Results are presented and discussed for the side reaction of Bunsen reaction at various operating conditions. Settling rates of Bunsen reaction product phases are presented in the subsection of this chapter. Chapter six gives the conclusion of the thesis based on the key finding of the research study. Recommendations for future studies are also presented in this chapter.

2 LITERATURE SURVEY

2.1 Introduction

A literature survey is presented in this chapter. Initially different hydrogen production technologies are described. Later detailed literature survey of Bunsen reaction is described. Bunsen reaction has been carried out in the literature in different modes such as semi-batch, continuous mode. The conditions of experiments, results are discussed. Liquid-Liquid phase separation experiments are conducted in the literature by premixing product solutions. The results of these studies are briefly discussed. Further side reactions experiment details and results are presented. There are different methods to carry out Bunsen reaction such as adding solvents etc… which are also covered in this chapter. Gap areas in the literature are identified.

2.2 Hydrogen Production Technologies

Hydrogen can be manufactured from diversified raw materials; such as from fossil-based resources and renewable sources. Different technologies can be adopted, such as chemical, electrolytic, biological, photolytic, and thermo-chemical. Different process technology has distinctive features, advantages, and challenges. Type of feedstock, technology readiness, applications, and costs are the influencing factors for hydrogen production. A brief description of process technologies is presented in this chapter.

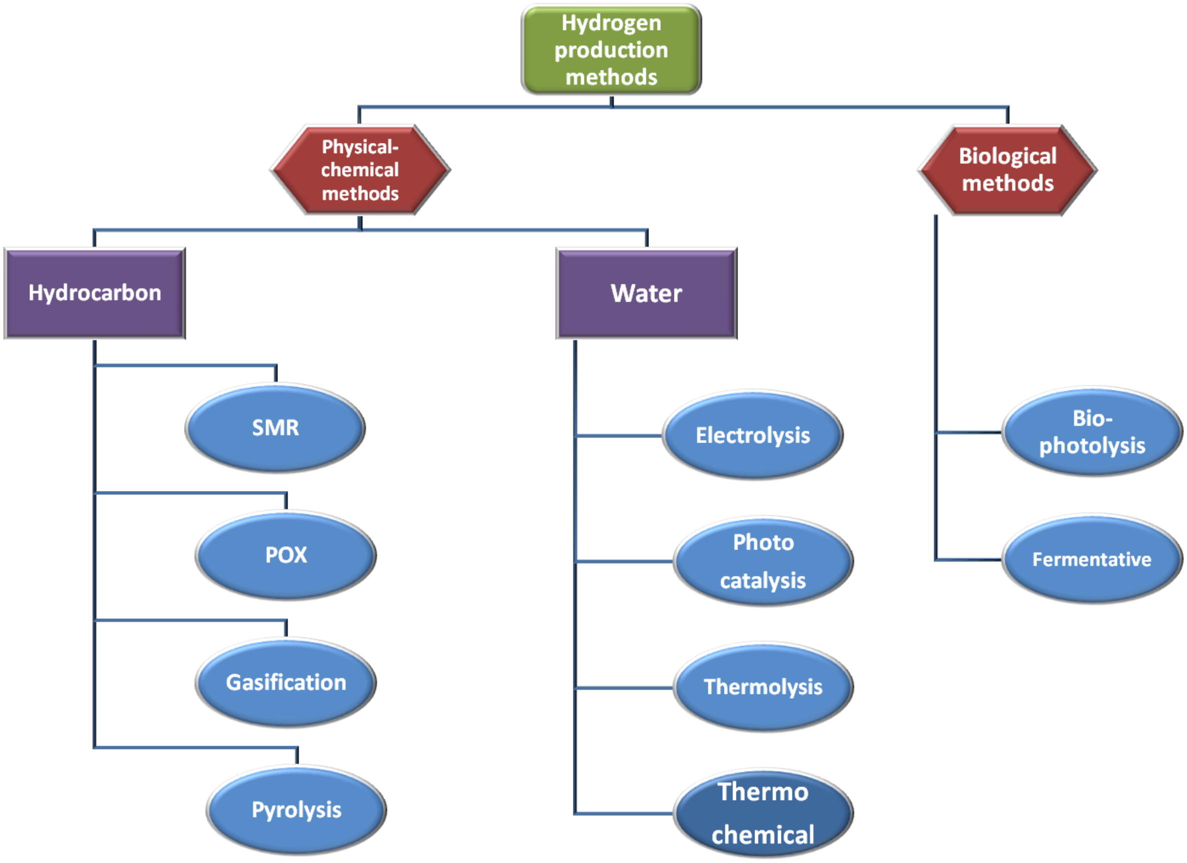


Fig. 2-1 Hydrogen production Methods

2.2.1 Role of Hydrocarbon-to-Hydrogen Technologies

Hydrocarbons (natural gas (NG) and petroleum) account for approximately 50% and 30%, respectively of the global production of hydrogen. Most of the hydrogen produced is based from petroleum feed material such as residual oil and refinery off-gases and is consumed with in refineries. About 4% of hydrogen is produced by electrolysis of water.

Overall, the oxidative based processes from hydrocarbons to hydrogen are proven technologies. Industrial hydrogen production processes such as steam methane reforming, partial oxidation, auto thermal reforming fit in this group. The water spitting process is not very well established except for water electrolysis. Hence any research input becomes an important contribution to establishing the processes involving the thermochemical splitting of water.

2.2.2 Steam Methane Reforming (SMR)

SMR is a widely used process for the industrial manufacture of hydrogen. The process know-how is well established and economically accessible at a extensive volume range, from tonnes per hour H_2 for minor distributed units to around 100 t/h H_2 for big ammonia production units [28].

Steam and methane as a mixture is flowed in the jacket heated tubes call as reformers. The tubes are filled with Ni catalyst, the reaction occurs in the mixture and finally it converts to CO and H_2 at 850‑900°C as given in the equation:

$$CH_4 + H_2O \rightarrow 3H_2 + CO \quad \Delta H = 206 \text{ kJ/mol} \qquad (2.1)$$

It is a highly endothermic reaction and enhances by low pressures.

Stream reacts with CO on a bed of catalyst forming H_2 and CO_2.

$$CO + H_2O \rightarrow H_2 + CO_2 \qquad (2.2)$$

Reaction 2.2 is exothermic.

For the hydrogen plant with a capacity of 1.5×10^6 Nm^3/day, the energy efficacy was 89% (basis of high heating value). In comparison to the I-S process of 4×10^6 Nm^3/day, the efficiency comes around 41 %. The major pros of the SMR are that it is an established technology suitable for massive hydrogen production. However, it contributes to greenhouse gas emissions. The fuel which it adopts will exhaust in the near future.

2.2.3 Partial Oxidation (POx) of Hydrocarbons

The partial oxidation of hydrocarbons is alternative way to produce hydrogen on an industrial level. In this process, hydrocarbons and air (or oxygen) are mixed in amounts such that fuel is transformed into a stream of H_2 and CO.

The synthesis gas is produced based on catalytic gas-solid reactions using oxidant O_2 (or air) and is denoted as catalytic POx (CPO). The CPO of natural gas is given by the following equation:

$$CH_4+1/2O_2 \rightarrow CO+2H_2 \qquad (2.3)$$

Both oxygen and air might be deployed in the CPO reaction. One of the major cons of this process is that it utilizes higher molecular weight hydrocarbons which in turn lead to more CO_2 emissions. The efficiency of this process is slightly lesser than SMR.

2.2.4 Autothermal Reforming

The Auto thermal reforming (ATR) method is a grouping of SMR and POx methods in this the heat energy to produce synthesis gas is obtained from combustion of the feed of hydrocarbon in an adiabatic reactor. The autothermal reformer has 3 divisions as shown in Figure 2.2 and they are combustion, thermal, and catalytic division. The feed is introduced to the combustion zone and mixed with steam and oxygen or air. The combustion reaction can be shown as follows:

$$CH_4 +3/2O_2 \rightarrow CO +2H_2O \qquad (2.4)$$

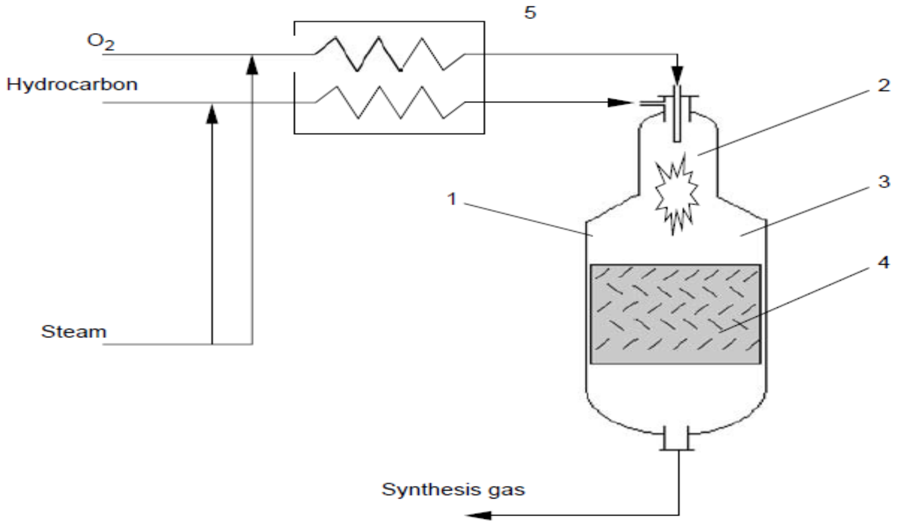


Fig. 2-2 Schematic illustration of the ATR reactor from hydrocarbons. 1- reformer, 2- flame generation section, 3- combustion section, 4-catalyst, 5-heater.

In the thermal division, over the bed of catalyst, more conversion happens by gas-phase reactions by homogeneously. The key reactions in the thermal division are gas-phase SMR homogeneous reaction and shift reactions.

In the catalytic division, a bed of Ni based catalyst performs the steam reforming of hydrocarbons in the pressure range of 1.8‑6.7 MPa [28]. This process has the benefit of utilizing the pros of both SMR and POX processes. But the problem of emissions remains that of greenhouse gas emissions. The fuel used in this process is limited in the earth's reserves.

2.2.5 Hydrogen Production from Coal

Production of hydrogen from water by using coal in an oxidation and reduction chemical reaction.

$$C + H_2O \rightarrow H_2 + CO \tag{2.5}$$

Production of hydrogen from coal, in which O_2 or water vapor is flowed on the bed of coal producing H_2, CO, and CO_2 from where H_2 is removed (Figure 2.3).

Throughout the earlier numerous years, hydrogen produced from coal is mostly utilized in zones to produce methane, methanol, ammonia, and Fischer‑Tropsch products as described in Figure 2.4.

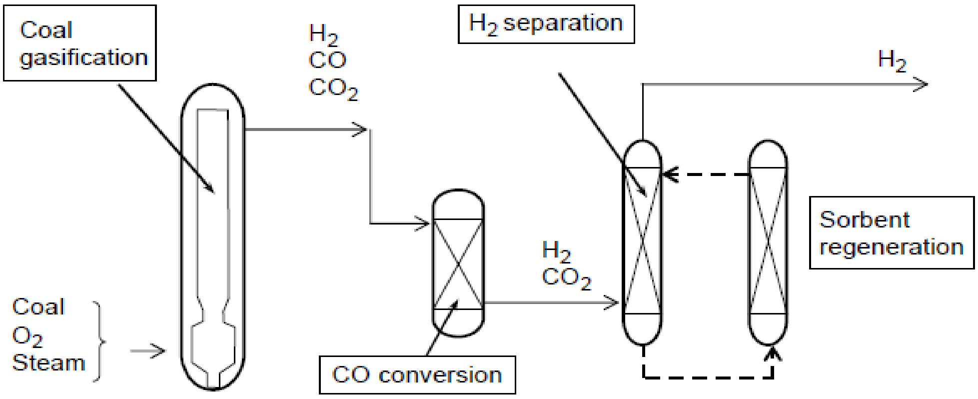


Fig. 2-3 Production of H_2 from Coal gasification

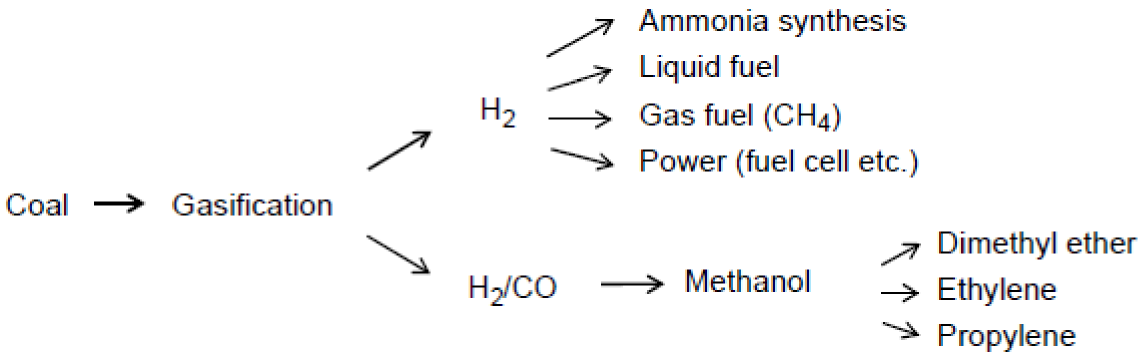


Fig. 2-4 Current uses H_2 derived from Coal

Hydrogen production from coal is expensive process compared to using feed stock of oil or natural gas. But hydrogen produced from coal can be used wherever natural gas is not easily available and also coal is plentifully available. This process leads to the highest CO_2 emissions. This is a suitable process for a short-term basis only with sequestration of CO_2.

2.2.6 Coal Gasification

In the process the conversion of coal into syngas is given by following reactions:

$$C + O_2 \rightarrow 2CO \text{ (gasification of oxygen)} \tag{2.6}$$

$$C + H_2O \rightarrow H_2 + CO \text{ (steam gasification)} \tag{2.7}$$

$$C + 2H_2 \rightarrow CH_4 \text{ (hydrogasification)} \tag{2.8}$$

The water gas shift reaction is a gas-phase reaction. It is an vital reaction which dictates the equilibrium amongst CO, H_2, CO_2, and H_2O.

$$CO + H_2O \rightarrow H_2 + CO_2 \text{ (water-gas shift reaction)} \tag{2.9}$$

2.3 Electrolysis of Water

Electrolysis of water is a method of producing hydrogen, and by-product oxygen, by the direct decomposition of water molecules using electric energy [64]. Water electrolysis is already commercially practiced in the 1890s. Some installations are operating around the beginning of the twentieth century. In the 1920s and 1930s, several plants in over 10 MWe size are constructed [65,66]. Industrial research and development to improve the economic performance of the method has continued to this very date [67-69]. The newly developed electrolysis cells include the high-pressure designs and state-of-the-art membrane electrolyte designs.

The electrolysis of water is a combination of two half-reactions as shown below. The equations are different by electrolyte type.

Acid electrolyte:

$$\text{Anode: } H_2O \rightarrow 2H^+ + 0.5O_2 + 2e^- \tag{2.10}$$

$$\text{Cathode: } 2H^+ + 2e^- \rightarrow H_2 \tag{2.11}$$

Alkaline electrolyte:

$$\text{Anode: } 2OH^- \rightarrow H_2O + 0.5O_2 + 2e^- \tag{2.12}$$

$$\text{Cathode: } 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{2.13}$$

Figure 2.5 is a schematic of an alkaline-water electrolysis (AWE) cell. A porous diaphragm acts as a barrier by preventing the mixture of product gases and through contact of electrodes. Though asbestos is used first, alternative materials are being researched [70]. The major disadvantage of this process is that the process has a lower efficiency of around 20-22 %. This process is not suitable for massive hydrogen production.

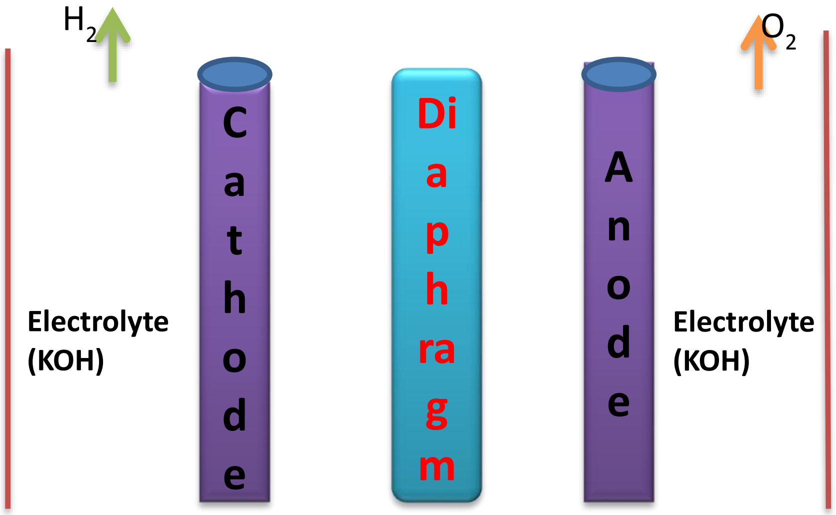


Fig. 2-5 Schematic of an alkaline-water electrolysis cell

The process of the high-temperature electrolysis (HTE) of steam is a reaction in reverse direction when compared with solid-oxide fuel cell (SOFC) [71-73].

$$H_2O\,(g) + 2e^- \rightarrow H_2(g) + O^{2-} \tag{2.14}$$

Reactions on the two electrodes are given as,

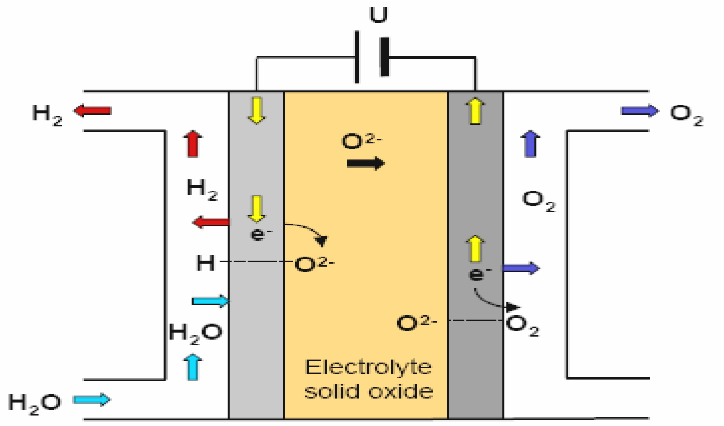
Cathode reaction:

$$H_2O + 2e^- \rightarrow H_2 + O^{2-} \tag{2.15}$$

Anode reaction:

$$O^{2-} \rightarrow \tfrac{1}{2}O_2 + 2e^- \tag{2.16}$$

The porous cathode is Ni-YSZ and the porous anode is LSM-YSZ [71-73]. This process is having higher efficiency of around 42 %. This process is also not advisable for large scale hydrogen production.



Cathode Anode

Fig. 2-6 High-Temperature Cell

2.4 Thermochemical Processes

2.4.1 Principle of Thermochemical Processes

Direct decomposition of water requires temperatures greater than 3500 °C. However, the incorporation of chemical reactions to the decomposition process can lower the temperature threshold of the heat to be required [74, 75]. Figures 2.7 - 2.9 explains the concept. The reactions are given below to satisfy these enthalpy/entropy balances.

$$\Delta H_{WS} = \sum_i \Delta H_i$$

$$\Delta S_{WS} = \sum_i \Delta S_i$$

$$\Delta G_i = \Delta H_i - T_i \Delta S_i$$

Reaction i proceeds without work input at the temperature of $\Delta Gi \leq 0$. When all the reactions are operated at Ti (= Δ Hi/ Δ Si), Δ Gi of all the reactions is 0. If Δ Hi is plus and Δ Si is minus, such Ti is impossible (case (1) in Figure 2.9). This is also the same in the case of Δ Hi is minus and Δ Si is plus (case (4)). And when both Δ Hi and Δ Si are plus in all the reactions, Ti is higher than Td at least one reaction shown as a line (1) in the upper diagram of Figure 2.8 Therefore, ΔHi must be plus and ΔSi must be minus in at least one reaction when all Ti is lower than Td, as line (1) of lower diagram of Figure 2.9. Figure 2.7 is an example of a 2-reaction process.

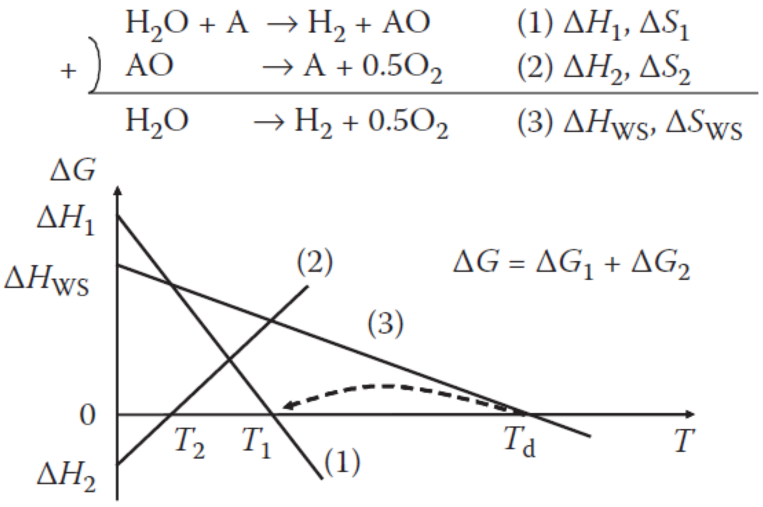


Fig. 2-7 Concept of thermochemical water splitting

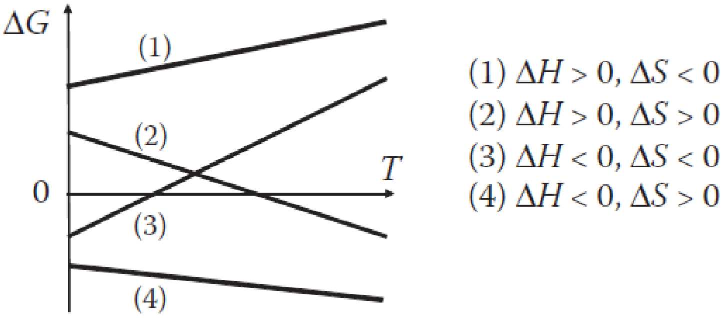


Fig. 2-8 Relation of reaction enthalpy, entropy and Gibbs energy

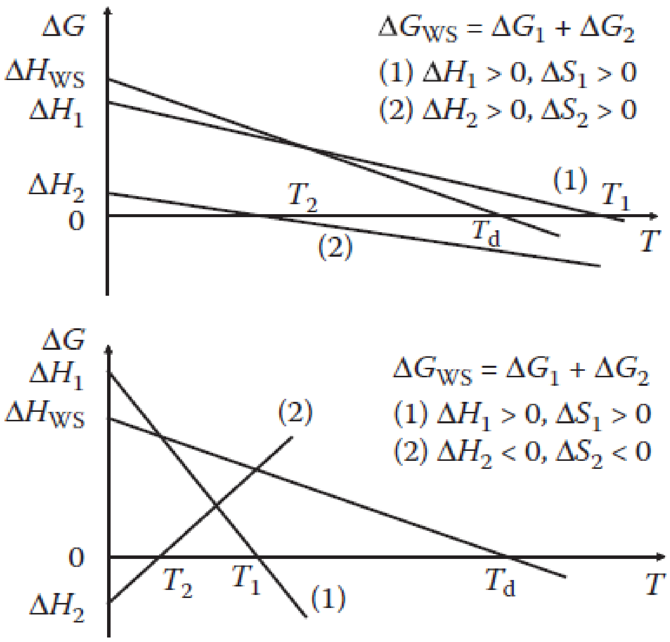


Fig. 2-9 G–T diagram of thermochemical water splitting.

2.4.2 History of Thermochemical Processes

The concept of thermochemical water splitting is not new [76]. A two-step HgO/Hg cycle is patented as early as in 1925 [77]. However, R&D of the concept is activated in the early 1960s by the theoretical proposition based on thermodynamics in the Energy Depot project of the U.S. Army and others [78]. Effective hydrogen production processes with two steps of thermal reaction are not found in the temperature range below 1100°C. Instead, a three-step Ta–Cl cycle and a four-step V–Cl cycle are proposed as examples [79].

The Joint Research Centre (JRC) Ispra, Italy, of the European Commission, has carried out a series of extensive research [80]. The research at JRC Ispra proceeded in three phases [81, 82]. In the first phase, verification of each reaction of the Mark 1 cycle by experiment, measurement of a thermodynamic property of $CaBr_2$, corrosion test of materials, flowsheet, and cost evaluation are performed [83].

Separation of H_2SO_4 and HI produced by Bunsen reaction is a major problem of the Mark 16 process. A variety of extracting agents is tried to separate them [65]. Nevertheless, this cycle is researched for a long time after the JRC study as S‑I or I-S process.

Rheinisch-Westfälische Technische Hochschule (RWTH) Aachen, Germany, has researched under Euratom, the same as JRC Ispra. The group has researched mainly on Fe-Cl cycles earlier and on I-S process later.

GA, SNL, and Commissariat à l'Énergie Atomique (CEA), France, have participated in the project on thermochemical hydrogen production called as International Nuclear Energy Research Initiative (I-NERI) program [84].

HYTHEC (Hydrogen THErmochemical Cycles) project, a project of the European Community Framework 6 program "Innovative Routes for High-Temperature Hydrogen Production (INNOHYP)," is carried out in collaboration with several European institutes, universities, and companies from 2004 to 2007 [85, 86].

I-S process is selected as the main target and some other cycles such as the Westinghouse process, UT-3 cycle as alternatives [65, 87- 98].

In Japan, the research on the I-S process by JAEA has continued [99-101]. South Korea and China also have researched the I-S process [102-104]. Tsinghua University, China, started R&D on hydrogen production through the I-S process in 2005 considering HTR-10, a High-Temperature Gas-cooled Reactor as a heat source [65].

Indian Scenario:

India is working on I-S, Cu-Cl, and HTSE processes for the Production of Hydrogen.

Hybrid processes that involve electrical energy as direct inputs to drive one of the chemical reactions are also being studied in the literature [105].

2.4.3 Iron-Chlorine (Fe-Cl) Cycle

Fe-Cl is a chlorine family thermochemical cycle. This cycle is capable to explore due to the richness of Iron as a substance and cheaper cost compared to the other materials.

During the valuations by Lewis et al. [84] in 2011, Fe-Cl was suggested for additional examination due to the material richness and feasibility of the reactions. The early research on iron-chlorine TWSC was performed by RheinischWestfalische Technische Hochschule (RWTH) Aachen in the late 1970s [106]. Fe-Cl was recognized as a feasible cycle while the main challenges were found to be poor reactivity of thermal decomposition of $FeCl_3$ and hydrolysis of $FeCl_2$.

Chlorification of Fe_3O_4 with Cl_2 and/or HCl to iron chlorides ($FeCl_2$, $FeCl_3$, etc.), reverse Deacon reaction (Equation 2.20) are taken as feasible considering chemical engineering.

The following four-step reaction is recommended for the cycle.

$$3FeCl_2 + 4H_2O \rightarrow Fe_3O_4 + 6HCl + H_2 \text{ at } 650\ ^{o}C \tag{2.17}$$

$$Fe_3O_4 + 8HCl \rightarrow FeCl_2 + 2FeCl_3 + 4H_2O \text{ at } 125\ ^{o}C \tag{2.18}$$

$$2FeCl_3 \rightarrow 2FeCl_2 + Cl_2 \text{ at } 425\ ^{o}C \tag{2.19}$$

$$Cl_2 + H_2O \rightarrow 2HCl + 0.5\ O_2 \quad \text{at } 650\ ^{o}C \tag{2.20}$$

$$H_2O \rightarrow H_2 + 0.5\ O_2 \tag{2.21}$$

The benefits of the cycle are the low material costs, the chemistry of iron compounds is well known. The hydrolysis and reverse Deacon steps are endothermic while chlorination and thermal decomposition steps are highly exothermic. One of the key problems is the thermal decomposition of $FeCl_3$. Decomposition of $FeCl_3$ with a two-step reaction by using CO (Equations 2.22 and 2.23) is proposed.

$$2FeCl_3 + CO \rightarrow 2FeCl_2 + COCl_2 \tag{2.22}$$

$$COCl_2 \rightarrow CO + Cl_2 \tag{2.23}$$

Thermal decomposition reaction, lowering the temperature of reverse Deacon reaction and hydrolysis as well as the separation of the HCl and solid products are reported as the key issues of this cycle.

2.4.4 Copper-Chlorine (Cu‑Cl) Cycles

The copper–chlorine cycles are of different types. The characterization is done based on the number of major steps involved [109-111]. The cycle consists of three, four, and five-steps. The five-step cycle is compared with three and four step cycles.

Chlorination reaction

$$2Cu(s) + 2HCl(g) \rightarrow 2CuCl(molten) + H_2(g),\ 450\ °C \quad (2.24)$$

Disproportionation reaction -electrolysis

$$4CuCl(aq) \rightarrow 2Cu(s) + 2CuCl_2(aq),\ 30–80\ °C \quad (2.25)$$

Drying step

$$CuCl_2(aq) + nfH_2O(l) \rightarrow CuCl_2 \cdot nhH_2O(s) + (nf - nh)H_2O \quad (2.26)$$

nf > 7.5, nh is 0–4, at 100–260 °C (spray drying) or 30–80 °C (crystallization)

Hydrolysis reaction

$$2CuCl_2 \cdot nhH_2O(s) + H_2O(g) \rightarrow CuOCuCl_2(s) + 2HCl(g) + nhH_2O(g),\ 375\ °C \quad (2.27)$$

Decomposition reaction

$$CuOCuCl_2(s) = 2CuCl(molten) + 0.5O_2\ (g),\ 530\ °C \quad (2.28)$$

Four-step copper–chlorine cycle

Chlorination reaction

$$2Cu(s) + 2HCl(g) \rightarrow 2CuCl(molten) + H_2(g),\ 450\ °C \quad (2.29)$$

Disproportionation reaction

$$4CuCl(s) \rightarrow 2Cu(s) + 2CuCl_2(aq)\ \ 30–80\ °C \quad (2.30)$$

Oxychlorination reaction

$$CuCl_2(aq) + nfH_2O(l) \rightarrow CuOCuCl_2(s) + 2HCl(g) + (nf - 1)H_2O(g),\ 375\ °C \quad (2.31)$$

Decomposition reaction

$$CuOCuCl_2(s) \rightarrow 2CuCl(molten) + 0.5O_2\,(g), \text{ at } 530\ °C \qquad (2.32)$$

Three-step copper–chlorine cycle

Chlorination reaction

$$2Cu(s) + 2HCl(g) \rightarrow 2CuCl(molten) + H_2(g), \text{ at } 450\ °C \qquad (2.33)$$

Disproportionation reaction

$$4CuCl(s) \rightarrow 2Cu(s) + 2CuCl_2(aq), \text{ in HCl acid at } 30–80\ °C \qquad (2.34)$$

Oxychlorination reaction

$$CuCl_2(aq) + nfH_2O(l) \rightarrow 2CuCl(molten) + (nf - 1)H_2O(g) + 2HCl(g) + 0.5O_2(g), \text{at } 530\ °C \qquad (2.35)$$

It can be found that Oxychlorination reaction is approximately comparable to the combination of reactions 3 and 4 of the four-step cycle or the combination of reactions 3, 4 and 5 of the five-step cycle.

Advantages of the copper–chlorine cycle are mainly medium temperature operation, the capability to use waste heat thereby improving energy efficiency, and lower material cost. In relation to other thermochemical cycles, the Cu–Cl process requires temperatures of up to 530 °C. The electrochemical step requires a relatively low voltage (0.6 to 1.0 V) [110]. The estimated overall efficiency of the Cu–Cl cycle is 43% [111].

The major disadvantage of the process is the handling of solids and corrosive reagents this is a challenge for the development of engineering scale equipment.

2.4.5 Hybrid-Sulfur process Cycle

The hybrid-Sulfur process, a sulfur-based process, is one of the efficient and green technologies for the production of hydrogen which uses direct heat energy [112].

The hybrid-Sulphur process is a two-step process for hydrogen production by splitting water. Two reactions are shown here.

1. $SO_2+H_2O \rightarrow H_2SO_4+H_2$ (Electrochemical step, ~25-80°C)

2. $H_2SO_4 \rightarrow SO_2+H_2O+O_2$ (Endothermic reaction, ~800-900°C)

Process inputs are water, heat (either solar/nuclear), and electrical energy (either solar/grid) with recycle of all other intermediate chemicals (H_2SO_4 & SO_2). This process has a predicted maximum thermal efficiency of 45% [114]. Small and medium scale hydrogen production plants in the near future are viable through HyS process.

SO_2 Depolarised electrolysis is an electrochemical reaction step, where hydrogen and sulfuric acid are formed from SO_2 and H_2O. This is a low-temperature step in the range of 25 to 80°C. Sulphuric acid produced in electrolysis is decomposed in the acid decomposition step and produces SO_2, O_2 & H_2O, in which SO_2 & H_2O are recycled back to the electrolysis step. The acid decomposition step is the high-temperature step (~800-900°C) of the process. The pros of the process are high efficiency, two-step process but it involves corrosive chemicals.

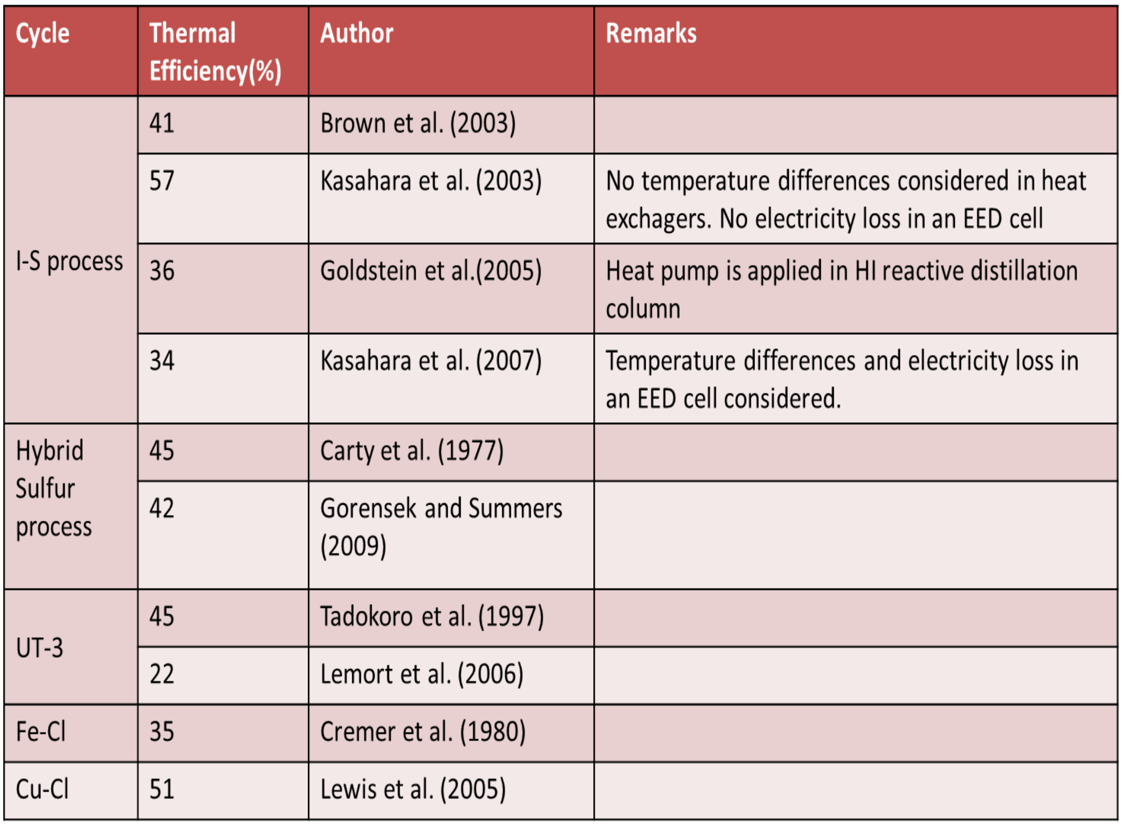
2.4.6 Process Thermal Efficiency

Thermal efficiency is an important performance indicator of the water-splitting processes. Although many definitions of efficiency exist, the most desirable definition is based on thermodynamics as follows:

$$\eta_{\mathrm{WS}} = \frac{\Delta H_{\mathrm{HHV}}}{\sum_i Q_{\mathrm{WS},i} + \sum_i W_{\mathrm{WS},i}/\eta_{\mathrm{WG}}} \qquad (2.36)$$

This definition applies to any type of method including pure thermochemical cycles, hybrid cycles, and electrolysis because it takes electric energy generation into account. HHV is more appropriate because liquid water is fed to the water-splitting processes and H_2O is liquid at 25°C [86, 101, 113-114]. Table 2.1 summarizes thermal efficiency by studying the flow sheets.

Table 2-1 Efficiencies of different thermo-chemical cycles



Cycle	Thermal Efficiency(%)	Author	Remarks
I-S process	41	Brown et al. (2003)	
	57	Kasahara et al. (2003)	No temperature differences considered in heat exchagers. No electricity loss in an EED cell
	36	Goldstein et al.(2005)	Heat pump is applied in HI reactive distillation column
	34	Kasahara et al. (2007)	Temperature differences and electricity loss in an EED cell considered.
Hybrid Sulfur process	45	Carty et al. (1977)	
	42	Gorensek and Summers (2009)	
UT-3	45	Tadokoro et al. (1997)	
	22	Lemort et al. (2006)	
Fe-Cl	35	Cremer et al. (1980)	
Cu-Cl	51	Lewis et al. (2005)	

2.5 Iodine-Sulfur Thermochemical process

Thermochemical cycles produce hydrogen from a sequence of chemical reactions, where the net reaction is the hydrogen and oxygen production by spitting water at a much lower temperature than the indirect thermal decomposition of water [20]. The Closed-loop Iodine-sulfur process is a high temperature nuclear reactor/solar heat based pure thermochemical cycle. It is one of the most efficient thermochemical processes [115]. It contains three chemical reactions and is considered suitable for large scale cost-effective production of environmentally attractive hydrogen.

The iodine sulfur thermochemical cycle is developed at General Atomics subsequently numerous important features in the three reactions were studied and identified. The features involve catalytic reactions, phase separations, etc. The initial objective of General Atomics is to study three reactions reasonably well in the laboratory. Thereafter study related to estimating the energy efficiency of this cycle is taken up. It has encouraging efficiency (to ~47%) to investigate further development. Research is principally inclined towards the engineering aspects of the cycle, which includes a bench-scale unit, engineering design, and economics. [21].

Department of Energy through General Atomics in the year 1977 started the design and construction of a bench-scale unit to perform the iodine-sulfur thermochemical cycle as one continuous operation. The purpose of the bench-scale work is generally to study the actual processing steps and their interactions by conduction key continuous flow reactions and separation steps. The purpose of the study also includes fluid handling, key operation behaviour, and the effects of incomplete physical separations and possible side reactions [116].

Bunsen reaction (exothermic at 20-120^{0}C)

$$I_2 + SO_2 + 2\ H_2O \rightarrow 2HI + H_2SO_4 \qquad (2.37)$$

Hydroiodic acid decomposition (endothermic at 300-450^{0}C)

$$2HI \rightarrow H_2 + I_2 \qquad (2.38)$$

Sulfuric acid decomposition (endothermic at 800-900^{0}C)

$$H_2SO_4 \rightarrow H_2O + SO_2 + 0.5\ O_2 \qquad (2.39)$$

Reaction (2.37) is a Bunsen reaction. Reactions (2.38) and (2.39) are catalytic sulphuric acid and hydroiodic acid decomposition reactions at high and medium temperatures respectively. Here water, SO_2, and iodine are reused and H_2 and O_2 are out as a product.

While the excess water in the Bunsen process is required to make the process spontaneous, the heat released at low temperatures cannot be effectively exploited resulting in a substantial loss in energy. The energy obtained at low temperatures cannot be efficiently utilized and the irreversible process decreases the cycle efficacy.

Bunsen reaction is known as the Karl fisher reaction and is utilized in aquametry. In this reaction [117], it is essential to invest minimum energy for the separation of phases.

The characteristics of the I-S process are that this process is all fluid (liquids, gases) process, therefore well suited for continuous operation. It is a closed system without any effluents. The recycle streams contain corrosive components namely iodine, sulfur dioxide, hydriodic acid, sulfuric acid; therefore, this requires superior materials for engineering scale process equipment. This process heat can be obtained from solar, nuclear-based sources.

The literature survey on the Bunsen section mainly classifies into four parts. The first part includes reaction studies which include reaction equilibrium and kinetics studies. The second part includes studies on liquid-liquid phase separation studies. The third part includes side reaction studies during and after the Bunsen reaction. Apart from these studies some of the researchers focussed on alternative methods to carry out Bunsen reaction and phase separation such as the electrochemical route, use of solvents, use of precipitating agents, etc are covered in the fourth part.

2.5.1 Studies on Bunsen reaction

Davis M E *et al* (1982) have carried out the analysis of efficiency and entropy production of the Bunsen reaction. Theoretical calculations are carried out to study the efficiency of the Bunsen reaction. The study determined that the selection of operating conditions for the Bunsen reaction is integrally connected to the total process flow sheet [118]. But the study is not backed by experiments to assure the calculated efficiencies of Bunsen reaction are correct. Shimizu et al (1992) has studied the Bunsen reaction at 20^oC in a wide range of H_2O, $I_{2,}$ and HI concentrations at ambient temperature in the bench-scale studies. The study has adopted a lower temperature because of the easier handling of chemicals at room temperature in the apparatus. Experiments are conducted by passing SO_2 along with N_2 gas to the H_2O-I_2-HI mixture which reacts rapidly. Feeding of reactant SO_2 was stopped when the concentration of SO_2 in the tail gas from the Bunsen reactor grew to 500 ppm. In the study during the experimentation cyclic operation was frequently stopped due to the disappearance of the two-phase separation. The study has discussed the role of the excess of H_2O and iodine in Bunsen reaction on the formation of a homogeneous solution of HI and H_2SO_4 at lower concentrations of the former chemicals. Further, the study has obtained the correlation between the molar fraction of H_2O, for HI-H_2SO_4-H_2O system and density at 20°C under conditions of iodine saturation. The conclusions of the study were, at a molar fraction of feedwater below 0.92 two-phase separation occurs. Decreasing water amount in the feed has led to an increase in HIx phase density. However, the density of the sulfuric acid phase remained constant at 1.4 g/cc [119]. The study is limited to a temperature of 20°C where cross-contamination levels of the two phases are high. It is thus required to explore wide operating ranges.

Leybros J et al (2009) has discussed a conceptual design of the Bunsen reactor. The design of the Bunsen reactor has incorporated reaction cum separation in a single counter-current reactor. The design has considered the separation of SO_2 and O_2 before the introduction into the Bunsen reactor. The study emphasized two criteria which must be considered, the first one is the reaction time must be minimized to avoid side reactions (volume of the reactor for the reaction is limited) and enough heat exchange area to remove the exothermic heat and maintain isothermal conditions. The combination of these two constraints results in a reactor consisting of a series of continuously stirred reactors in the axial direction in the form of a mechanically stirred column-type liquid-liquid contactor. Turbine impellers in every section of the reactor maintain conditions required for the chemical reaction. Further, the mixers facilitate heat transfer through the walls of the reactor to jackets to remove the exothermic heat of the reaction [120]. However, the design does not consider the reaction parameters which give partial sizing of the reactor.

Giaconia et al (2010) have carried out basic experimental studies using a glass reactor to characterize the Bunsen reaction between temperatures of 30-120°C and different initial compositions. Apart from the Bunsen reaction, purification of the HIx phase by removal of

H_2SO_4 and residual SO_2 is also discussed in the article. Also, iodine removal from the sulfuric acid stream is studied. A continuous lab-scale setup to study the Bunsen reaction and subsequent purification of the products acids are carried out. The reactor was firstly charged with iodine and 57 wt % HI (remaining water) solution, and heating arrangement is done. Gaseous SO_2 was fed and the reaction is carried out, upon completion of the reaction SO_2 is detected at the sensor both the reactor outlet and the alkaline (NaOH) trap outlet. The exothermicity of Bunsen reaction leads to a decreased amount of SO_2 being absorbed and reacted. However, the study is limited to atmospheric pressures and the inert gas is used as nitrogen.

The article discussed a continuous reactor configuration. In a continuous reactor, after absorption, SO_2 reacts with the dissolved iodine and water according to the Bunsen reaction stoichiometry and lighter sulfuric phase droplets nucleate, grow and approach interface on the top of the column; concurrently, the denser HIx phase settles at the bottom [121].

Parisi et al (2011) has carried out the Bunsen reaction by varying temperature and iodine content. Operation temperatures in the study have been varied from 30 ^{o}C up to 120 ^{o}C by saturating $HI-I_2-H_2O$ solutions with gaseous SO_2, and the iodine content has been changed between 0.22 and 0.57-mole fraction. At 30 ^{o}C and 45 ^{o}C tests have been completed at unsaturated conditions and also saturated conditions. The purpose of the study is to scrutinize the iodine concentration effect and also the temperature on the Bunsen reaction. Temperature and dissolved iodine are dependent, as the solubility of iodine depends on temperature. The solubility of iodine defines side reactions occurrences also, below a lower bound. It is observed in the study that at temperatures lower than 35 ^{o}C, the separation of the two phases is quite slow unless a great excess of water is adopted. Besides that, an increase in temperature and iodine concentration leads to a decrease in the solubility of the sulfur dioxide and reaction conversion but leads to a decrease in contamination of sulfates in the HIx phase, and thus improving the purification of acid. Particularly, at high enough temperature and the iodine content, it is probable to remove the sulfates from the HIx phase without the happening of secondary reactions [122]. The study is limited to atmospheric pressures without considering oxygen as a carrier gas.

Kim YH et al (2012a) have studied the features of Bunsen reaction on the reactor shape and temperature by using a counter-current continuous reactor. Experiments are carried out at ~90°C, with the molar ratio of I_2/HO varying from 0.250 to 0.450. The length to diameter ratios of a reactor was set at three different conditions those are 9.25, 13.71, and 21.67. The author studied the semi-batch Bunsen reaction initially. Later, the author has conducted the continuous Bunsen reaction at the same conditions of semi-batch experiments. The length to diameter ratio of the reactor has slightly affected the composition of each phase obtained from the continuous reaction. The author also studied the phase separation characteristics at different temperatures, in the continuous Bunsen reaction. It was observed that the molar ratio of HI/H_2SO_4 (an impurity) in an H_2SO_4 phase decreased from 0.08 to 0.03 by increasing the temperature and I_2 content. And the molar ratio of H_2SO_4/HI (an impurity) in a HIx phase decreased from 0.21 to 0.04 by increasing the temperature and I_2 content [123]. Though the study attempted continuous operation, the higher-pressure operation is not carried out.

Kim YH et al (2012b) have conducted the Bunsen reaction using a continuous counter-current reactor at the pressurized condition to investigate the characteristics of phase separation of Bunsen reaction. The results of the study indicated a steady-state operation. This is inferred from the constant composition of Bunsen products at the outlet. The conversion of the reactant increased at the pressurized condition. This is because of increased SO_2 solubility in water with pressure. In the study, the material of the construction of the counter-current flow reactor is of glass. This is to observe visually the phase separation of products. From the results, it was seen that the composition of the H_2SO_4 phase was barely influenced by the feed molar ratio of

I_2/H_2O. The study reported no side reaction products under pressurized operation [124]. Though the study has attempted higher pressure operation, the pressure is limited to 2 bar (g). The solubility of SO_2 still increases with pressure; hence there is a scope to explore higher pressure operation.

Kim YH et al (2012c) have studied the Bunsen reaction to obtain the effect of O_2 on the Bunsen reaction by supplying SO_2-O_2 mixture gases in the presence of HIx solution. The experiments have been conducted at I_2 saturation points of respective temperature with SO_2 and SO_2-O_2 mixture gases. The study has completed a series of the experiment at 60^{o}C with O_2/SO_2 molar ratios in the range of 0.2~0.5 to find the role of the amount of O_2 in SO_2-O_2 mixture gases. The results of the study were; irrespective of the operating temperature, the amount of unreacted I_2 with the feed of SO_2-O_2 mixture gases was very small, higher than those under the feed of SO_2 gas only. While the HI product quantity was relatively decreased. The amount of H_2SO_4 solution has decreased with increasing the O_2/SO_2 molar ratio. The important conclusion of the study is the amount of impurities in each phase produced from the Bunsen reaction with the HIx solution was barely influenced by the O_2/SO_2 molar ratios [125]. This study has been conducted at atmospheric pressures.

Kim HS et al (2013) have studied the Bunsen reaction using a counter-current continuous reactor, the Bunsen reaction and product separation steps are performed simultaneously, and the composition difference of each phase settled at the top and bottom of the reactor was examined. The process parameters are the molar ratio of I_2/H_2O, SO_2 feed flow, operating temperature. The study found that by maintaining steady feed flow and continuous product outflow, the concentrations remained steady even after 120 min of reaction time, demonstrating a steady-state process. The phase separation of the Bunsen reaction is marginally influenced by the SO_2 feed rate. The amount of I_2 fed increased with increasing temperature, but the volume of the H_2SO_4 phase from the top phase was unaffected, while that of the HIx phase settled from the lower phase increased correspondingly. In the study, the average molar composition of the H_2SO_4 phase ($H_2SO_4/H_2O/HI$) obtained at a typical operation condition (80 ^oC, I_2/H_2O molar ratio of 0.406) was 1/5.30-5.39/0.02-0.04, and the composition of the HIx phase ($HI/I_2/H_2O/H_2SO_4$) was 1/2.81-3.09/5.67-6.40/0.04-0.06 [126]. However, the study is not conducted at higher pressures and without O_2 as a carrier gas.

Ying Z et al (2013) have studied the effect of the initial HI amount in the feed solution and the operating temperature on the thermodynamics and kinetics of the Bunsen reaction. The author found that increasing the initial HI concentration in the feed or temperature (30 ^oC - 85^oC) has resulted in amplification of the reaction kinetic rate, and this led to the faster formation of liquid-liquid separation and a short time to attain the thermodynamic equilibrium. But the separation became tough by a further increase of the initial HI content. The liquid-liquid equilibrium (LLE) separation is improved with a rise in temperature. An increase in the initial HI content to some extent deteriorated the LLE phase separation at a lower temperature, while at 72^oC and 85^oC, the LLE phase separation characteristics showed little variation in the HI/H_2O molar ratio. The study obtained an over-azeotropic HI concentration in the HIx phase with feeding HI. The conversion of SO_2 lowered as the initial HI content and the temperature was increased [127]. However, this study also has been carried out at atmospheric pressures without oxygen as a carrier gas.

Zhu Q et al (2013) have conducted a series of experiments by charging the mixture of SO_2/N_2 in an iodine-water mixture in the temperature range of 63^oC-85^oC to study the kinetics and thermodynamics of the Bunsen reaction. The role of different operating parameters such as temperature, SO_2 flow rate, I_2 content, and H_2O content on the efficiency of SO_2 conversion and kinetic rate are reported. The results of the study exhibited that the SO_2 conversion ratio is nearly unaffected with a decrease in the SO_2 flow rate. In the experiments, it is reported that at the SO_2 flow rate of 50-70 mL/min, the input SO_2 is completely absorbed into the aqueous solution until the saturation of the reaction is detected. An increase in the I_2 or H_2O content drives the Bunsen reaction, leading to a higher SO_2 conversion ratio. The addition of surplus I_2 and H_2O has improved the separation of the two liquid phases and thermodynamically drives the reaction. The study has proposed a fundamental kinetic model to explain the kinetic route of the Bunsen reaction, but the role of the mass transfer and diffusion between SO_2 and reactant solution, and the dilution effect of H_2O is ignored [128].

Zhang Y et al (2014) have carried out the Bunsen reaction to study the flow of SO_2, ratio of iodine and water in the feed. The study projected the Bunsen reaction mechanism keeping given the kinetic characteristics. The results of the study shown that an increase in iodine amount and a decrease in water amount enhanced LLE separation characteristics. The H_2S formation reaction has happened with the rise in water content and reduction in iodine content. The study has projected the ideal operating condition for the inlet SO_2 mole fraction >0.12 and initial I_2/H_2O molar ratio >0.284 on the experimental results, with a focus on improving the separation characteristics and preventing side reactions [129]. But the study is carried out at atmospheric pressures and without oxygen as an inert gas. Further, the study has not considered mass transfer effects.

Rao AS et al (2015) have carried out a semi-batch Bunsen reaction. The study involves a parametric study of Bunsen reaction. Experiments are conducted in a Bunsen reactor of tubular construction at various pressure and temperature with sulfur dioxide. The study has detected that there is an increase in the overall reaction rate with pressure. The overall reaction decreases with an increase in temperature. Later studies have been performed with N_2 and SO_2, to comprehend the influence of gas film resistance on the conversion and overall reaction rate. It is found that the Bunsen reaction rate has increased with an increase in pressure operating at a specific operating temperature and the reaction rate has decreased with an increase in temperature for a specified operating pressure. The conclusions of the study are the role of temperature on reaction length or reaction rate is more dominant in comparison to the role of pressure on reaction rate [130, 131]. The study has done only in semi-batch mode; continuous operation gives a better understanding of hydrodynamics. Further, the study has considered nitrogen as a carrier gas.

Kim HS et al (2016) have studied the features of the Bunsen reaction with the usage of the HIx solution in a co-current continuous mode operation. The role of the operating variables such as feed flow rates of reactants, H_2O, and I_2 feed compositions, temperature, and reaction volume on the Bunsen reaction is studied. The results of the study are, decreasing the I_2 feed concentration and increasing the H_2O feed concentration improved the extent of the Bunsen reaction. When the temperature increases, the Bunsen products' purity has enhanced, but the SO_2 conversion has decreased. The study has concluded that the characteristics of the Bunsen reaction are not influenced by the variation in the reaction volume and $SO_2/HI/I_2/H_2O$ feed molar ratio maintained in the ranges of 1/1.8-2.0/3.9-4.1/14.8-15.6 to get high SO_2 conversion and enhance separation performance of the Bunsen products at 60 ^{o}C [132]. The study has limited the operating pressure of the experiments at atmospheric pressures.

Kim HS et al (2016) have examined the features of the Bunsen reaction at different operating conditions such as pressure, temperature, $I_{2,}$ and H_2O feed concentrations. In the study, a mixture of HI, $I_{2,}$ and H_2O is used as the reactant. The results of the study are, when the pressure is increased, the degree of Bunsen reaction is improved. This is because of an increase in the solubility of SO_2 gas in the HIx solution. Further, the H_2SO_4 phase solution quantity is increased. Increasing temperature has improved the phase separation of the Bunsen products, while the degree of Bunsen reaction has decreased. When the feed concentration of I_2 is increased, the side reaction is repressed, but the degree of phase separation of the Bunsen products is decreased. The important conclusion of the study is, though increasing H_2O feed concentration is desired for the high-pressure Bunsen reaction, the H_2O feed concentration should be maintained by taking in to account the solubility of I_2 in the HIx Solution [133]. The pressure in the study is limited to 2 bar g only.

Zhou C et al (2017a) have studied the Bunsen reaction kinetics by comparing the pressure decrease of SO_2 gas with progress of reaction. The author has examined the absorption behaviour of SO_2 in HI acid under different conditions, with diverse HI concentration, absorption temperature, and SO_2 partial pressures. The results of the study showed that the absorption amount of SO_2 in HI solution increases with the HI acid concentration and pressure of the SO_2, while the role of temperature on SO_2 absorption in HI solution is complex. S and SO_4^{2-} are noticed in HI solutions afterward SO_2 absorption, and iodine is found in HI solution in the conditions of high pressure or high temperature, representing chemical absorption has occurred [134]. But the effect of mass transfer is not considered in evaluating kinetic parameters.

Zhou C et al (2017b) have conducted a Bunsen reaction to obtain kinetic parameters by initial rate method. During the study, the role of important parameters, are SO_2 partial pressure, I_2 concentration, agitation speed, and reaction temperature, on reaction rate, are methodically examined by monitoring the change in SO_2 pressure with progress of reaction. The initial rate analysis method obtained the Bunsen reaction rates from there 0.23 and 0.77 order w.r.t SO_2 pressure and I_2 concentration are found. The apparent activation energy is 5.86 kJ/mol. An expression for the rate of the Bunsen reaction is obtained [135]. The study has not considered the effect of mass transfer while evaluating the rate parameters.

2.5.2 Studies on Liquid-Liquid phase separation

Sakurai *et al* (1999) have studied the role of iodine concentration in the feed on the separation characteristic of liquid-liquid phase solutions at $0^{O}C$. The experiment is conducted by using raw material with a constant composition $HI/H_2SO_4/H_2O$ – 0.07/0.048/0.882 in a molar fraction in a flask and different amounts of iodine are added to the mixture. Phase separation has enhanced as iodine fraction in feed increased to 0.43. Phase separation got disturbed below the certain limit of iodine concentration, phase separation didn't occur. Further, a saturation of iodine content occurs at the upper limit, and solidification of excess iodine occurred [136]. Most of the phase separation studies have studied the characteristics by premixing the HIx and H_2SO_4 without conducting the Bunsen reaction.

Sakurai *et al* (2000b) in his further investigation has carried out phase separation studies to a broader temperature range. The study is carried out to get the role of iodine and temperature in $HI/H_2SO_4/I_2/H_2O$ solution on liquid-liquid equilibrium phase behaviour in 0 °C - 95 °C. The solution of a mixture of HI, H_2SO_4, I_2, and H_2O is made in a glass vessel with a jacket to keep the constant temperature. The initial molar ratio of HI, H_2SO_4 and H_2O of the solution: 0.070/0.048/0.882, for 0, 28, 40, 60, 80 and 95 °C; 0.085/0.058/0.857, 0.049/0.069/0.882, for 40 °C. In this study, the HI to sulfuric acid ratio is different from 2, this value is stoichiometric of products of Bunsen reaction. The study shows that the mole fraction of the iodine amount in feed solution results in a higher amount of I_2 and a lower amount of HI and H_2SO_4 in the product HIx phase at different operating temperatures. It also results in a lower fraction of HI and I_2 in the H_2SO_4 phase at different operating temperatures. The role of operating temperature on the I_2 concentration for the starting point of separation to that I_2 saturates are studied and it was found that separation point and saturation point increases with temperature. Finally, the important findings of the study are: (a) amount of iodine content enhances the liquid-liquid separation features and (b) rise in temperature enhances the iodine solubility by broadening the permissible iodine range [137]. This study has conducted experiments by premixing Hix and H_2SO_4 solutions.

Lee *et al* (2005) have studied the role of water on side reaction and phase separation in the composition range of 0.047:0.093:0.860, 0.038:0.075:0.887, 0.030:0.061:0. 909: H_2SO_4: HI: H_2O at 20 °C. In this study, H_2S generation is the objective. Excess water content in raw material resulted in decreased H_2S formation, but Bunsen product phase separation is not observed. The main conclusion from the study is that the feedwater range is important to avoid undesired product creation and process the two-phase separation [138].

Kang *et al* (2006) have investigated the process characteristics of the H_2SO_4-HI-H_2O-I_2 mixture system for separating into two liquid phases and the circulation of H_2O to each phase. The study considered the feed composition in the range of $H_2SO_4/HI/H_2O/I_2$ =1/2/14~20/0.5~8.0 from 25 ^oC ~ 80 ^oC. One of the main results of the study is that the minimum impurity concentrations of the HI phase and sulfuric acid are identified at the excess iodine moles of 8.0 and the temperature of 80 ^oC. The best result for the reduction of impurities (HI and I_2 in the H_2SO_4 phase and H_2SO_4 in HIx phase) in each phase is obtained in an optimum condition with the highest temperature of 80 ^oC and the highest I_2 molar composition. At this condition, the level of impurity of HI in the sulfuric acid phase is 0.024 and sulfuric acid impurity in the HIx phase is 0.028. For the distribution of H_2O to each phase, the cohesiveness between HIx and H_2O is more significant than between H_2SO_4 and H_2O. This property between HIx and H_2O is decreased with increasing temperature, instead, the same property is increased with increasing I_2 concentration [139].

Colette SC *et al* (2006) have studied the $H_2SO_4/HI/I_2/H_2O$ system for the phase separation region by mixing products of Bunsen reaction. The mixtures of H_2SO_4, HI, I_2 and H_2O are charged in a vessel made of glass with a jacket. The solution is stirred with a magnetic stirrer; the temperature is retained at 35 ^oC by passing through the jacket a fluid from a thermostatic liquid bath. The initial study has been done with the focus on the influence of water on phase separation with $H_2SO_4/HI/I_2/H_2O$ = 1/2/3/n mixtures, n varying from 13 to 32. Later the role of iodine on separation is studied with $H_2SO_4/HI/I_2/H_2O$ = 1/2/x/14 mixtures, x varying between 1 and 4.2. The conclusions of the studies are sulfuric acid phase density steadied around 1400 kg/m^3 while in the HIx phase the density frequently decreases when the feed water content increases. It has been shown that decreasing water and increasing iodine in the mixtures favours liquid phase separation [140].

Giaconia *et al* (2007) have investigated phase separation characteristics of the four-component $H_2SO_4/HI/H_2O/I_2$ mixtures using a 50mL jacketed quartz test tube. Feed concentration varies for iodine are 4~16 moles and 11~16 moles of water, at 80, 95, and 120 ^oC. Temperature and iodine content have a slight effect on the sulfuric acid and HI concentrations in the two phases. Increasing water excess leads to dilution of the acids, but HI concentration in the lower phase is continuously above the azeotrope point. The purity of two phases is virtually uninfluenced by iodine concentration and operating temperature, without the use of a very large amount of iodine at 120 ^oC. Iodide and HI in the sulfuric phase are continuously 1–2% of the total, while sulfates in the hydriodic phase are continuously higher than 15% of the total. Secondary reactions are never observed in experiments if the components are firstly mixed at a temperature below 80 ^oC. According to the work of Sakurai et al. [2000b], in order not to have secondary reactions, iodine excess should be larger than 3.4 mol I_2/mol H_2SO_4. In these experiments, the lowest iodine concentration is 3.9 mol I_2/mol H_2SO_4, and the only other way is to increase the excess water but, this severely decreases the concentration of the acid. It follows from the study that a temperature of 80^oC and an initial molar fraction of $HI/H_2O/I_2/H_2SO_4 = 0.11/0.61/0.22/0.06$ is the best choice for Bunsen reaction mixture [141].

Lee [2006] has carried out many of the liquid-liquid phase separation experiments. The important observations of the study are: (a) temperature don't have an important effect on the SO_2 solubility and the phase separation, but its increase improves the solubility of iodine, and (b) the characteristics of phase separation improves with increasing iodine concentration in the feed but is weakened by increasing the water concentration, and is particularly ineffectual when the water concentration is over 0.88 in mole fraction. The study observed that the H_2S

formation increases with the temperature, but decreases with the water and iodine content; mainly, no H_2S formation is observed at a mole fraction of $H_2O < 0.909$ [142].

Lee *et al* (2008) have conducted studies from the experimental data of Sakurai *et al* (2010b), Giaconia *et al* (2007), Kang *et al* (2006), and Lee *et al* (2005) to deduce an optimal operating range. The recommended ideal excess moles are between 4 and 6 moles for iodine, 11 and 13 moles for water, and 57 ~ 77 ^{o}C of the temperature range. The excess iodine of 4 is considered as the lower limit concerning sulfur formation. Excess iodine of 6 moles is based on the saturation limit. Alternatively, as the excess iodine increases, the molar ratio of water-to-H_2SO_4 drastically drops and decays smoothly to about 5. Impurities in the Sulfuric acid phase and HIx phase increased with an increase in water content in the feed. This occurs because of the dilution of iodine with an increase in water content. But the amount of water in the sulfuric acid phase does not vary significantly in the sulfuric acid phase whereas it changes linearly in the HIx phase. The feedwater amount can be varied to control HIx concentration. As the temperature increases, the water content for a given iodine content decreases in the HIx phase and increases in the sulfuric acid phase. This is because water tends to move in the direction of the top phase at higher temperatures. As the iodine content is increased, this leaning becomes weaker. A lower limit of 11 moles of additional water is demarcated as to lessen water content to keep HI concentration over azeotrope. An higher limit of 13 moles of excess water was demarcated since the HI concentration became lesser than azeotrope over 13. In relations of temperature range 57 ^{o}C is opted as the lower limit to enhance the exothermic features of the Bunsen reaction and 77 ^{o}C is opted as the higher limit to extend the iodine operation range [143].

Yoon HJ et al (2009) have studied the liquid-liquid separation characteristics with attention to get over azeotropic HI mixture in the heavy HIx phase. The feed is a quaternary liquid mixture of $H_2SO_4/HI/H_2O/I_2$ and charged in a 50 mL jacketed quartz test setup. The varying Molar ratio of I_2/H_2SO_4 from 2 to 4 then the molar ratio of $HI/(HI + H_2O)$ in the HIx phase is enhanced from 0.157 to 0.22, which is high enough to get highly pure HI gas through flashing. A lower temperature is more favourable to increase the HI concentration. The inverse Bunsen and the sulfur formation reaction become leading as the temperature increases and the molar ratio of I_2/H_2SO_4 was low. 10–50 wt% of HI in the feed turned into I_2 when the inverse Bunsen and the sulfur formation reaction occurred. When the molar ratio of I_2/H_2SO_4 in the feed was increased, impurities in both phases are reduced; HI and I_2 in the sulfuric acid phase are more complex than H_2SO_4 in the HIx phase. Besides, the majority of I_2 in the feed shifts to the lower HIx phase, which increased the density of the lower phase. Since the density variance among the two phases is the driving force of liquid-liquid phase separation [103].

Maatouk *et al* (2009) have conducted initial studies at 35 ^{o}C to perform phase separation with iodine between 1-4.2 mole and excess water between 10-35. The study detected that an increase in the feed iodine concentration and a decrease in the water content enhanced the separation of the two liquid phases. But, when the water content is low, side reactions between HI and H_2SO_4 are also promoted. It is observed that an increase in the amount of H_2SO_4 enhanced the purity of the two phases and seemed to make a certain degree of dehydration of the HIx phase. Iodine favours the HIx phase viewing density difference amongst two phases and lessening water in the system favours liquid phase separation [144].

Zhu Q *et al* (2012) have conducted several experiments to examine the separation behaviour of the liquid-liquid phase in the $H_2SO_4/HI/I_2/H_2O$ quaternary solution produced by Bunsen reaction. The role of the solution composition in the feed and the temperature on the separation behaviour is analysed to find better-operating conditions in the Bunsen section. The increases in the iodine concentration and the temperature improved the separation behaviour of the liquid-liquid phase but the study ignored the formation of secondary reactions. The quantity of impurities in two phases decreased as the iodine concentration is increased. The consequence of the iodine concentration is more important compared to that of the temperature. The study projected optimal operating conditions to attain the over azeotropic composition concentrations of HI in the HIx phase. The I_2/HI molar ratio in the HIx phase linearly increased with the increase in the I_2/H_2SO_4 molar ratio, this phenomenon may be explained by the strong complexation between I^- and I_2. A higher amount of I_2 dissolved in the HIx phase at higher solution temperatures. The H_2O/HI molar ratio approximately inclined toward the value 5.41, which is equivalent to the HI azeotropic concentration in the HI/H_2O binary system when the I_2/H_2SO_4 molar ratio and temperature are steadily increased. As the I_2/H_2SO_4 molar ratio was above 2.2, the H_2SO_4/HI ratio in the HIx phase was maintained at less than 0.05.

The HI/H_2SO_4 and I_2/H_2SO_4 molar ratios in the H_2SO_4 phase drastically decreased in terms of excess iodine [145].

Kim HS et al (2014) have studied the role of temperature, iodine concentration, and water concentration to recognize the phase separation behaviour of Bunsen reaction products using the HIx feed with SO_2. The main conclusions from the study are, the amount of sulfuric acid phase increased with the temperature and decreased the impurity levels in both the phase. Increasing the iodine feed content slightly decreased the quantity of the H_2SO_4 phase, though the density variance among the phases increased. The amount of H_2SO_4 that separated into the H_2SO_4 phase was very small under most of the conditions. The excess feed water during the phase separation step is suggested to enhance the separation of the H_2SO_4 phase solution without the occurrence of side reactions [146].

Kamel *et al* (2009) have projected a model for the Bunsen section. At moderate temperature and pressures, the UNIQUAC model with Engels' solvation model is adopted. Model is discussed in the study, with HI solvation by water and by iodine as well as H_2SO_4 solvation by water, resulting in a very high complexity with nearly a hundred parameters to be estimated from experimental data. Considering the water excess, an effective condensed model with only

15 parameters is suggested by introducing new apparent species [63]. The model is limited to certain concentrations of feed solution.

Bunsen reaction and phase separation can be combined in a single reactor in counter-current mode of operation. One of the candidate reactors for that operation is an oscillatory baffled Bunsen reactor. But the counter-current operation increases the probability of occurrence of side reactions.

2.5.3 Studies on Side reaction

Sakurai *et al* (2000b) have studied the likelihood of side reaction in $HI/H_2SO_4/I_2/H_2O$ solution at 95 ^oC. The role of the temperature, iodine concentration, and the ratio of H_2SO_4 and HI on the sulfur formation is studied. Experimental conditions in this study are $[H^+]$ = 4-11 mol/kg-H_2O; $2[H_2SO_4]/[HI]$ = 0.3, 0.8; x of HIx = 1-4.41; reaction temperature is 22 ^oC - 95 ^oC. The two likely side reactions of HI and H_2SO_4 as reactants are S and H_2S gas formation. The factors for the occurrence of side reactions are high temperature and HI concentration, and low excess iodine. At 22 ^oC, sulfur formation is not observed. In the temperature range above 40 ^oC, sulfur is formed in a certain region and the region spread out with an increase in reaction temperature. It is found that sulfur is simply generated with the increase in acid content and the decrease in iodine content. Excess moles of iodine are suggested in between 4.41 & 11.99 to avoid side reaction in lower limit and iodine solidification at a higher limit [147]. The study is conducted by adding premixed Bunsen reaction products.

Hwang GJ et al (2005) have studied the side reaction and effect of the I_2 fraction in the 2-liquid phase separation of Bunsen reaction in the temperature range, from 25 to 80 ^oC. The solution of a mixture H_2SO_4, HI, H_2O and I_2 are placed in the glass vessel with a jacket. The solution temperature is maintained to constant by passing temperature-controlled water. The study has selected the initial molar ratio of H_2SO_4, HI, and H_2O: 1/2/14, 1/2/16, 1/2/18, 1/2/20, 1/1.5/14. At 25 ^oC, H_2S production quantity is very low and has the almost same value with an increase in I_2 fraction. H_2S production quantity at 40 °C increased with an increase in I_2 fraction, and showed maximum value at about 0.48 of I_2 fraction, and then decreased. At 60 °C, H_2S production quantity increased with an increase in I_2 fraction, and showed maximum value at about 0.5 of I_2 fraction, and then decreased. H_2S production quantity at 80 °C increased with an increase in I_2 fraction, and showed maximum value at about 0.52 of I_2 fraction, and then decreased. The study concluded that the amount of impurity could be reduced by increasing the temperature and I_2 concentration of the production solution in the Bunsen reaction [148].

2.5.4 Alternate route to carry out Bunsen reaction and Phase Separation

Several methods have been proposed to deal with H_2SO_4/HI mixtures; these methods are based on the following:

- ✓ electrochemical separation
- ✓ use of different types of solvents
- ✓ use of liquid SO_2
- ✓ use of aromatic polymers
- ✓ use of precipitation agent and solid salt formation
- ✓ iodine excess addition

The most widely used strategy relies on iodine excess addition (discussed in section 2.3) that causes the separation of the aqueous solution into two distinct phases, each one migrating to a well-defined spatial location in the solution.

Dakiya M et al (1979) has performed the Bunsen reaction as a short circuit cell reaction and used a cell with a cation-exchange membrane as a diaphragm and separator, resulting in the H_2SO_4 and HI to be produced distinctly in the anode and cathode chambers [149].

Beni De G *et al* (1980) is one of the first to publish on Bunsen reaction using organic solvents. In his research, he has discussed different methods to improve the yield of Bunsen reaction using organic solvents. Initially, the author conducted a series of experiments using liquid sulfur dioxide. Later experiments are conducted using organic compounds. A selection of organic compounds is made based on their chemical and physical properties. The study has concluded that when low boiling organic solvents are utilized, the recovery of HI from the sulfur dioxide phase is feasible, but needs enormous amounts of energy. The use of high boiling solvents avoids side reaction and reduces the energy required for HI recovery [150].

Vincenzo Barbarossa *et al* (2009) have studied a creative way to separate the acids by using an intermediate insoluble sulfonic acid which forms during the process. The new method consists of using an aromatic polymer to seize the sulfuric acid so that a sulfonic polymer is created. If an insoluble polymer is used, the sulfonic polymer can be simply separated by filtration. At this point, an acid desulfonation restores the sulfuric acid and the initial aromatic polymer. The formation of sulfonic-poly styrene-divinyl-benzene (S-PSDVB) and its desulfonation are studied, and their introduction in the sulfur-iodine thermochemical cycle for hydrogen production is proposed by the author. The results have shown satisfactory sulfuric acid recovery of about 56% concerning the total SO_2 injected into the Bunsen reaction [151].

Giaconia et al (2009) have studied experimentally the viability of three diverse methods for performing the Bunsen reaction and separation of acid products. The use of a reaction solvent other than water is considered first. Reducing the recycled water flow rate can increase the overall efficiency by decreasing the thermal burden during the acid concentration steps. Another technique that doesn’t require an excess of iodine in the Bunsen reaction includes the use of the ion-exchange method, in which the formation of insoluble solid salts takes place. By adding a precipitating agent such as lead sulfate results in iodide elimination by precipitation of the insoluble PbI_2 salt. The third method is a redox process, the Bunsen reaction can be performed electrochemically with SO_2 oxidation to H_2SO_4 and I_2 reduction to HI [152].

Taylor et al (2013a) have explored dibutyl-butyl phosphonate (DBBP) and Cyanex-923 as alternatives to Tri Butyl Phosphate as a solvent in Bunsen reaction. The study concluded the need for further work to measure the behaviour of the Bunsen reaction in each of these solvents and to find methods of recovering the HI from the solvents [153]

Taylor et al (2013b) has examined ionic liquids as solvents for the Bunsen reaction. Several possible ionic liquids are recognized considering anion properties. The HI extraction in the ionic liquid is experimentally examined. All the ionic liquids tested are not appropriate for use in the Bunsen reaction, but the properties of an ionic liquid can be custom-made by the choice of anion and cation. Further examination of ionic liquids is essential before ruling it out. [154].

The Bunsen reaction through the electrochemical route has been suggested as an alternative and encouraging method in relation to the traditional Bunsen reaction, and its kinetics are studied in this work. Polarization curves are obtained by using a platinum electrode in the diverse ranges of $SO_2/H_2SO_4/H_2O$ and $I_2/HI/H_2O$ solutions at a temperature of 30-80 ^oC. The activation energy and pre-exponential factor for the reactions at the electrode are obtained using the Arrhenius equation [155]. A gas-liquid-liquid system kinetics of Bunsen reaction with the iodine-toluene solution is also studied [156].

2.6 Gap areas in the literature and motivation of the research

Bunsen reaction is a very complex reaction that involves multi phases and a key step, as overall process feasibility; stability & efficiency are determined by this step. In this process step, water is reacted with iodine (I_2) and sulfur dioxide (SO_2) to obtain hydriodic acid and sulfuric acid.

The crucial role of operating conditions like temperature, compositions, etc is not well understood until now. They must be optimally selected to achieve high purity of product phases, conversion & yield. Phase and chemical equilibria of this highly nonideal reacting system are not completely studied in the literature. The contacting scheme, reactor type, and size also have a severe bearing on reaction and phase separation. Published literature on these aspects of the I-S process is scanty.

- Bunsen reaction is carried out only up to 2 bar(g), which shows better yield and product purity, but beyond 2 bar(g) data is not available in the literature, hence to fill that gap it is planned to carry out the reaction at high pressures.
- Most of the studies carried out phase separation using premixed Bunsen reaction products without carrying out Bunsen reaction which may not give the correct picture of phase separation because the product acid forms nucleate, and then coalesce to form two phases.
- Most of the studies have focussed on carrying Bunsen reaction in semi-batch mode and a few studies in continuous mode.
- Kinetic studies on Bunsen reaction have been carried out by few researches. But the approach to evaluating the kinetics for a multiphase reaction is not fully followed. Especially for gas-liquid reactions, there are various regimes of reaction such as slow, fast, instantaneous, etc which need to be accounted for during the studies.

Problem identified: Based on the literature survey to understand the role of parameters on the Bunsen reaction system which includes reactor temperature, reactor pressure, feed concentrations. Further, to study parallel reactions and cross contaminations of the phases during the Bunsen reaction to maximize the yield and purity will be evaluated and optimized.

The study is planned to carry out phase separation studies during/after reaction without premixing the product components. The kinetics of the Bunsen reaction depends on both chemical reaction resistances as well as mass transfer resistances. The kinetics date for a gas-liquid reaction is required for the design and scale-up of the reactor. To evaluate the kinetics of the Bunsen reaction experimental methodology has been adopted and several experiments have been carried out. A methodology will be developed to study the Bunsen reaction which incorporates the effects of mass transfer and obtain the kinetic parameters.

Table 2-2 Summary of Literature Survey

Authors / Para Meters	Mode of Experiment	Temperature Range (°C)	Pressure Range (bar g)	SO_2 Partial Pressure	I_2/H_2O ratio	Kinetics	Kinetics with Mass transfer
Desired or required attribute for scale up	Continuous	30-80	High	50-95%	> 80 % of Sat*	Y	Y
Shimizu et al (1992)	Semi Batch	20	Atm	100%	0-0.2	N	N
Sakurai et al (1999)	Batch	0	Atm	-	0.32	N	N
Colletter et al (2007)	Batch	35	Atm	-	0.1-0.3	N	N
Giaconia et al (2010)	Semi Batch	30-120	Atm	100%	Sat*	N	N
Kim YH (2012c)	Semi batch	40-70	Atm	50% (O_2)	0.38-0.56	N	N
Zhou C et al (2017a)	Semi batch	40-80	2	100%	Sat*	Y (SO2+ HI)	N
Parisi et al (2011)	Semi Batch	30-120	Atm	100%	0.3-0.7	N	N
Kim et al (2012a)	continuous	40-90	Atm	100%	0.25-0.45	N	N
Kim YH et al (2012 b)	Continuous	90-120	2	100%	0.4-0.7	N	N
Kim HS et al (2013)	Continuous	40-110	Atm	100%	0.25-0.45	N	N
Ying Z et al (2013)	Semi Batch	30-85	Atm	25-50%	0.18-0.32	N	N
Zhu Q et al (2013)	Semi Batch	63-85	Atm	20-50%	0.21-0.32	Y	N
Zhang Y et al (2014)	Semi Batch	72	Atm	10-20%	0.25-0.32	N	N
Rao et al (2015)	Semi batch	40-80	4	80-100%	0.25	N	N
Kim HS et al (2016)	Continuous	60-80	Atm	100%	0.33-0.37	N	N
Zhou C et al (2017b)	Semi batch	25-50	2.2	100%		Y	N
Zhou C et al (2017a)	Semi batch	40-80	2	100%	Sat*	Y (SO2+ HI)	N
Present work	Semi batch & Continuous	30 to 80	0-6	50-95 %	0.25-0.4	Y	Y

Sat-Saturated amount of iodine in HI solution, Y-Studied, N-Not studied

3 EXPERIMENTAL SETUP AND ANALYTICAL METHODOLOGY

3.1 Preamble

Three different types of experimental facilities are described in this chapter to achieve the objective of research i.e. evaluation of Bunsen reaction and phase separation in a continuous reactor. The first facility is used to study the best operating ranges of Bunsen reaction and product phase cross-contamination as shown in figure 4.1. The operating mode for the reactant is in co-current mode. The material of construction of the reactor is tantalum and the material of construction for the jacket is SS316. The experimental facility is set up to handle high pressure and moderate temperatures. The second facility is used to generate the kinetic data for the Bunsen reaction. The operating mode is a batch mode for both sulfur dioxide gas and liquid reactants. The material of construction of the reactor is glass with two PTFE coated agitator assembly. The third facility is used to study the best location of feed water during the Bunsen reaction. The material of the construction of the reactor is glass. Analytical methods for chemical analysis are also described in this chapter.

3.1.1 Studies on Bunsen reaction at elevated temperature and high pressure

Bunsen reaction is carried out in a co-current reactor to identify the effect of different operating conditions on concentrations of Bunsen reaction product mixture. The schematic is given in figure 4.1. Bunsen reaction studies have done in a tubular reactor, which is made of a tantalum tube and stainless-steel jacket as shown in figure 4.2. Feed flow rates of sulfur dioxide, HIx are varied during experiments. Experimental studies have carried out at different temperatures and pressures.

It is found that increasing operating temperature has increased the mole fraction of HI in the HIx phase and decreased the mole fraction of H_2SO_4 in the sulfuric acid phase.

3.1.2 Studies on phase separation of Bunsen reaction product mixture

Bunsen reaction is studied to identify the role of different operating conditions on the purity of Bunsen reaction product phases. The focus of this experiment is to find out the level of contamination in each of the Bunsen reaction product phases. Hydroiodic acid and iodine are contaminants in the sulfuric acid phase and sulfuric acid is a contaminant in the hydroiodic acid phase. Enhancing the level of purity in two product phases will reduce the burden on purification steps downstream of the I-S process.

3.1.3 Studies on reaction kinetics of Bunsen reaction

The SO_2 reaction with water and iodine solution is of wide importance in the I-S process and its kinetics is vital for whole modelling of the reactive absorption. The schematic is given in figure 4.5. An imprecise assessment of the kinetics of gas-liquid reactions may lead to an flawed design of the equipment. A stirred cell reactor is fabricated to obtain the kinetics of the Bunsen reaction. The stirred cell reactor is extensively useful, as its simple to construct and operate. This reactor can be operated under stringent isothermal environments and does not require carrying out liquid phase analysis.

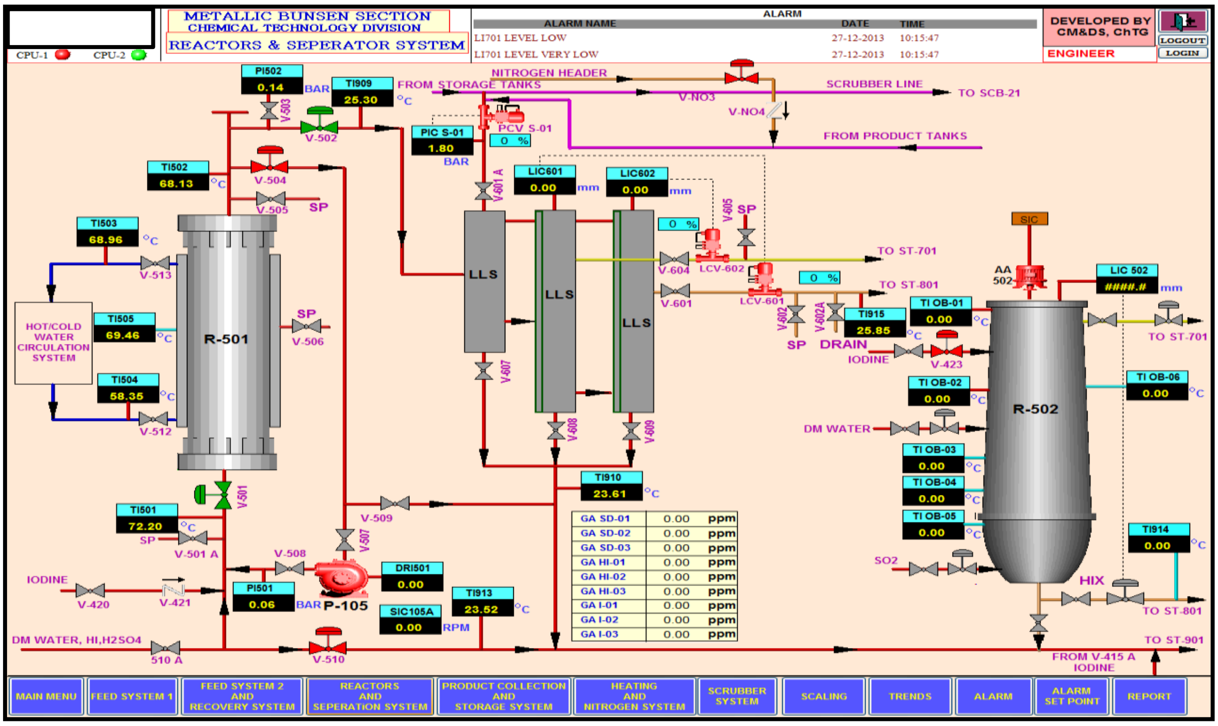
3.1.4 Studies on side reaction and settling rates of Bunsen reaction products

During Bunsen reaction under certain conditions, side reactions occur, which disturbs the closed-loop nature of the process. The side reaction products are sulfur and hydrogen sulfide. Sulfur remains in solid form which can cause additional trouble by chocking the process lines. To avoid side reactions experiments are conducted to identify the regime in which side reactions occur so that such conditions are completely avoided or minimized during closed-loop operation.

Settling rates are essential in sizing phase separation equipment. To obtain the characteristics of the dispersion and settling of Bunsen reaction product phases, experiments are carried out in a batch vessel. The preliminary experiments have been performed to investigate a batch settler to get a better understanding of the separation characteristics at different Iodine concentrations and temperatures.

3.2 Setting up of experimental facilities

An experimental facility is set up where data related to the Bunsen reaction can be collected by designing simple and safe experiments. Three types of experimental facilities are created to accomplish the objectives as envisaged in section 3.1. Since the chemicals involved in the Bunsen reaction are hazardous and toxic, it is necessary to have adequate instrumentation, controls, and safety measures incorporated in the system, which will not only serve to record the process data but also ensure the personnel and the equipment safety. One of the mimic screens for control and monitoring during experiments is shown in figure 3.1. The following steps have been adopted during the installation of the test facility to address safety concerns.



ALARM NAME	DATE	TIME
LI701 LEVEL LOW	27-12-2013	10:15:47
LI701 LEVEL VERY LOW	27-12-2013	10:15:47

GA SD-01	0.00	ppm
GA SD-02	0.00	ppm
GA SD-03	0.00	ppm
GA HI-01	0.00	ppm
GA HI-02	0.00	ppm
GA HI-03	0.00	ppm
GA I-01	0.00	ppm
GA I-02	0.00	ppm
GA I-03	0.00	ppm

Fig. 3-1 Schematic of control mimic of the reactor system

3.2.1 High pressure Bunsen reaction experimental facility

The experimental facility is used to carry out Bunsen reaction and product phase cross-contamination studies and the facility comprises of the following systems:

1. Feed System
2. Reactor & Separation System
3. Product collection & storage System
4. Scrubber System
5. Utility System

Feed system

The feed system introduces feed chemicals into the reactor. It consists of the following equipment

1. HIx feed Tank
2. SO_2 Cylinder
3. O_2 Cylinder

HIx Feed tank

The capacity of the HIx feed tank is 160 litres. The tank is having the jacketing arrangement for maintaining an operating temperature of 50-80°C inside the tank. The heating is provided by the thermic fluid heating system. The tank is used to simulate recycled conditions by recycling HI from the HI section.

Construction: Material of construction is glass-lined on Carbon steel.

Control Loop: In the outlet line from the tank, the flow control loop is present with a flow meter, control valve, and PID controller. The flow can be controlled with a parallel line using a diaphragm pump and VFD. The pressure in the tank can be set using a pressure transmitter, Electro-pneumatic valves. Nitrogen gas is used at the inlet to the tank to flush the contents of the tank. Temperature control in the tank is, by adjusting the thermic fluid flow rate through the jacket of the tank.

SO_2 Feeding System

The material of Construction: The cylinder is made of Carbon Steel

Volume: 47 litres of water capacity

Cylinder Pressure: 4 bar g at room temperature.

Control Loop: In the outlet line from the cylinder, flow is regulated by a mass flow controller (after cylinder regulator) which flows to the reactor. The cylinder pressure is monitored with a pressure transmitter and safety interlocks are invoked for any abnormal surges.

Oxygen Feeding System

Volume: 47 litres of water capacity

Cylinder Pressure: 120 bar g at room temperature

Material of Construction: The cylinder is made of Carbon Steel

Control Loop: In the outlet line from the cylinder, flow is regulated by a mass flow controller (after cylinder regulator) which flows to the reactor. The cylinder pressure is monitored with a pressure transmitter and safety interlocks are invoked for any abnormal surges.

Reactor & Separation System

This system consists of the following equipment

1. Co current reactor
2. Liquid - Liquid separator

Static Mixer Reactor

The Bunsen reactor is a tubular reactor with static mixer inserts and is a co-current type reactor. The temperature is maintained by cooling water flowing in the jacket to remove the exothermic heat from the Bunsen reaction.

The material of Construction: Tantalum tube and SS316 jacket

Construction: The tube is made of Tantalum and the shell is made of Stainless Steel.

Control Loop: The pressure in the reactor is controlled using a pressure transmitter and control valve at the outlet of the Liquid-liquid separator. Temperature control in the reactor is maintained by adjusting the jacket fluid flow rate.

Liquid-Liquid Separator

A liquid-liquid separator is for the separation of two acid products from the Bunsen reactor.

The material of construction: PFA lined on pipes made of (inner pipe & jacket) on mild steel.

Construction: The system consists of PFA lined on mild steel fittings.

Control Loop: Pressure above the liquid level is maintained by Pressure transmitter with a control valve, which in turn maintains the system pressure

Product collection & storage system

This system consists of the following equipment

1. H_2SO_4 Product tank
2. HIx Product tank
3. Waste liquid tank

Sulfuric Acid Product Tank

The capacity of the sulfuric acid product tank is 63 litres. The tank is having the jacketing arrangement for maintaining a temperature of 120°C inside the tank to maintain the temperature above the melting point of Iodine in case any Iodine is deposited inside the tank. The heating is provided by the thermic fluid heating system. The tank is used to collect the product sulfuric acid phase from the liquid-liquid phase separator.

Construction: Material of construction is glass-lined on Carbon steel.

Control Loop: Nitrogen gas is used to at the inlet to the tank to flush the contents of the tank. Temperature control in the tank is by adjusting the thermic fluid flow rate manually.

Hydroiodic Acid Product Tank

The capacity of the Hydroiodic acid product tank is 63 litres. The tank is having the jacketing arrangement for maintaining a temperature of 120°C inside the tank to maintain the temperature above the melting point of Iodine in case any Iodine is deposited inside the tank. The heating is provided by the thermic fluid heating system.

Construction: Material of construction is glass-lined on carbon steel

Control Loop: Nitrogen gas is used to at the inlet to the tank to flush the contents of the tank. Temperature control in the tank is by adjusting the thermic fluid flow rate manually.

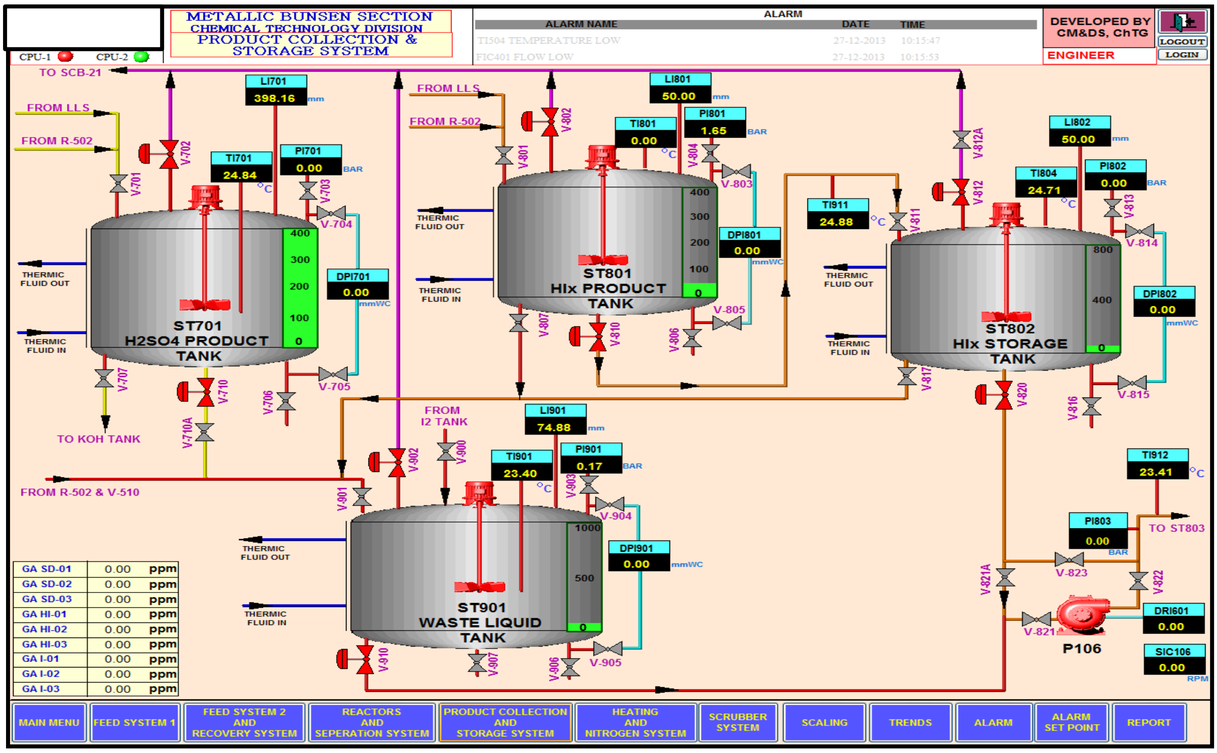
Waste Liquid tank

The capacity of the waste liquid tank is 630 litres. The tank is used to dump entire chemicals in case of leakages. The tank is having the jacketing arrangement for maintaining a temperature of 120˚C inside the tank to maintain the temperature above the melting point of Iodine in case any Iodine is deposited inside the tank. The heating is provided by the thermic fluid heating system.

Construction: Material of construction is glass-lined on carbon steel

Control Loop: Temperature control in the tank is by adjusting the thermic fluid flow rate.

The storage tanks and waste liquid tank mimic screen is shown in figure 3.2.



ALARM NAME	DATE	TIME
TI504 TEMPERATURE LOW	27-12-2013	10:15:47
FIC401 FLOW LOW	27-12-2013	10:15:53

GA SD-01	0.00	ppm
GA SD-02	0.00	ppm
GA SD-03	0.00	ppm
GA HI-01	0.00	ppm
GA HI-02	0.00	ppm
GA HI-03	0.00	ppm
GA I-01	0.00	ppm
GA I-02	0.00	ppm
GA I-03	0.00	ppm

Fig. 3-2 Schematic of control mimic of Product collection and storage system.

Scrubber System

This system consists of the following equipment

1. KOH tank-1
2. KOH tank-2
3. Scrubber

KOH Tank-1

The capacity of the tank is 160 litres. The tank is having the jacketing arrangement for removing heat for the neutralization reaction. It is used to scrub unconverted gases and fumes from the facility.

Construction: Material of construction is glass-lined on carbon steel

Control Loop: The level is controlled manually in the tank using a level transmitter, KOH discharge pumps to the tank. Temperature control in the tank is by adjusting the cooling water flow rate.

KOH Tank-2

The capacity of the tank is 63 litres. It is used to scrub unconverted gases and fumes from the facility. It is in addition to KOH tank-1.

Construction: Material of construction is glass-lined on carbon steel

Control Loop: The level is controlled manually in the tank using a level transmitter, KOH discharge pumps to the tank.

Scrubber

Type : Spray scrubber

Scrubber solution flow rate : 40 slpm

Gas flow rate : 40 slpm

KOH concentration : 10-20 %

Material of Construction : Monel

Heating System

The heating system consists of an electrical heating unit, accumulator tank, storage tank, thermic fluid circulating pumps to process system, and internal recirculation pumps. Dustproof, prewired modular control panel, contactors, temperature controllers cum indicators, are used in the system. Storage tank cum make up a tank is provided and the system can dump the entire thermic fluid holdup (800 litres) in the storage tank and accumulator tank together. At the outlet from the pump, the heating system piping network starts and branches out into three floors i.e. ground floor, first floor, and second floor. On each floor, the piping is branched and supplied to tanks, process piping. And the piping joins the return header which flows into the heating system again.

Safety interlocks are present for the low flow of thermic fluid, low & high temperature of the thermic fluid, low & high holdup/level of thermic fluid in the accumulator tank.

Operating Temperature : 155°C
Operating Pressure : 4 bar (g)
Flow rate : 200 lpm
Fluid handled : Therminol-55

Ventilation system

The system consists of 500 mm X 500 mm main exhaust duct and branches out into 300 mm X 300 mm ducts and these spreads throughout the process area with 11 dampers which are placed in critical areas. The gases are carried by ventilation duct from different areas of the plant are routed through the wet precipitator to stack.

Electrical System

The entire electrical requirement for the process is catered using an electrical panel housed in the rectifier room. Electrical equipment meets the safety requirements as per industrial safety rules.

Control and Instrumentation System

The control and instrumentation system of the metallic Bunsen section is designed to remotely control the plant during start-up, steady operation, safe, and emergency shutdown.

All analog process signals are connected through AI modules and final control elements are connected to AO modules. Digital inputs from and outputs to the process are connected to digital I/O modules. Two desktop PCs are used as operator stations and one laptop is provided as an engineering station for configuring and programming the system.

In this system, a dual redundant hot standby PLC CPU is used. All the components of the PLC system along with necessary input and output relay boards are housed in a control panel**.**

3.2.2 Integrity testing of experimental setup

Bunsen Section setup integrity testing has been carried out with water and air for leak tightness & functioning of equipment, piping & instruments, etc. The following activities have been carried out.

- ✓ Leak Testing
- ✓ The functionality of Equipment, instruments
- ✓ Controls
- ✓ Interlocks
- ✓ Alarms

3.2.2.1 System Integrity testing for Leakage

For testing the integrity of the system, the following equipment/ Tanks & piping have been leak-tested with air. The whole system is heated up to 100°C & pressurized up to 8 bar g. The system is put on hold for approximately one hour & then allowed to cool down. After cooling down to room temperature, leak testing has been carried out. Results are given in the following tables.

3.2.2.2 Equipment

All the tanks have been tested as follows. In leak testing, all the tanks have been taken with their pipe fittings for instruments and up to isolation valves. The details of leak testing are as follows: -

Feed & Product Storage Tanks: Iodine Feed Tank

System integrity for leakage: Pressure is stable @8.3 bar (g).

Component tested	Iodine Feed Tank
Test Medium	AIR.
Test pressure	8.3 bar (g).
Operating pressure	6.0 bar (g).
Testing time	2.0 Hrs.
P&ID section	Feed system 2 (tanks).
Pressure Indication Points	PT-401
Temperature Indication Points	TI-401
All joints to be soap bubble tested (Yes/No)	Yes.
Pneumatic test result	Satisfactory, No visible leakage found

Iodine feed line

The iodine feed line is up to reactor inlet –

Leak integrity: Pressure is stable @ 8.3 bar (g).

Component tested	Iodine feed line.
Test Medium	AIR
Test pressure	8.3 bar (g)

Operating pressure	6.0 bar (g)
Testing time	2.0 Hrs
P&ID section	Feed system 1 (tanks)
Pressure Indication Points	PT-401
Temperature Indication Points	TI-401
All joints to be soap bubble tested (Yes/No)	Yes
Pneumatic test result	Satisfactory, no visible leakage found

Utilities: Heating System

Leak testing of the heating system is done with Thermic fluid. This testing includes tank jackets, pipe jackets, heating system distribution & collection header, breaded hose connections.

Jacketed pipe and hoses are leaks tested using thermic oil @6 kg/cm^2 held for 30 minutes

Leak Integrity: No leak observed.

Nitrogen Purging System

Leak testing of the nitrogen purging system has been done with air. The testing includes piping from the nitrogen cylinder isolation valve to nitrogen line isolation valves on tanks.

System integrity for leakage: pressure is stable @ 8.6 bar (g).

Instrument Air System

Instrument air system leak testing has been done with air. The testing includes piping after the isolation valve in the experimental area to the instrument air header.

System integrity for leakage: No leak

Iodine Feed Pump

The functionality of the Iodine feed pump has been tested with water. The following tests have been carried out.

Rotation

Pump motor rotation, smoothness & direction have been checked. Motor rpm has also been checked in SCADA. Tested Ok

Oil

Pump Oil visual check for unwanted foreign material & level have been carried out. Oil leakage from the pump also has been checked.

Tested Ok

Current

With the help of electrical personnel, the testing for drawn current has been carried out for motor load checking at various motor rpm.

Flow

Flow testing has been carried out at following discharge pressures, stroke & rpm.

Pressure	1 bar (g), 3 bar (g), 5 bar (g), 7 bar (g), 8 bar (g)
Stroke	25%, 50%, 75%, 100%
RPM	25%, 50%, 75%, 100%

Temperature Transmitter

Temperature transmitters are checked for their functioning by reading in SCADA @ ambient temperature & hot water bath.

Pressure Transmitter

Pressure transmitters are checked for their working by reading in field indicator & SCADA at various pressures as follows

1 bar (g), 3 bar (g), 5 bar (g), 7 bar (g), 8 bar (g)

Level Transmitter & Differential Pressure Transmitter

Level transmitters & Differential pressure transmitters are checked for their working by reading in field indicator & SCADA at various levels as follows

Flow Transmitters

Flow transmitters are checked with collecting water in a measuring cylinder from sample points/drain points.

Heating System Testing

The heating system is tested for the following

Heater pump functioning, rotation, flow, discharge pressure.

User pump functioning, rotation, flow, discharge pressure.

Visual inspection of Thermic oil

Testing of the level switch in accumulator tank at

- High : 255 Litre
- Normal : 168 Litre
- Low : 108 Litre
- Very Low : 87.5 Litre

The pressure Switch in the Heater Pump discharge line has been set @ 0.5 bar (g): will indicate low flow to the heater. Testing of the pressure gauge in user pump discharge has been done.

Heater testing at 50, 75, 100, 120 ^{o}C temperatures is done.

Rotameters are tested for transmission & field indication.

Heating in Feed tanks is tested with respective TI in tanks.

Ventilation System Testing

The ventilation system is tested for its air changes per unit time capacity. All duct openings have been closed other than the experimental facility. Anemometer has been used to measure the velocity at all corners, middle point of sides &centre of all duct openings. The average of all these has been considered as average velocity from that duct opening. Two cases have been studied to evaluate the ventilation system.

1. When duct opening on all the floors closed other than the floor being tested.
2. When duct opening on all the floors opened together.

Monitoring & Detection System Testing

Gas monitors are tested for their field indication & panel indication. For testing respective, calibrated chemicals have been exposed in the vicinity of the sensor of the gas monitor & the alarm has been checked. For fire alarm the smoke introduced in the vicinity of the sensors & alarm tested.

After successful completion of integrity testing, experiments are conducted to ensure the correctness of results.

Fig. 4-1 shows the experimental apparatus. The Bunsen reactor is a tubular reactor having a capacity of 800 ml. Feed water, HI, and iodine are mixed as HIx solution and is pumped into the reactor, gaseous mixture of SO_2 and O_2 are fed along with HIx in co-current mode. SO_2 & O_2 are fed from respective compressed gas storage cylinders and through mass flow controllers (M5X, Bronkhorst). HIx solution is heated in the feed tank to the desired temperatures by the thermic fluid heating system (Etherm EH-015, Technomax) and then pumped into the reactor. Bunsen reaction products are collected in the storage tanks and unreacted SO_2 is scrubbed in alkali solution. The pressure of the system is controlled using a control valve and a pressure transmitter (7MF4033, Siemens).

The reactor is made of a tantalum tube with SS 316 jacket to remove the exothermic heat of the Bunsen reaction. The temperature is maintained by a thermic fluid heating system. Temperatures of the reaction, inlet, and outlet cooling water temperatures are measured using ‘K’ type thermocouples (TD548202, Thermal Instruments).

Samples are collected at the reactor inlet and outlet under high pressures using 3 valves strategy. The valves V1, V2, and V3 are connected in series at the sample location. Initially, V1 is opened and closed, then V2 is opened and closed and finally, V3 is opened and collected the sample. The valve opening sequence is done thrice to flush hold up and collect the real-time sample. After the collection of the sample in a transparent beaker, a top phase which is the sulfuric acid phase is sucked out using a pipette leaving HIx which is the bottom phase. Valves are PFA lined ball valves with 25 NB bore size.

3.2.3 Safety aspects of the experimental facilities

To ensure reliable functioning, the integrity of the setup components such as piping, valves, and instruments are checked thoroughly during the installation. The fabrication is carried out by skilled technicians under strict supervision and quality checks. All the weld joints, whether in equipment or piping, are liquid penetrant tested. The equipment and pipelines are subjected to hydro and pneumatic testing at pressures above the design pressure. The leakage testing of the pipelines is carried out using Nitrogen gas by a soap bubble test. Engineered safety features such as adequate ventilation and installation of the gas detectors are adopted to ensure personnel safety during operation. To carry out the periodic surveillance for leakage of the toxic gases such SO_2, Iodine, and HI, handheld detectors are also made available. Integrity testing is already described in an earlier subsection.

3.3 Analytical Methods

Analysis of feed solution iodine (dissolved in HI), product acids viz. sulfuric acid and hydriodic acid are required to be carried out for various species such as I^-, $H^{+,}$ and I_2. Alkali solution is analysed for KOH. Analysis of samples for the above species is done in a potentiometric titration unit (Metrohm, 836 Titrando).

3.3.1 H^+ analysis

The sulfuric acid analysis is carried out using the following standards.

Primary standard: Potassium Hydrogen Pthalate (KHP)($KHC_8H_4O_4$)

Secondary standard: Sodium Hydroxide (NaOH)

Electrode: pH glass electrode

Secondary standard NaOH was standardized with a known concentration of a standard primary solution of Potassium Hydrogen Phthalate.

$$\mathrm{KHC_8H_4O_4 + NaOH \rightarrow KNaC_8H_4O_4 + H_2O} \quad (3.1)$$

With the digital pipette, the sample is quantified. pH glass electrode is used to analyze the sample with standardized NaOH solution in an automated potentiometric titration unit.

$$\mathrm{2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O} \quad (3.2)$$

3.3.2 HI (I^-) analysis

HI, acid analysis is carried out using the following standards.

Primary standard: Sodium Chloride (NaCl)

Secondary standard: Silver Nitrate ($AgNO_3$)

Electrode: Ag_2S electrode

The secondary standard $AgNO_3$ solution is standardized with a known concentration of a standard primary solution of Sodium Chloride.

$$\mathrm{NaCl + AgNO_3 \rightarrow AgCl + NaNO_3} \quad (3.3)$$

With the digital pipette, the sample is quantified. To sample distilled water is added up to enough level. Ag_2S glass electrode is used to analyse the sample with standardized NaOH solution in an automated potentiometric titration unit.

$$\mathrm{HI + AgNO_3 \rightarrow AgI + HNO_3} \quad (3.4)$$

3.3.3 Iodine (I_2) analysis

Iodine analysis is carried out using the following standards.

Primary standard: Potassium Iodate (KIO_3)

Secondary standard: Sodium thiosulphate pentahydrate ($Na_2S_2O_3.5H_2O$)

Electrode: Platinum ring electrode

Secondary standard Sodium thiosulphate pentahydrate solution is standardized by adding known quantities of Potassium iodide salt and Sulfuric acid and then titrated with a known concentration of a standard primary solution of Potassium Iodate.

$$\mathrm{KIO_3 + 5KI + 3H_2SO_4 \rightarrow 3I_2 + 3H_2O + 3K_2SO_4} \quad (3.5)$$

$$\mathrm{Na_2S_2O_3 + 2I_2 \rightarrow 2NaI + S_4O_6^{2-}} \quad (3.6)$$

With the digital pipette, the sample is quantified, and to it, distilled water is added up to a sufficient level. A platinum ring electrode is used to analyse the sample with a standardized Sodium thiosulphate solution in an automated potentiometric titration unit.

3.3.4 KOH analysis

KOH analysis is carried out using the following standards.

Primary standard: Standard NaOH solution

Secondary standard: Oxalic Acid $(COOH)_2$

Electrode: pH glass electrode

The secondary standard of Oxalic Acid solution is standardized with a known concentration of a standard primary solution of NaOH.

With the digital pipette, the sample is quantified, and to it, distilled water is added up to a sufficient level. the pH glass electrode is used to analyse the sample with a standardized Oxalic Acid solution in an automated potentiometric titration unit.

$$\mathrm{C_2H_2O_4 + 2KOH \rightarrow K_2C_2O_4 + 2H_2O} \quad (3.7)$$

The error associated with the analysis of total concentration is$< \pm1\%$, H^+ & I^- is $< \pm1\%$. The accumulated error in the calculation of H_2SO_4 and H_2O is$< \pm2\%$ & $\pm5\%$ respectively.

3.4 Fluid Properties

Fluid properties of acids and mixture of acids were derived from Chemical process simulation software PRO SIM, France.

4 EXPERIMENTAL STUDIES

4.1 Studies on phase separation of Bunsen reaction product mixture

4.1.1 Preamble

Bunsen reaction as described earlier in chapter 2 involves a reaction between sulfur dioxide, water, and iodine to produce two acid mixtures. In the present section, studies on cross-contamination in the production phases of Bunsen reaction are presented. I-S process becomes feasible when the Bunsen reaction produces two immiscible pure phases i.e. sulfuric acid and HIx phase (a mixture of HI, water, and iodine). Although Bunsen reaction looks less critical due to negligible energy demand and relatively mild temperatures of operations, it represents a key process step to be optimized. As the compositions of its product streams strongly affect energy consumption in the operations downstream.

During the phase separation, HI & I_2 are contaminants in the H_2SO_4 phase and H_2SO_4 is a contaminant in the HIx phase, the cross-contamination amount needs to be minimized/removed. The cross-contamination poses great problems in downstream sections [122,157-162]. One of the major problems is iodine gets precipitated at lower temperatures in the process piping. Iodine can chock the small-diameter pipelines in the sulfuric acid section. Apart from iodine chocking, cross-contamination can lead to the occurrence of side reactions (reaction 1.2 & 1.3), especially during HIx purification. Sulfuric acid and hydroiodic acid solution react to form sulfur and hydrogen sulfide, under lower iodine concentration and higher temperatures.

The formation of sulfur due to side reaction can lead to poisoning of catalyst in HI decomposer. To avoid these problems temperature, pressure, and feed compositions need to be optimized.

SO_2 solubility in water decreases as the temperature is increased. To increase the SO_2 solubility, higher pressures are required. Pressurized conditions are favourable for the integrated operation of the Bunsen reaction. It is observed that the conversion of SO_2 increases as pressure is increased which is highly desirable. In the article, Rao et al. have observed that the increase in pressure and decrease in temperature leads to increase in overall reaction rate.

The data on the level of cross-contamination in the two liquid phases at high pressures are available only up to pressures of 2 bar (g).

Liquid-liquid phase separation has been studied earlier without carrying out Bunsen reaction in which impurities of the two phases are discussed at atmospheric pressures. These are extensively discussed in the literature survey.

To obtain the level of impurities in the sulfuric acid phase and hydroiodic acid phase of Bunsen reaction products, experiments have been performed up to pressures of 6 bar (g) in continuous mode operation.

In the closed-loop operation of the I-S process, oxygen and sulfur dioxide are produced during sulfur trioxide decomposition as shown in fig. 1-2. The produced oxygen in the sulfuric acid section can be recycled along with sulfur dioxide in the Bunsen section. This leads to a reduction in additional separation step for removal of O_2 from SO_2. The O_2 has been used as an inert gas in experiments along with feed SO_2, wherein SO_2 gets consumed in the reactor thus separating O_2 [125]. If higher pressures give better purity levels in the two product phases of the Bunsen reaction, then the burden on downstream sections will greatly reduce. Experiments have been carried out at higher pressures and temperatures using O_2 as inert. The pressures have been limited to 6 bar (g) as the solubility of SO_2 in aqueous medium does not greatly enhance after 6 bar (g) [163].

4.1.2 Experimental schematic

The experimental schematic is described in Fig. 4.1. Fig. 4.2 is the experimental setup of the Bunsen reactor and fig 4.3 describes the typical gas-liquid reaction in which sulfur dioxide is the gas reactant which is bubbled through iodine and water in hydroiodic acid which are the liquid reactants.

As discussed earlier, the reactor tube is made of a tantalum tube. Jacketing is provided to remove the exothermic heat of the Bunsen reaction and it is made of SS 316 as shown in figure 4.2. The temperature is maintained by a thermic fluid heating system. Temperatures of the reaction, inlet, and outlet cooling water temperatures are measured using ‘K’ type thermocouples. Pressures and levels are monitored using pressure transmitter and differential pressure transmitters (7MF4033, Siemens). The feed concentrations of HIx ($HI/I_2/H_2O$) are studied in the molar ratios of 1/1.5-2.8/6.32-8. The experiments are conducted at temperatures from 50 ^oC to 75 ^oC. The operating pressures are in the range of 2-6 bar (g). The SO_2 flow rates varied from 0.06 g/s to 0.24 g/s and O_2 flow rates varied from 0.008 g/s to 0.016 g/s.

Experimental conditions are selected such that there is a maximum amount of purity is obtained. Since the Bunsen reaction is exothermic, increasing temperature leads to a reverse reaction. An increase in temperature will also increase the probability of side reaction occurrence. Hence temperature is limited to 75 ^oC. The rate constant improves at higher temperatures and there should be an appreciable amount of iodine that should be made available for better phase separation. Iodine solubility in the HIx solution strongly depends on temperature. So nearly 70-80 % iodine saturation limit of the respective temperature of operation has opted in this study. SO_2 and HIx flow rates are kept in such a way that gives an equivalent hydrogen throughput of 150 Nlph. In most of the studies, sulfur dioxide to oxygen ratio is maintained as per stoichiometry of sulfur trioxide decomposition from the sulfuric acid section.

Samples are collected at the outlet of the liquid-liquid separator under high pressures using 3 valves strategy as described in section 3.2.1 of chapter 3. After the collection of the sample in a transparent beaker, the top phase which is the sulfuric acid phase is sucked out using a pipette leaving HIx in the bottom.

The HI and I_2 concentrations are measured by titrating I^- and I_2 with 0.1 N $AgNO_3$ and 0.1 N $Na_2S_2O_3$ standard solutions, respectively. H^+ is titrated with 0.1 N NaOH standard solutions. H_2SO_4 concentration is calculated by subtracting the amount of HI from the amount of H^+ titrated. H_2O concentration is calculated assuming that only HI, H_2SO_4, H_2O, and I_2 are present in each phase.

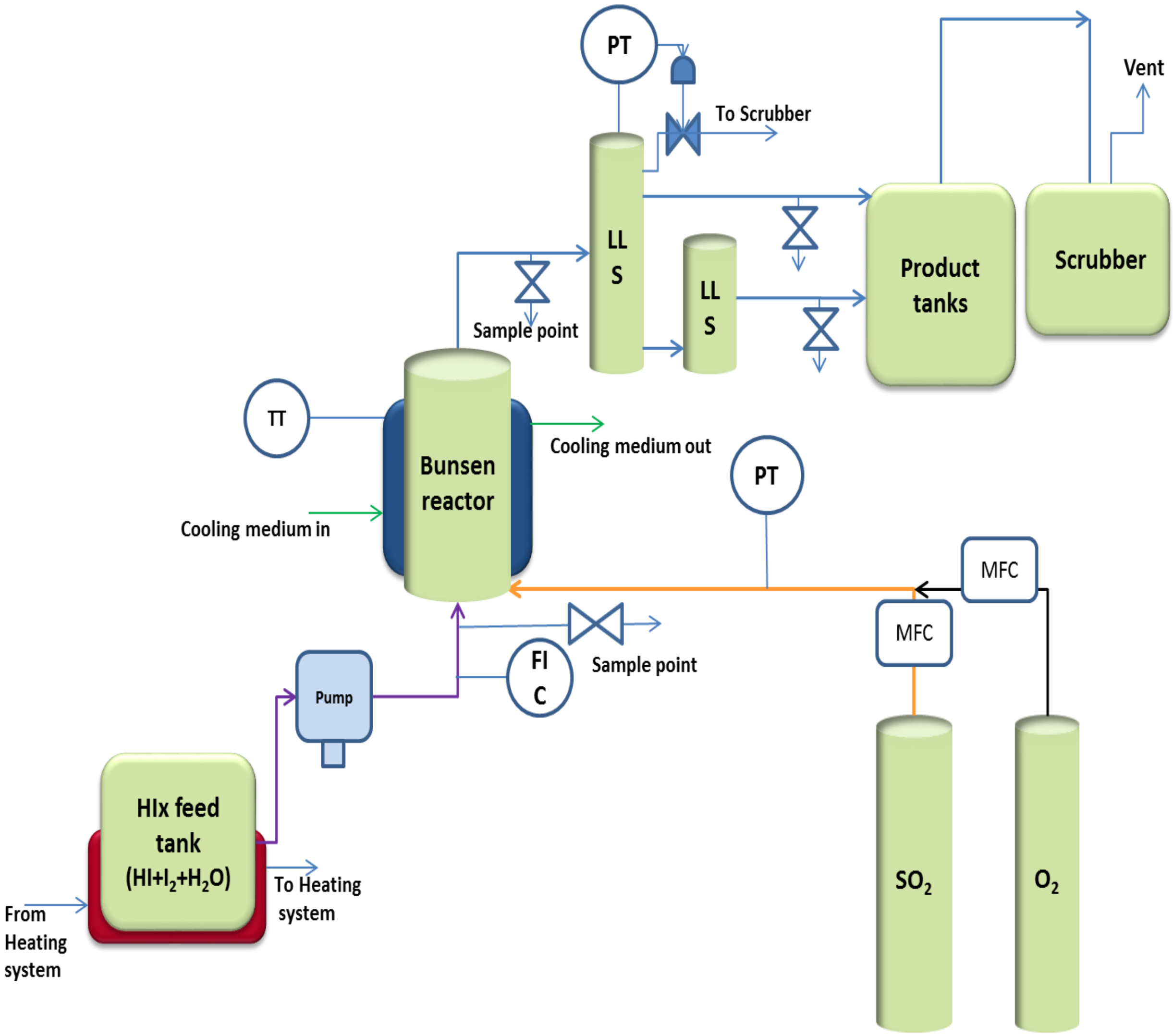


Fig. 4-1 Simplified experimental schematic

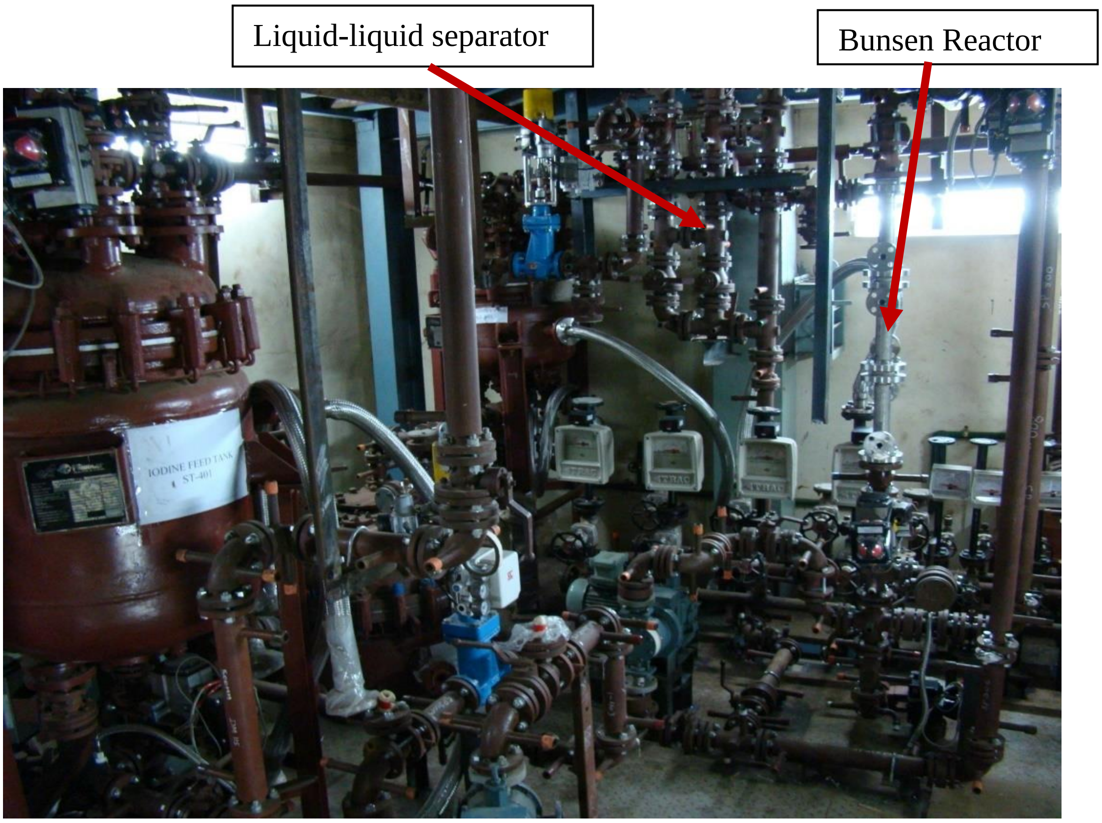


Fig. 4-2 Bunsen Reactor and Liquid-liquid separator

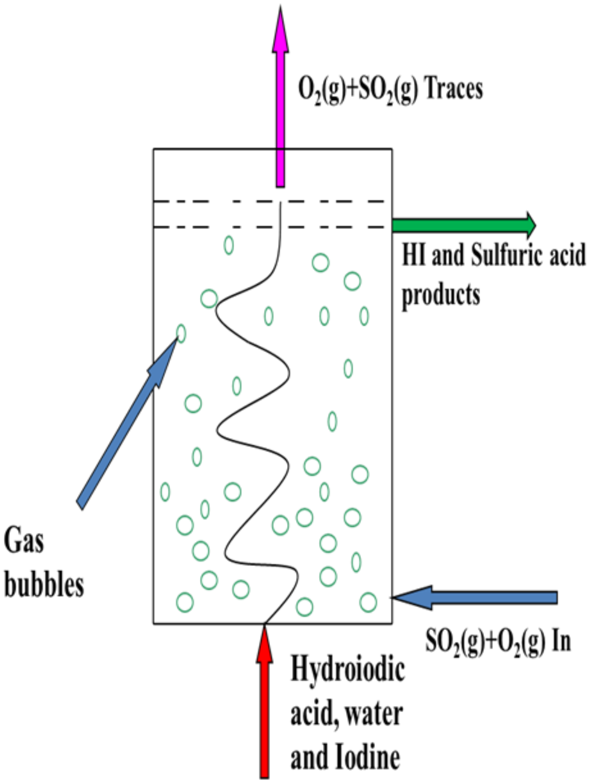


Fig. 4-3 Schematic of Bunsen Reaction

4.2 Studies on Bunsen reaction at elevated temperature and high pressure

4.2.1 Preamble

In the present section, Bunsen reaction studies at high pressures and elevated temperatures are presented.

As discussed in the previous chapter, an increase in Bunsen reaction operating temperature leads to a decrease in SO_2 solubility. Higher pressure operating conditions are favourable for the integrated operation of the Bunsen reaction. An increase in pressure shifts the HI azeotrope to a higher value and reduces the pumping power required to compress hydrogen produced. Bunsen reaction and phase separation has been studied extensively under various operating conditions.

As mentioned in the literature survey, the Bunsen reaction is also carried out in counter-current flow mode to achieve reaction and phase separation in the same equipment by varying the SO_2 flow rate and partial pressure. In the literature, Bunsen reaction has been carried out at pressures up to 2 bar (g) in continuous mode and up to pressures 4.5 bar (g) in semi-batch mode.

In this study, O_2 has been fed along with SO_2 instead of N_2 at pressures up to 6 bar (g) in continuous mode by varying feed flow rates and temperature from 50 ^oC to 80 ^oC. This separation of O_2 from SO_2, which is produced in the H_2SO_4 decomposition section can be achieved in the Bunsen reaction without additional equipment. The pressures have been limited to 6 bar (g) as the solubility of SO_2 in aqueous medium does not greatly enhance after 6 bar (g) [163]. HI is used along with water and iodine in the feed because in the closed-loop integrated operation of the I-S process iodine and water are recycled along with unconverted HI.

4.2.2 Experiential Schematic

The experimental schematic is described and shown in fig.3.1 in section 3.2.1 of chapter 3. The setup consists of a tubular reactor, feed, and product tanks. Feedwater, HI, and iodine are premixed as HIx solution and fed into the reactor, gaseous reactant SO_2 with O_2 are fed in co-current mode. SO_2 and O_2 are fed through gas cylinders and mass flow controllers with an accuracy of ±0.5% full scale. Heating of feed HIx is carried out through the thermic fluid heating system. Bunsen reaction products are collected in the storage tanks and unreacted SO_2 is scrubbed in alkali solution. System pressurization is achieved by a control valve and pressure transmitter with an accuracy of ±0.5% measured value.

Fig. 4.4 is the experimental setup of the Bunsen reactor. The reactor is made of tantalum tubes having a capacity of 800 ml with a Stainless Steel 316 jacket to remove the exothermic heat of the Bunsen reaction. Temperatures of the reaction, inlet, and outlet cooling water temperatures are measured using thermocouples with an accuracy of $\pm 0.2\ ^{o}C$. The Experiments are carried out by varying flow rates of HIx, $SO_{2,}$ and $O_{2,}$ temperature, and pressure with feed HIx ($HI/I_2/H_2O$) in the ranges of 1/1.6-2.6/6.3-7.

Fig. 4-4 Bunsen reactor setup

The sample collection strategy is described in section 3.2.1 of chapter 3.

4.3 Studies on reaction kinetics of Bunsen reaction

4.3.1 Preamble

Bunsen reaction is a heterogeneous gas-liquid reaction system in which the mass transfer of sulfur dioxide to the reaction system is enhanced by chemical reaction [165]. Thus, the kinetics of the Bunsen reaction depends on both chemical reaction resistances as well as mass transfer resistances.

Evaluation of the kinetic parameters for gas-liquid reactions is required for the design of reactors. An error in the estimation of these parameters will lead to an over or under the design of the reactor. Further, the accuracy of process modelling invariably depends on accurate model parameters.

Bunsen reaction studies have been carried out with the focus on best operating conditions for the operation, phase separation characteristics, side reactions, thermodynamics, and use of solvents for phase separation. Bunsen reaction studies are carried out by researchers and the same is given in chapter 2.

Evaluation of kinetic parameters has been carried out for the Bunsen reaction. Kinetic studies in a semi-batch reactor are studied by varying feed flow rates and reactant concentrations, but effects of mass transfer are not described and the reaction is carried out at ambient pressure conditions. Reaction kinetics of the electrochemical Bunsen reaction using polarization curves measurement studied but the applicability of data for conventional reactor design is limited. Using solvents, reaction kinetics have been studied in detail, but the reaction mechanism will be entirely different without solvent.

Bunsen reaction kinetics studies carried out using a stirred cell reactor and from pressure decrease profiles and obtained the reaction parameters. However, absorption rates of SO_2 in HIx solution should be in a fast pseudo-first-order regime to correlate kinetic absorption rates with experimentally determined absorption rates. To ensure the reaction regime is to be in fast pseudo-first-order, several experiments have been conducted in this study and obtained the kinetic rate constant.

There are diverse kinds of apparatus to quantify the rate of gas-liquid reactions. The widely accepted and studied are laminar jet, wetted wall apparatus of diverse contacts, and a stirred cell [165]. Mainly, the interface area between the phases and physical mass transfer coefficients necessarily to be available in such setups, to identify the consequence of the chemical reaction in the presence of diffusion mass transfer.

The gas-liquid mass transfer phenomenon is explained by several theories in the literature, such as models built on the two-film theory and others evaluated on the penetration and surface renewal theories. Out of all these models, the film theory model is most often considered [167] because it is mathematically less complicated over penetration theory. In the film theory, mass transfer phenomena occur by diffusion at molecular level in a stagnant liquid/gas layer of thickness δ, but the bulk of liquid/gas is considered to be well mixed. All the resistance to mass transfer is in a thin film δ. Outside the film the concentration of the solute is assumed to be uniform. The film is assumed to be stagnant. The absorption process is by steady-state diffusion irrespective of; the entire column is operating at a steady-state or unsteady state. Typical concentration profiles of components for the general case of absorption with chemical reaction are illustrated in Fig. 4.5.

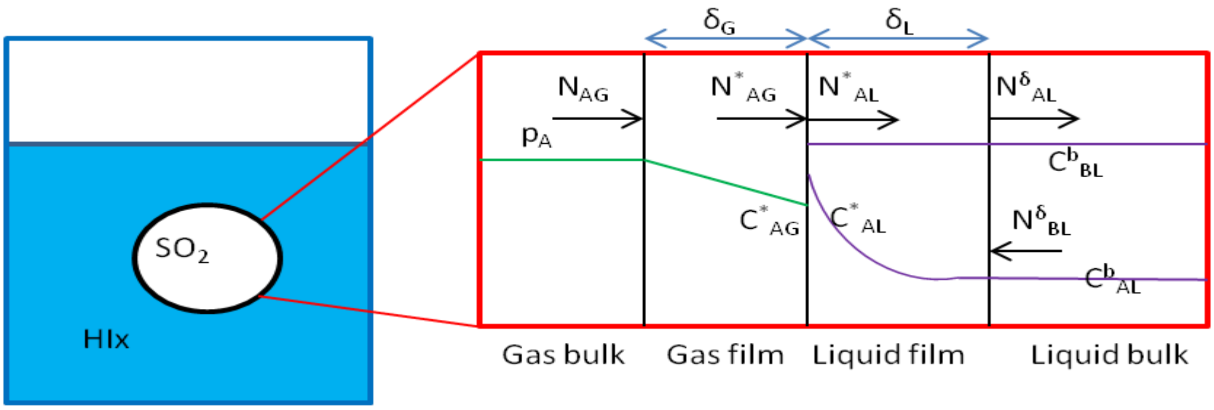


Fig. 4-5 Mechanism of gas transfer into the liquid bulk

Sulfur dioxide absorption rate into an aqueous solution followed by reaction in the absence of gas-phase limitation can be represented by the following equation

$$N_{AL}^{*} = E_A k_{AL} \left(C_{AL}^{*} - C_{AL}^{b} \right) \qquad ---(4.3)$$

N_{AL}^{*} is the flux of A into the liquid phase, E_A enhancement factor, k_{AL} is the coefficient of mass transfer of SO_2 in the liquid medium, C_{AL}^{*} and C_{AL}^{b} are the concentrations at interface and bulk. The enhancement factor E_A describes the effect of a chemical reaction on the mass transfer rate. The enhancement factor is the ratio of the rate of absorption of a component in gas into the liquid phase in the occurrence of a chemical reaction to the rate of absorption in the absence of a reaction at the same driving force of concentration. This factor encompasses all the effects of chemical reaction on the absorption rate. However, to evaluate the enhancement factor there is no general analytical expression.

Diverse approaches for the evaluating the enhancement factor is available in the literature. Based on the film model and through analytical approach, enhancement factor are obtained for some asymptotic cases with certain assumptions with regard to the reaction regime.

For the case of C_{AL}^{b}=0 Eq. (4.3) can be simplified to:

$$N_{AL}^{*} = E_A k_{AL} C_{AL}^{*} \qquad ---(4.4)$$

Analytically expressions are derived for the calculation of enhancement factors that are possible for some of the cases only but over a wide range of process conditions expressions are not possible because of the complexity of mathematical equations it involves. Alternatively, estimation of the mass transfer rate through the enhancement factor, utilizing approximation approaches for the account of the given absorption case can be obtained. Diverse approaches for the calculation of enhancement factors are given in [168].

Bunsen reaction can be represented in the form of a gas-liquid reaction with A as SO_2 gas and B as liquid reactant here it is H_2O dissolved in HIx solution which includes I_2. Considering the liquid solution to be non-volatile and proceeds in a forward direction further analysis is carried out.

$$A(g) + b'\,B(l) \xrightarrow{k_2} C(l) \qquad ---\ (4.5)$$

$$-r_A = kC_AC_B$$

C_{Bb} = Concentration of B in liquid (bulk)

C_A^*= Concentration of A in equilibrium with the gas partial pressure and it is the concentration of A at the gas-liquid interface.

The governing equation in the gas-liquid film is given by

$$D_A \frac{d^2C_A}{dx^2} = kC_AC_B \qquad ---\ (4.6)$$

$$D_B \frac{d^2C_B}{dx^2} = b'\,kC_AC_B \qquad ---\ (4.7)$$

Boundary conditions are given by

$$\text{At } x=0,\ C_A=C_A^*,\ \frac{dC_B}{dx} = 0 \qquad ---\ (4.8)$$

$$\text{At } x=\delta,\ C_A=C_{Ab},\ C_B=C_{Bb} \qquad ---(4.9)$$

When the above equations are non-dimensionalize by substituting

$$a = \frac{C_A}{C_A^*} \qquad ---\ (4.10)$$

$$b = \frac{C_B}{C_{Bb}} \qquad ---\ (4.11)$$

$$\psi = \frac{x}{\delta} \qquad ---\ (4.12)$$

We get

$$\frac{d^2a}{d\psi^2} = \left(\delta^2 \frac{kC_{Bb}}{D_A}\right) ab \qquad ---\ (4.13)$$

$$\delta^2 \frac{kC_{Bb}}{D_A} = Ha^2 \qquad --- (4.14)$$

$$\frac{d^2b}{d\psi^2} = \left(\delta^2 \frac{kC_{Bb}}{D_A}\right)\left(\frac{b' D_A C_A^*}{C_{Bb}}\right) ab \qquad --- (4.15)$$

$$q = \frac{D_B C_{Bb}}{b' D_A C_A^*} \qquad --- (4.15a)$$

$$\frac{d^2b}{d\psi^2} = \left(\frac{Ha^2}{q}\right) ab \qquad --- (4.16)$$

Boundary conditions:

$$\Psi=0,\ a=1,\ \frac{db}{d\psi} = 0 \qquad --- (4.17)$$

$$\Psi=1,\ a=a_b=\frac{C_{Ab}}{C_A^*},\ b=1 \qquad ---(4.18)$$

As described earlier effect of chemical reaction on mass transfer is given using enhancement factor. The enhancement factor depends on the two parameters, the Hatta number, Ha and the enhancement factor of an infinitely fast reaction, E_∞. Ha is the ratio of the characteristic time for diffusion with the characteristic time for reaction or it is relating the reaction rate with the diffusion rate and is given by

$$Ha = \frac{\sqrt{k_2 D_{AL} C_{BL}^b}}{K_{AL}} \qquad --- (4.19)$$

When Ha is large it means that, the characteristic time for reaction is much slower than the characteristic time for diffusion or reaction is much faster than diffusion. If Ha is small it means, the characteristic time of diffusion is much smaller than the characteristic time for reaction; which means, the diffusion is a much faster process than reaction. The Hatta number is can be seen as the measure for the reaction happens entirely in the liquid bulk or entirely in the liquid film.

$$E_{\infty} = 1 + \frac{D_{BL}C_{BL}^{b}}{b'D_{AL}C_{AL}^{*}} = 1 + q \qquad ---(4.20)$$

For a system, for which the concentration of B is fixed, the concentration of A is fixed. E_{∞} reflects the maximum enhancement that can occur in mass transfer because of chemical reaction and therefore, a subscript E_{∞} here is the the maximum value of enhancement factor for a given system or enhancement in the case of instantaneous reaction.

As the Hatta number is increased the chemical reaction is tending towards the gas-liquid boundary and the enhancement factor is restricted by the value specified by E_{∞}.

Based on the value of Hatta number and the relation between Ha and E_{∞} different regimes of reaction can happen. Experiments that are done at a steady liquid concentration and at a defined hydrodynamic environment categorized by a certain k_{AL}, varying the gas partial pressure might affect the influence of a chemical reaction on the SO_2 (A) absorption rate.

When the Hatta number, Ha is far less than the infinite enhancement factor, E_{∞}, then the concentration of H_2O (B) is almost same in the liquid bulk and liquid film. This can also be interpreted as the relative abundance q is high in the gas-liquid interface. This results in uniform concentration of H_2O (B) in the gas-liquid interface.

As concentration of H_2O in the liquid film is nearly steady, reaction in the liquid film is dependent only on the concentration of SO_2. Hence the reaction can be considered to be pseudo first order with respect to SO_2 in the liquid film.

When Ha>2, the reaction is said to be fast in the liquid film.

$$2 < Ha \ll E_{\infty} \qquad ---(4.21)$$

Inequality (4.21) represents the case of fast pseudo first order reaction in the liquid film.

In this case integrating twice equation 4.16 gives b=1

By substituting b=1 in equation 4.13 gives

$$\frac{d^2 a}{d\psi^2} = \left(\delta^2 \frac{kC_{Bb}}{D_A}\right) a \qquad ---(4.22)$$

Solving 4.23, gives

$$a = \frac{1}{sinhHa}[a_b \sinh{(Ha.\psi)} + \sinh{(Ha(1-\psi))}] \qquad ---(4.23)$$

Absorption flux is given by

$$N_A = -D_A \frac{dC_A}{dx}|_{x=0} = -\frac{D_A C_A^*}{\delta}\frac{da}{d\psi}|_{\psi=0} \qquad ---(4.24)$$

Incorporating equation 4.23 in 4.24 we get

$$\frac{da}{d\psi}|_{\psi=0} = \frac{a_b Ha - Ha.\cosh{(Ha)}}{\sinh{(Ha)}} \qquad ---(4.25)$$

$$N_A = -\frac{D_A C_A^*}{\delta}\left(\frac{Ha}{\tanh(Ha)}\right)\left(1 - \frac{a_b}{\cosh(Ha)}\right) \qquad ---(4.26)$$

For the case of a_b~0 which is a fair assumption for fast reactions.

We know

$$k_L = \frac{D_A}{\delta} \qquad ---(4.27)$$

Rewriting 4.28 in the following form by substituting 4.27,

$$N_A = k_L\left(\frac{Ha}{\tanh{(Ha)}}\right)C_A^* \qquad ---(4.28)$$

By comparing equation 4.28 and 4.4, the expression for enhancement factor is given by,

$$E_A = \frac{Ha}{\tanh{(Ha)}} \qquad ---(4.29)$$

The interfacial concentration of SO_2 is related to its partial pressure in gas and can be represented by Henry`s law.

$$C_{AL}^* = \frac{p_A}{H} \qquad ---(4.30)$$

For Ha>3, it can be seen that

$$\tanh{(Ha)} \sim 1 \qquad ---(4.31)$$

For this case by introducing (4.30) into (4.4) results in

$$N_{AL}^{*} = \frac{\sqrt{k`D_{AL}}p_A}{H} \qquad --- (4.32)$$

k` is the overall reaction rate constant. k` = k$_2$ C_{BL}^{b}

By satisfying equation (4.21) the reaction of SO_2 with H_2O in HIx solution is thought to occur in the fast pseudo first order reaction regime. It indicates the chemical reaction to be in first order relative to SO_2 and content of H_2O in the liquid film is constant. By considering equation (4.32), partial pressure observation gives the absorption rate of SO_2 in liquid. Hence reaction rate constant can be obtained experimentally from the partial pressure data from equation (4.32) by knowing Henry's constant and diffusion coefficient.

There are different experimental techniques to obtain kinetic rate data. The hydrodynamics, mass transfer resistances and the interfacial area must be known correctly for the different apparatus which is being used to obtain the kinetic data. As described earlier different apparatus includes a laminar jet, the wetted wall column, the wetted sphere absorber and a stirred cell. In order to obtain kinetics data, mass transfer coefficients should be as high as possible which results in smaller impact of diffusion phenomena on the absorption rate. The gas-liquid interfacial area and mass transfer coefficient may extensively be varied in a laminar jet reactor. By changing jet length and the flow rate of liquid, the interfacial area and k_{AL} can be altered. With respect to different setup, the interfacial area is static by sizes of a specified equipment size. The benefit of knowledge of the interfacial area and mass transfer coefficient aprior is that the reaction kinetics and mass transfer can be assessed independently. Then the obtained rate data can be studied to evaluate the kinetics of gas-liquid reactions. The stirred cell reactor is extensively useful as its simple to construct and operate and hence adopted in this study. This reactor can be operated under strict isothermal environments and can also be useful to evaluate gas solubility in a liquid. It can also be deployed in gas-liquid-solid reactions [167-169].

A typical reactor of that type is a cylindrical vessel with a stirring device as shown in fig. 4.6. The shown apparatus is defined as a well-mixed reactor or a stirred reactor because there is a uniform composition and temperature of the reaction in all areas of the vessel. The upper part of the reactor top encompasses the shaft seal and the essential nozzles for introducing the liquid phase. For an axially located stirrer, agitation introduces rotational motion. This can be prevented by introducing the baffles on the circumference. Stirring devices are having the issue of mechanical and sealing problems particularly in under pressure operations. The stirrer is the turbine type with four blades and both the gas and liquid phases are agitated by two stirrers which rotate in opposite direction.

As Bunsen reaction is exothermic reaction, there is a possibility of temperature increase due to exothermicity. This can create variation in mass transfer rate because of changes in coefficients of mass transfer and reduction in solubility of the absorbed gas. Uniform temperatures are very important during the chemical reaction rate which are generally very sensitive to temperature, the cooling and heating in a stirred vessel are attained by having jackets throughout the reactor vessel.

4.3.2 Experimental Schematic

Stirred cell reactors are functioned in batchwise in relation to the liquid phase. With regard to the gas phase, the experiments can be achieved in a batchwise or semi-batchwise mode. In batch experiments with respect to both gas and liquid phases, the absorption process is observed by monitoring the rate of pressure decrease in the reactor. At the start of the experiment, the gas is charged into the reactor instantaneously. The liquid reactant or solvent is initially charged before the introduction of the gas-phase and the desired temperature is obtained through jacket heating. As soon as the gas is introduced stirring is started, the absorption process is initiated. The SO_2 rate of absorption is evaluated from the experimental data by the mass balance in the reactor gas phase as:

$$N_{AL}^{*} = -\frac{V_G}{RTA`}\frac{dp_A}{dt} \qquad ---(4.33)$$

$$N_{AL}^{*} = k_{AL}\left(C_{AL}^{*} - C_{AL}^{b}\right) \qquad ---(4.34)$$

Where $V_G$the volume of gas phase in the reactor, T is the temperature, R is the gas constant, and A` is the interfacial area. In Eq. (4.34), the ideal gas phase behaviour was applied. Characteristically, at partial pressures near to atmospheric pressure, ideal gas law behaviour predicts the PVT relation well without causing significant errors relative to the real gas equations. The absorption rate is calculated from equation (4.34) by obtaining the pressure decrease profile for each experiment. In the absorption of SO_2 into the water, chemical reactions can be neglected. This system is used to examine the physical absorption behaviour of the reactor and obtain the appropriate mass transfer coefficients. Experiments are carried out by introducing SO_2 into the stirred vessel in a very short time (~3-4 seconds) over a liquid surface which contains only water. It has to be ensured that the mass transfer process is independent of stirring speed to reach a fast reaction regime. Hence, initial experiments are carried out only to evaluate the liquid side mass transfer coefficient i.e. water by varying stirring speeds from 0 rpm to 360 rpm. After obtaining the desired rpm, HIx is introduced into the vessel. Experiments are repeated to obtain the kinetic rate constant as described in equation (4.32).

From equations (4.31), (4.33) and (4.34) following relation can be derived to evaluate k_{AL} for the case of $C_{AL}^{b} \sim 0$.

$$\frac{dp_i}{dt} = -\frac{RT}{V_G}k_{AL}\frac{p_i}{H} \qquad ---(4.35)$$

Equation (4.36) is obtained by integrating equation (4.35) from initial pressure $p_{i,o}$to p_i in time interval t

$$\frac{p_i}{p_{i,o}} = exp\left(-\frac{RTA`k_{AL}}{V_G H}\ t\right) \qquad ---(4.36)$$

Similarly, from equation (4.30), (4.32) and (4.33), the following relation can be derived

$$\frac{dp_i}{dt} = -\frac{RTA`\sqrt{k`D_{AL}}}{V_G}\frac{p_i}{H} \qquad --- (4.37)$$

Equation (4.38) is obtained by integrating equation (4.37) from initial pressure $p_{i,o}$ to p_i in time interval t

$$\frac{p_i}{p_{i,o}} = exp\left(-\frac{RTA`}{V_G H}\sqrt{k`D_{AL}}\ t\right) \qquad --- (4.38)$$

Eq. (4.36 & 4.38) describes the pressure course during an experiment. Eq (4.36) is used for a direct numerical estimation of the mass transfer coefficient, k_{AL}. The latter is the only parameter to be fitted. Eq (4.38) is used for a direct numerical estimation of the reaction rate constant included in the overall kinetic rate constant k`. The latter is the only parameter to be fitted. This estimation is accomplished with the help of the least-square optimization which minimizes the residue between calculated and experimental values.

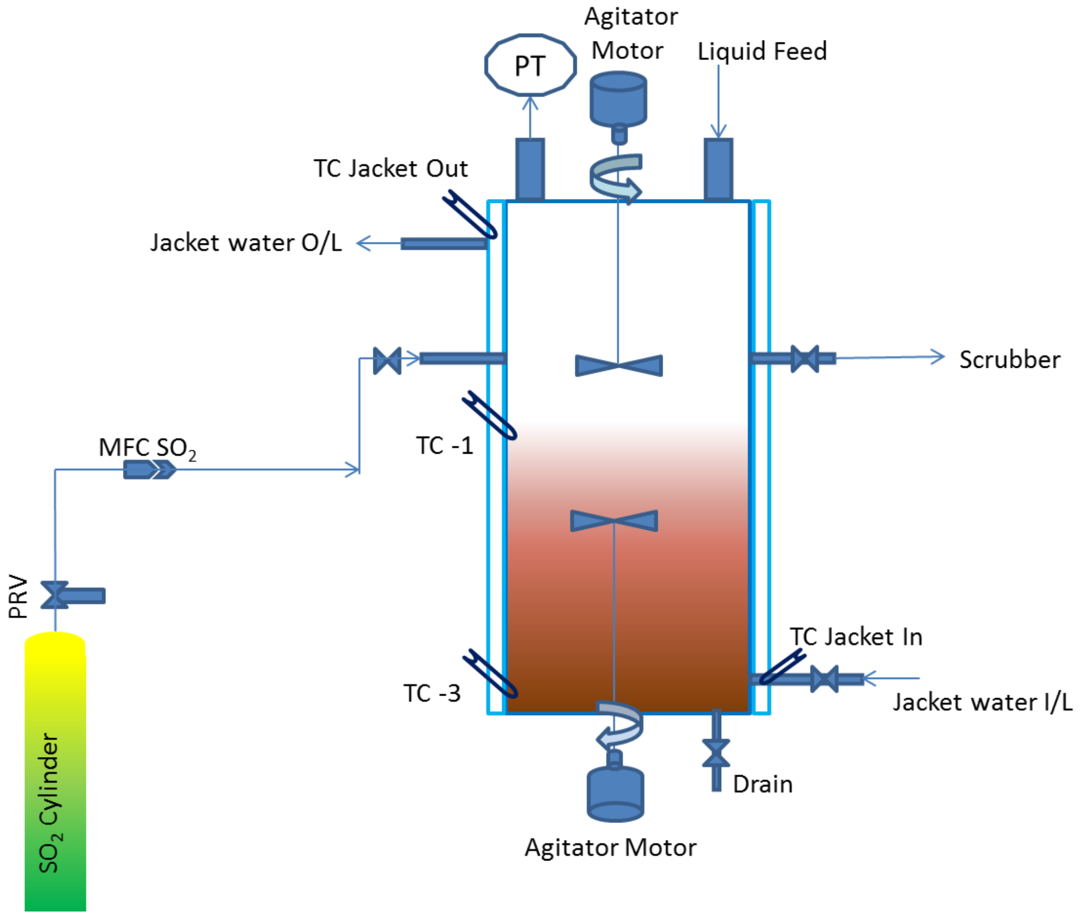


Fig. 4-6 Schematic of experimental setup

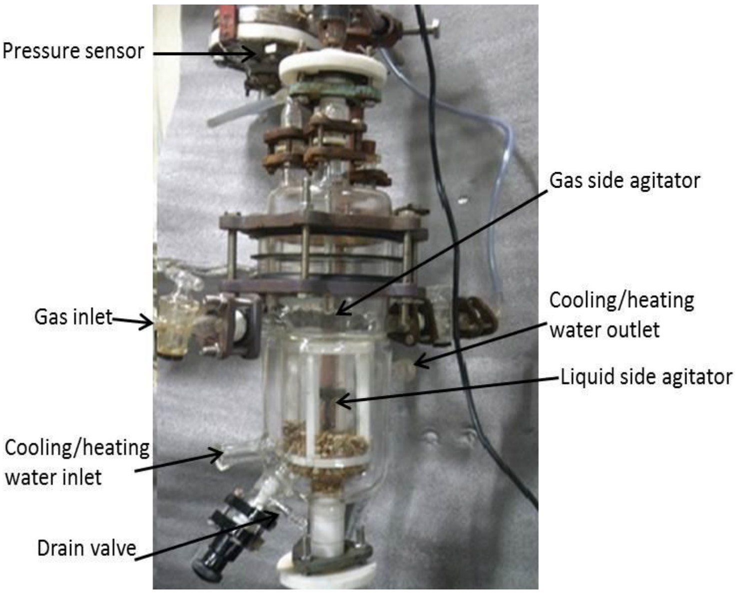


Fig. 4-7 Glass stirred cell reactor

The experimental schematic is shown in fig. 4.6. The setup consists of a stirred glass reactor with liquid hold up of 200 ml and 1200 ml vapor volume as shown in fig. 4.7. The temperature is maintained by water circulating through the jackets. Temperatures are monitored using ‘K’ type thermocouples. The liquid molar ratio of HIx ($HI/I_2/H_2O$) is 1/1.57/5.32. The temperatures and pressures of study are from 30 ^oC to 50 ^oC and up to 0.5 bar (g) respectively, varying stirring speed from 0 to 360 rpm. SO_2 gas is charged in the glass reactor from the gas cylinder using mass flow controller operation. The pressure is monitored using a pressure transmitter. The stirred glass reactor is shown in fig. 4.7.

Initially, HIx liquid is loaded and the desired temperature is obtained through jacket heating then the gas is charged into the reactor instantaneously i.e < 3 seconds, and stirring is started. Initially, experiments are carried out with the SO_2-H_2O system and evaluated the mass transfer coefficient at different stirring speeds. As stirring speed is increased, the rate of absorption increases, and beyond 300 rpm (in this study) stirring speed the mass transfer coefficient will not vary significantly and the absorption process of SO_2 in reaction media (HIx) is entirely governed by chemical reaction as given in equation (4.38). In all the experiments pure SO_2 gas is used as feed and therefore gas side mass transfer resistance is neglected.

Hence, initial experiments are carried out only to evaluate the liquid side mass transfer coefficient by varying stirring speeds from 0 rpm to 360 rpm. Later experiments are carried out with HIx liquid phase and a similar procedure is followed. Experiments are repeated to obtain the kinetic rate constant as described in equation (4.32).

4.4 Studies on side reaction and settling rates of Bunsen reaction products

4.4.1 Preamble

Bunsen reaction is operated in an aqueous medium (water acting as solvent and reactant) with a large excess of iodine to facilitate separation of the two product acids, to improve chemical equilibrium, to eliminate side reactions and can be represented as follows

$$(x+1)I_2 + SO_2 + (2+y+z)\,H_2O = (2HI + xI_2 + yH_2O) + (H_2SO_4 + zH_2O) \qquad (4.39)$$

where x,y,z are the iodine and water molar excess quantities respectively.

As discussed earlier during Bunsen reaction (4.39) under certain concentrations of iodine and water, side reactions as shown in (1.2) and (1.3) forms which are highly undesirable in a closed cycle operation.

Undesired side products are hydrogen sulfide and sulfur. To eliminate such undesired products and maximize the yield, Iodine content & temperature play a vital role that needs to be selected. Under lower amounts of excess I_2, there is a formation of side products, as I_2 presence makes a strong complex formation with HI and H_2O. At lower concentrations of I_2, HI readily reacts to form side products.

Settling rate data is crucial for sizing a phase separator. Experiments to determine settling rates of Bunsen reaction product phases are carried out at different concentrations of Iodine.

The objective of the experiments is to obtain the regime in which side reactions occur. It includes the study of side reactions at different temperatures, I_2 concentration, and excess H_2O

concentration. The study is required so that such conditions can be avoided during the actual operation of the Bunsen reaction.

4.4.2 Side Reaction experimental setup

Experiments have been performed in a glass reactor of 1 litre capacity. A schematic of the setup is shown in figure 4.8. Initial compositions of HIx and H_2SO_4 phases are charged in the reactor. The temperature of the reaction mixture is maintained using a coil heater. One condenser is provided at the outlet of the reactor for any vapor escape to be refluxed back to the reactor. Only uncondensed vapor will pass through the alkali scrubber and to the ventilation ducts. Constant stirring is given to the reaction mixture to maintain uniform mixing and temperature in the reaction zone. Experiments have been carried out at two reaction temperatures 80 ^oC and 90 ^oC. Samples are collected every 10 minutes interval. Analysis of the samples is carried out for H^+, I^-, I_2 using an automatic potentiometric titrator. H^+ is analysed using NaOH as a standard solution, I^- is analysed using Silver Nitrate as a standard solution, I_2 is analysed using Sodium thiosulfate as a standard solution. The results of the analysis are discussed in the next section.

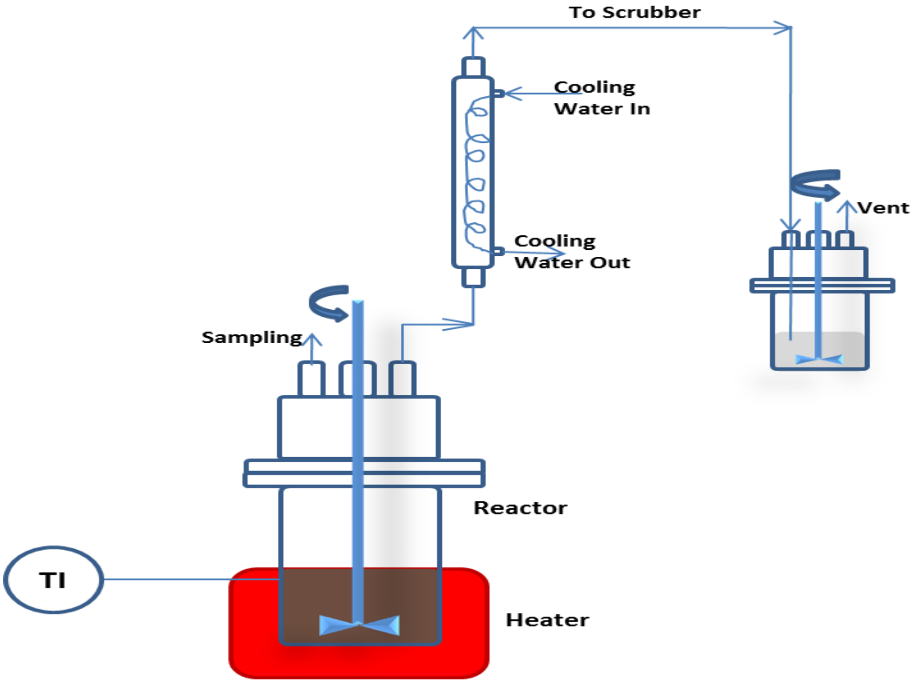


Fig. 4-8 Schematic of Side reaction setup

4.4.3 Phase separation experiments

Bunsen Reaction product mixer needs to be separated with the aid of gravity separation. To know the characteristics of the settling of these two phases experiments are carried out in a batch vessel. The preliminary experiments have been performed to investigate a batch settler to obtain a better understanding of the separation characteristics at different Iodine concentrations.

HIx and Sulfuric acid phases are prepared with known concentrations. The concentration of sulfuric acid is 64 wt % and HI 57 wt % at different volume ratios of I_2/HI. Experiments are carried out at room temperature and atmospheric pressure. Initially, the sulfuric acid phase is charged in the vessel then the HIx solution is charged. Settling is observed for different vessel diameters and at different mixing intensities.

The results are given in chapter 5. The first three experimental (1, 2, and 3) runs are carried out in 100 ml beaker by varying I_2/HI ratio of 0.5, 1, and 1.5. At an I_2/HI ratio of 0.5-layer separation is observed but after 8 minutes of the initial charge. At higher ratios of I_2/HI, the phase separation is immediate. This is because I_2 readily forms complex with HI and makes it immiscible with the H_2SO_4 phase. To evaluate the role of surface area in the settling of two phases different beaker sizes are used. Experiment no 4-6 are carried out with different surface area for settling. The settling rate has increased with an increase in surface area. The surface area plays an important role in the coalescence of dispersed phase drops and thereby increasing the settling rate.

5 RESULTS AND DISCUSSION

5.1 Results of studies on phase separation of Bunsen reaction product mixture

Experiments have been performed at various concentrations of $HI/H_2O/I_2$, flow rates of HIx, SO_2 & O_2 by varying temperature and pressure. Iodine is below the detection limit in the sulfuric acid phase in all experimental runs.

All the experiments are repeated 4 times. The error of the experimentations is found to within ±6.3 %. The t-values are calculated for all the experiments and the confidence interval is found to be more than 99.9 % in all the experiments. Hence all the experiments are considered to be statistically significant.

Bunsen reaction occurs in the liquid phase when the SO_2 is dissolved in the HIx, in which iodine and water are available sulfuric acid and HI. With the progress of the reaction, phase separation happens as an excess amount of iodine is present. The experimental setup and conditions are described in detail in section 4.1 of chapter 4.

$$\mathbf{mH_2O + I_3^- + H^+ \Leftrightarrow \{H_3O^+ + (m\text{-}1)\, H_2O + I_3^-\}} \qquad \mathbf{(5.1)}$$

$$\mathbf{I_2 + I^- \Leftrightarrow I_3^-} \qquad \mathbf{(5.2)}$$

5.1.1 Role of Temperature

Table 5.1 and fig. 5.1 show that contamination of sulfuric acid in the HIx phase increases initially and decreases as the temperature is increased further. This is because of the combating effect, firstly the increase in temperature results in, the decreased saturation level of I_2. The impurity of the HIx phase increases with decreased iodine saturation. Iodine content plays a major role in phase separation, by forming polyiodide species in HIx phase following complexation reaction between iodine and iodides species as shown in equation (5.1). When the temperature is increased the complexation, effect is reduced as given in equation (5.1). This affects the phase immiscibility. It can be seen that, the increase in contamination of H_2SO_4 in HIx phase is up to the temperature of 65°C further there is a decreasing trend. There is a parallel phenomenon occurring with an increase in temperature. Water is migrating to sulfuric acid as the temperature is increased. When the temperature is raised beyond 65°C, water migration to the sulfuric acid phase dominates, because of hygroscopic nature and hydration of sulfuric acid at higher temperatures. This leads to an increase in I_2 concentration in the HIx phase which in turn improves its purity.

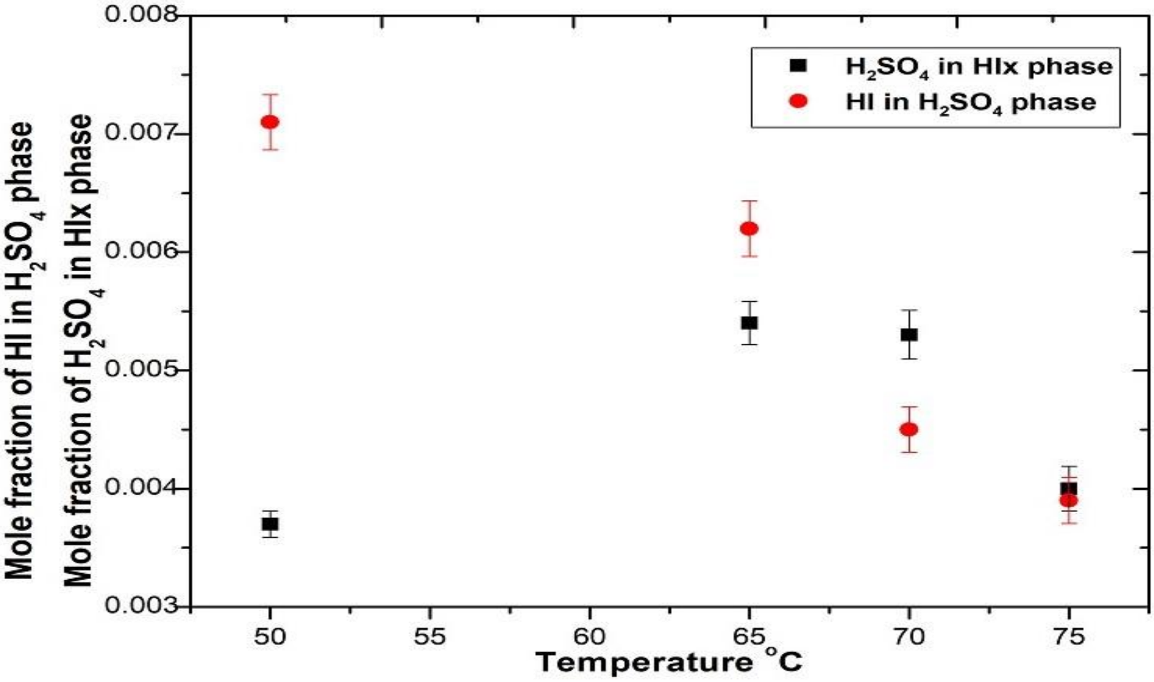


Fig. 5-1 Variation of sulfuric acid in HIx Phase and HI in sulfuric acid phase with temperature at constant pressure, SO_2, HIx, O_2 flow rates, mole ratios of feed-$HI/I_2/H_2O$:1/2.8/7.

Table 5-1: Mole fraction of sulfuric acid in HIx at various temperatures. Mole ratios of feed $HI/I_2/H_2O$:1/2.8/7.7, at P= 2 bar (g), HIx flow = 2.5 l/h, SO_2 flow= 0.1 g/s, O_2 flow = 0.01g/s

Temperature °C	Mole fraction of H_2SO_4 in HIx Phase	Mole fraction of HI in H_2SO_4 Phase	Concentration (mol/lit) ratio of I_2 in HIx Phase/feed
50	0.0037	0.0071	0.45

65	0.0054	0.0062	0.85
70	0.0053	0.0045	1.02
75	0.004	0.004	1.06

Fig. 5.1 shows that the impurity of HI in the H_2SO_4 phase has reduced as the temperature is increased. The water in the HIx phase migrates to the H_2SO_4 phase at higher temperatures [143] which leads to an increase of I_2 concentration in the HIx phase, which in turn improves phase separation and purity of phases.

5.1.2 Role of SO_2 flow rate

Table 5 and fig. 5.2 shows that the sulfuric acid impurity in the HIx phase has reduced as the flow rate of SO_2 is increased. It is because; increase in SO_2 flow rate has increased the extent of reaction. The increased flow rate has decreased the mass transfer resistances in heterogeneous reaction thereby increasing the consumption of other reactants i.e water and iodine. This leads to a reduction in the amount of water for distribution in the product phases as more feed water is consumed in the reaction. The decrease in water content reduces the dilution effect in the HIx phase, thereby increases the density of the HIx phase. This promotes the effective demixing of the two phases. These effects improve the phase separation and therefore the purity of phases.

Table 5-2: Mole fraction of sulfuric acid in HIx at various SO_2 flow rate. Feed mole ratios of $HI/I_2/H_2O$:1/2.8/7.7, at P= 4 bar (g), T= 60 ^oC, HIx flow = 2.5 l/h.

SO_2 flow g/s	O_2 flow g/s	Mole fraction of H_2SO_4 in HIx Phase	Concentration (mol/lit) ratio of I_2 in HIx Phase/feed
0.01	0.01	0.0061	0.61
0.06	0.01	0.0050	0.67

0.12	0.01	0.0045	0.99
0.24	0.01	0.0039	1.02

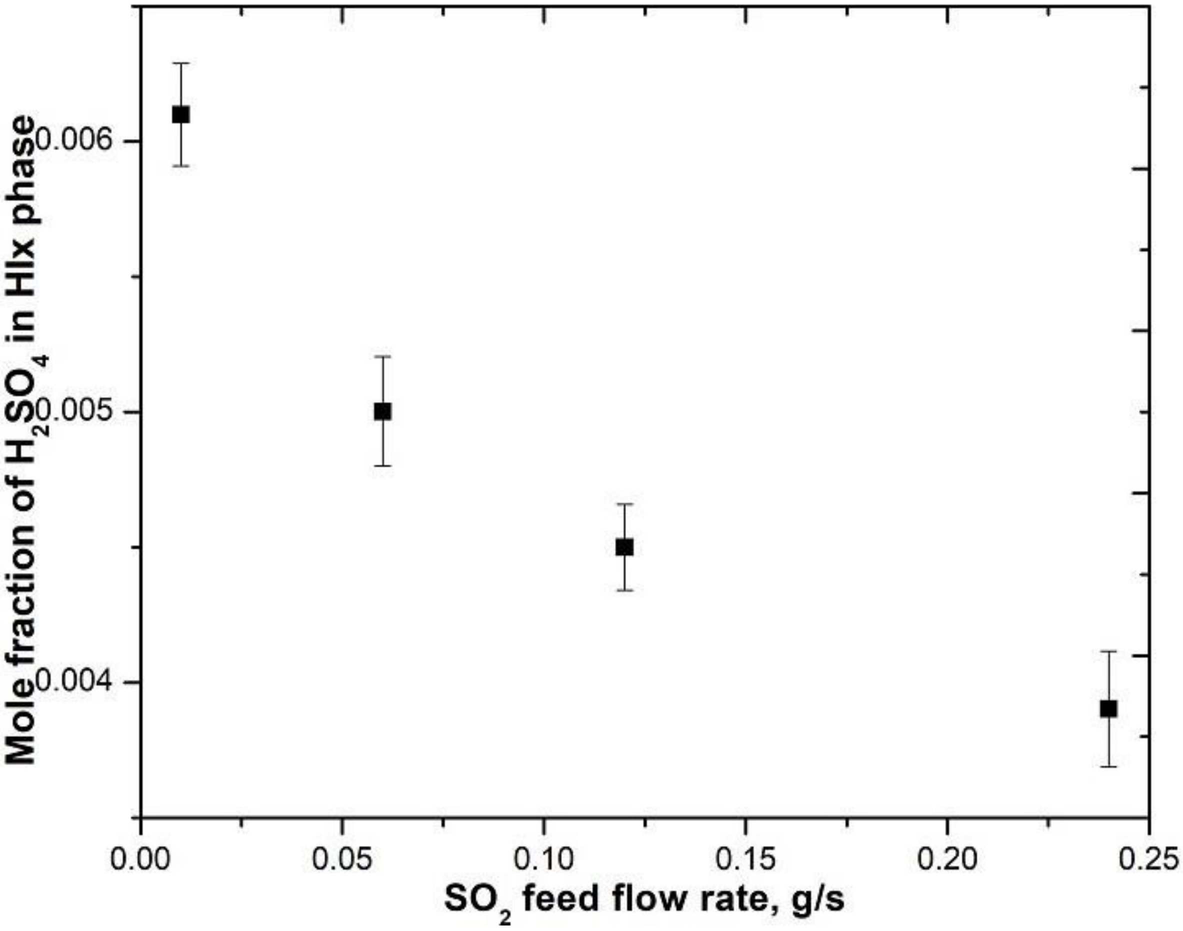


Fig. 5-2 Variation of Sulfuric Acid in HIx with SO_2 flow rate at const P, T, HIx, O_2 flow rates. Mole ratios of feed $HI/I_2/H_2O$:1/2.8/7.7

Table 5.3 shows that at higher pressures and higher flow rates, there is a significant purity enhancement in the sulfuric acid phase compared to lower pressures and lower flow rates of SO_2. From the earlier literature [143] it is seen that the HI mole fraction of 0.001 in the sulfuric acid phase is achieved at the I_2/H_2O ratio of 0.93, a temperature of 120 °C at atmospheric pressure. However similar HI mole fraction in the sulfuric acid phase is obtained at a very less I_2/H_2O ratio of 0.36, the temperature of 70°C, and a pressure of 4 bar (g) in this study. This is mainly because of the increased solubility of SO_2 under higher pressures. Further higher flow rates improve the mass transfer characteristics thereby reducing mass transfer resistances in the liquid film.

Table 5-3 Mole fraction of HI in sulfuric acid phase at various SO_2 flow rate. Feed mole ratios of $HI/I_2/H_2O$:1/2.8/7.7, at P= 4 bar (g), T= 70 ^oC, HIx flow = 1.8 l/h.

SO_2 flow g/s	O_2 flow g/s	Mole fraction of HI in H_2SO_4 Phase	Concentration (mol/lit) ratio of I_2 in HIx Phase/feed
0.12	0.008	0.0025	1.39
0.24	0.016	0.0015	1.82

5.1.3 Role of HIx flow rate

Table 5.4 and fig. 5.3 show that the mole fraction of H_2SO_4 in the HIx phase has increased as the feed HIx flow rate is increased. An increase in feed HIx flow rate reduces the conversion of SO_2 because of a reduction in residence time of reactants in the reactor. This results in increased water concentration and also dilution of the HIx product phase. Because of increased water content the effective collusions between the reaction components decreases and also the nucleation of sulphuric acid phase droplets also gets affected. Thereby disturbing the demixing of two phases. This leads to an increase in the level of contamination of H_2SO_4 in the HIx product phase.

Table 5-4: Mole fraction of sulfuric acid in HIx at various HIx flow rate. Feed mole ratio $HI/I_2/H_2O$:1/2.6/7, at P= 2 bar (g), T= 75 ^oC, SO_2 flow = 0.12 g/s, O_2 flow = 0.01 g/s

HIx flow l/h	Mole fraction of H_2SO_4 in HIx Phase	Concentration (mol/lit) ratio of I_2 in HIx Phase/feed
1.2	0.0034	1.07
1.4	0.0048	0.95
2.4	0.0062	1.00
2.9	0.0077	0.94

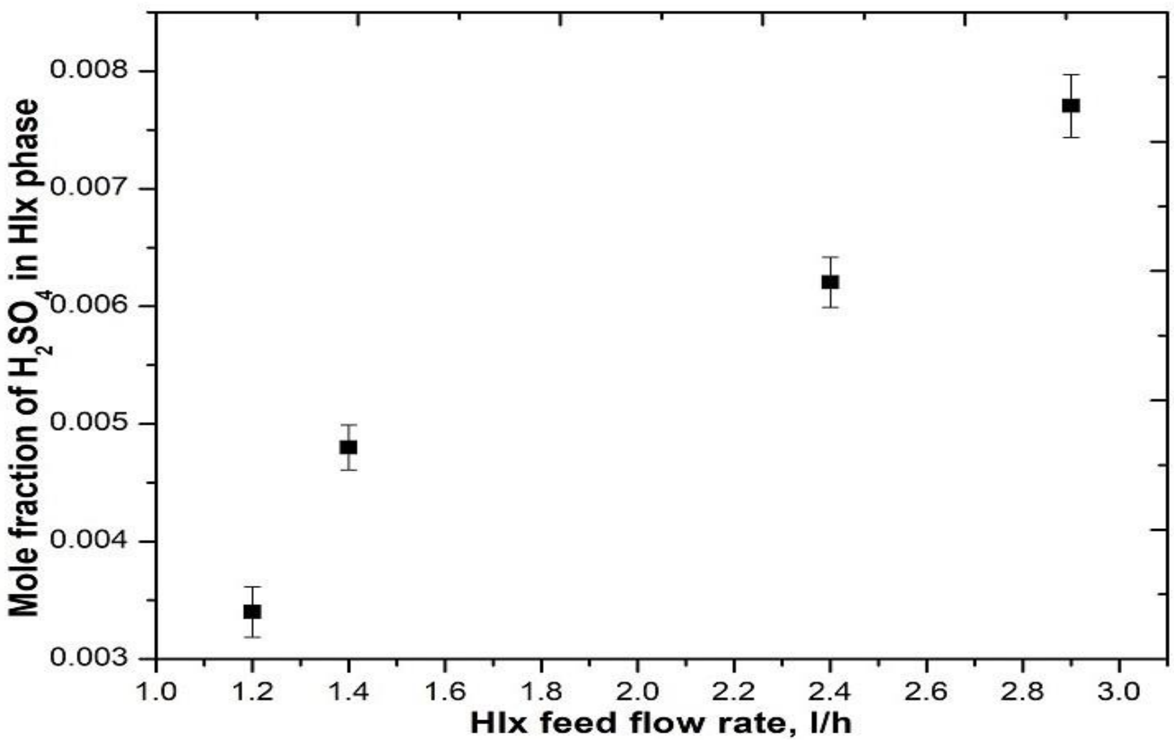


Fig. 5-3 Variation of Sulfuric Acid in HIx Phase with HIx flow rate at constant P, T, SO_2, O_2 flow rates. Feed mole ratio $HI/I_2/H_2O$:1/2.6/7

5.1.4 Role of Pressure

The mole fraction of H_2SO_4 in the HIx phase and HI in the H_2SO_4 phase at different pressures is shown in table 5.5 and fig. 5.4. Table 5.5 shows that the impurity has reduced till pressures of 4 bar (g). This is because at higher pressure, the solubility of SO_2 in HIx increases which leads to a higher yield of H_2SO_4 & HI. This results in higher consumption of feed H_2O. Reduction in excess water, minimizes dilution effect in the HIx phase. This also enhances the iodine concentration in the HIx phase which improves the phase separation through complexation reactions between iodine and iodide species. As pressure is increases up to 6 bar (g) consumption of feed I_2 and production of HI increases predominantly. This leads to a decrease in the level of iodine saturation (I_2 in the HIx phase) and also complexation reactions of iodine and iodides species. This phenomenon increases the impurity in both the phases (which can be seen from the concentration ratio of I_2 in HIx phase/feed-in table 5.5).

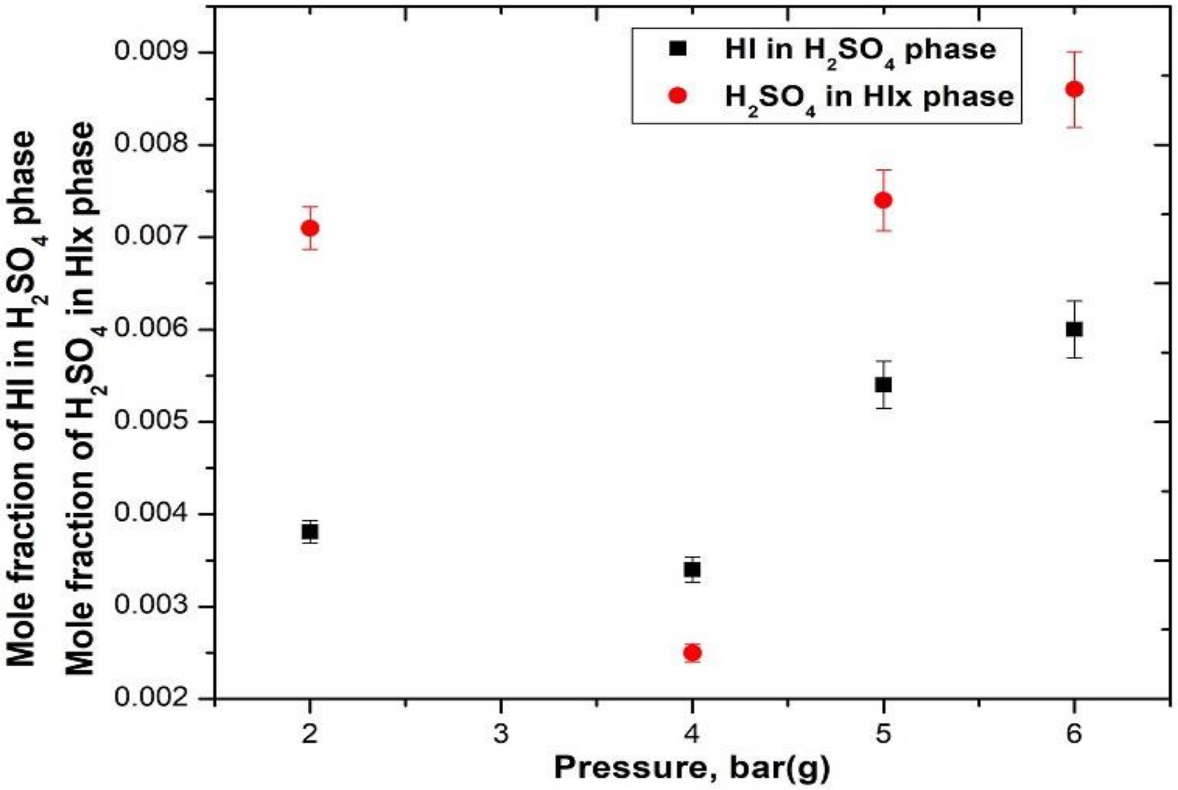


Fig. 5-4 Variation of sulfuric acid in HIx Phase and HI in sulfuric acid phase with pressure at mole ratios of feed $HI/I_2/H_2O$:1/2.8/7.7

Table 5-5 Mole fraction sulfuric acid in HIx Phase and HI in sulfuric acid phase with pressure at mole ratios of feed $HI/I_2/H_2O$:1/2.8/7.7; at T= 60 °C, HIx flow = 1.5 l/h, SO_2 flow= 0.12 g/s, O_2 flow = 0.008 g/s

Pressure bar (g)	Mole fraction of H_2SO_4 in HIx Phase	Mole fraction of HI in H_2SO_4 Phase	Concentration (mol/lit) ratio of I_2 in HIx Phase/feed
2	0.0038	0.0071	0.50
4	0.0034	0.0025	1.43
5	0.0054	0.0074	0.86
6	0.006	0.0086	0.56

To study the purity levels of two product phases, operating conditions have been varied and found that higher pressures of up to 4 bar (g), temperatures of 60-70 °C, feed HIx and SO_2 flow rate ranges of 1.5-1.8 l/h and 0.12-0.24 g/s respectively played a positive effect on obtaining higher purity levels. At 4 bar (g) and 70 °C, the purity levels in the sulfuric acid phase are highest which has 0.0015 HI mole fraction in sulfuric acid phase. At this, the HIx and SO_2 flow rates are 1.8 l/h and 0.24 g/s respectively. At 4 bar (g) and 60°C, the purity levels in the HIx phase are highest which has 0.0034 H_2SO_4 mole fraction in the HIx phase. At this, HIx and SO_2 flow rates are 1.5 l/h and 0.12 g/s respectively. The purity levels of the HIx phase are more significant in comparison to the sulfuric acid phase. The presence of sulfuric acid in HIx leads to side reactions at temperatures beyond 90 °C under certain iodine concentrations [147]. Side reactions lead to loss of recycled material and poor mass balance. Furthermore, sulfur which is a product of one of the side reactions acts like poison for catalyst in HI decomposer. To achieve better purification of phases it is desirable to operate the reactor at around 4 bar (g), 60°C with feed concentrations of $HI/I_2/H_2O$:1/2.8/7.7.

5.2 Results of studies on Bunsen reaction at elevated temperature and high pressure

Experiments have been performed with $HI/I_2/ H_2O$ mole ratios in the ranges of 1/1.6-2.6/6.3-7 at flow rates of HIx between 1.2 l/h to 3 l/h, SO_2 0.02 g/s – 0.24 g/s, and O_2 0.008 g/s -0.016 g/s. Varying temperatures of reaction up to 80 °C and pressures up to 6 bar (g). The experimental setup is described in detail in section 4.2 of chapter 4.

All the experiments are repeated 4 times. The error of the experimentations is ± 2.9 %. The t-values are calculated for Bunsen reaction experiments and the confidence interval is found to be more than 99.9 % in all the experiments. Hence the experiments are considered to be statistically significant.

5.2.1 Effect of I_2/H_2O ratio

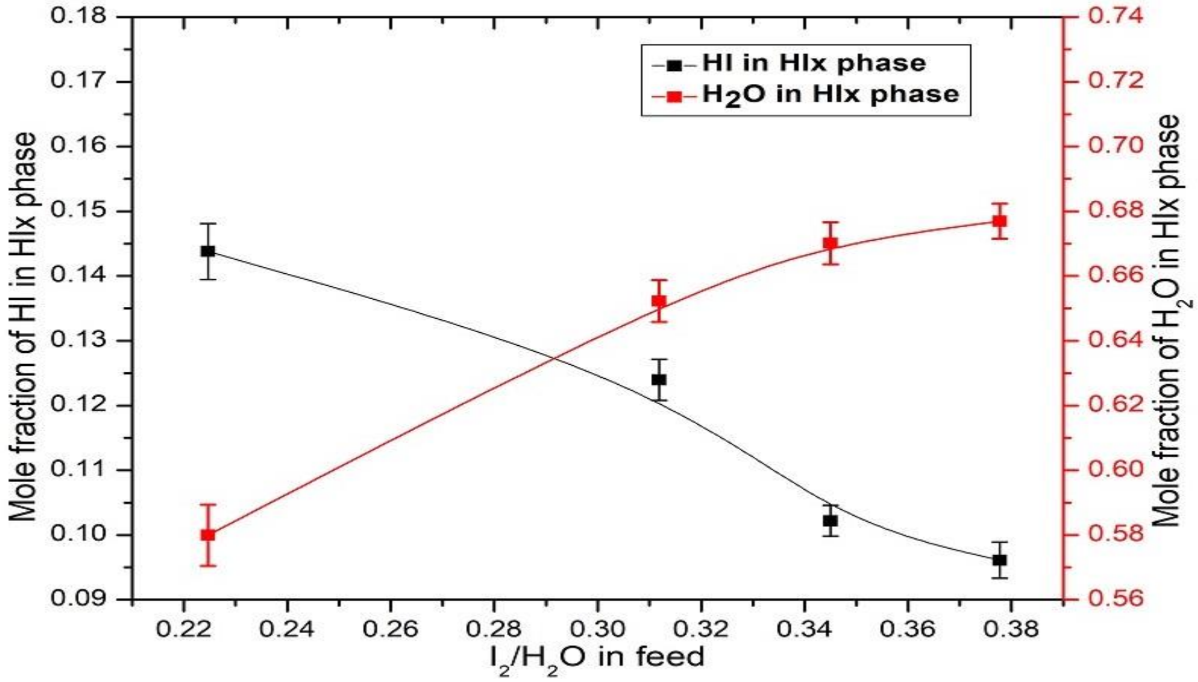


Fig. 5-5 Variation of HI, H_2O in HIx Phase with I_2/H_2O at T=60°C, P=2 bar(g), SO_2=0.12g/s, O_2=0.008g/s, HIx=2 l/h

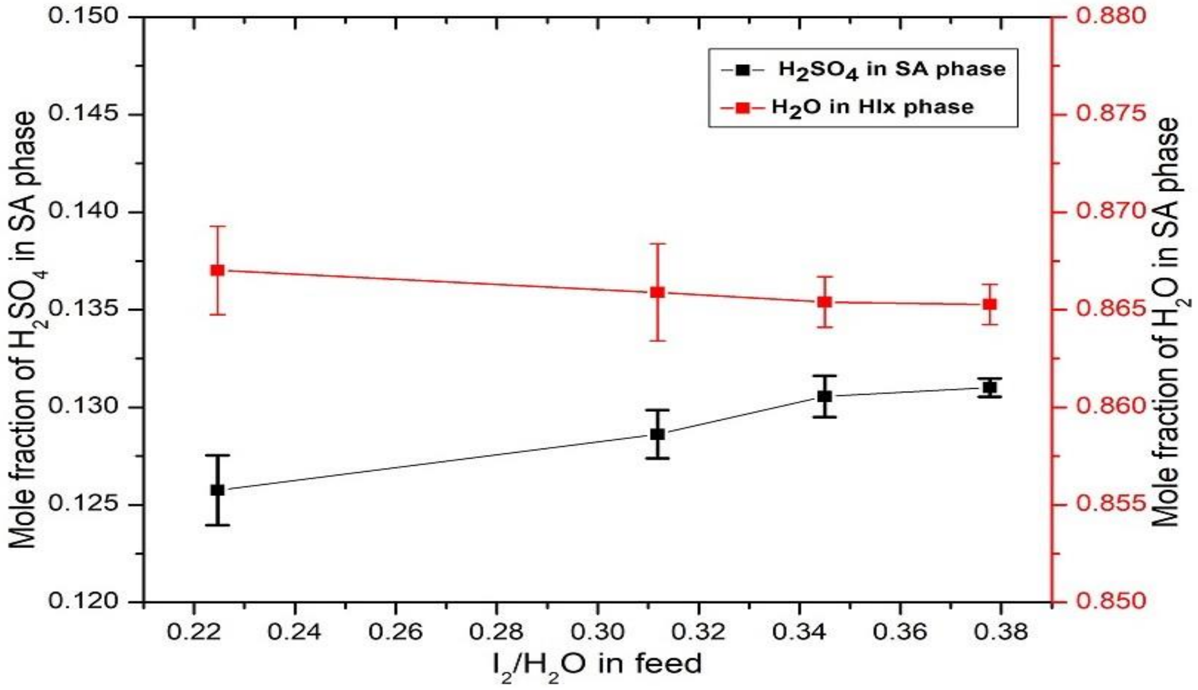


Fig. 5-6 Variation of H_2SO_4, H_2O in sulfuric acid phase with I_2/H_2O at T=60°C, P=2 bar(g), SO_2=0.12g/s, O_2=0.008g/s, HIx=2 l/h

Fig. 5.5 shows that the mole fraction of HI decreases in the HIx phase as the I_2/H_2O feed ratio is increased and steadied after I_2/H_2O ratio of 0.35 and higher. It is because of the transport of excess I_2 towards the HIx phase, as the I_2 affinity towards the HIx phase is higher than the sulfuric acid phase. Further increase in the I_2/H_2O ratio saturates the iodine in HIx. But the mole fraction of H_2O in the HIx phase is increased with an increase in I_2/H_2O ratio. In presence of excess I_2, H_2O migrates from the sulfuric acid phase to the HIx phase, this can be seen from a increase of H_2O asymptotically in the HIx phase and the decrease of H_2O in the sulfuric acid phase in fig. 5.5 and 5.6 respectively. This is due to the hydration reaction of H_2O with I_2 in the presence of I^- ions as shown in equation (5.1). Further increase in I_2 content also enhances the complexations reaction between iodine and iodide species resulting in improved immiscibility between the phases.

Fig. 5.6 shows that the mole fraction of H_2SO_4 in the sulfuric acid phase has increased. This is because an increase in the amount of iodine results in better phase separation of 2 phases and hence the sulfuric acid which is present in the HIx phase moves towards the sulfuric acid phase thus increasing sulfuric acid mole fraction. From kinetics point of view increase in concentration of I_2 results in increased Hatta number that improves reaction rate of overall Bunsen reaction. This leads to increase in both HI and H_2SO_4 concentration as can be seen from both figures 5.5 & 5.6.

In the literature [132], at I_2/H_2O ratio of 0.31, HI and H_2O mole fraction of 0.149 and 0.61 respectively are obtained at a pressure of 2 bar (g), the temperature of 60 ^{o}C. In the present experiment, HI and H_2O mole fractions of 0.124 and 0.667 respectively are obtained. In the present study the HIx flow rate of 2 l/h is kept and, in the literature, [132] it is 0.126-0.144 lph. Variation from the literature [132] is because of the increased residence time of HIx in the reactor which increases HI mole fraction.

5.2.2 Effect of Temperature

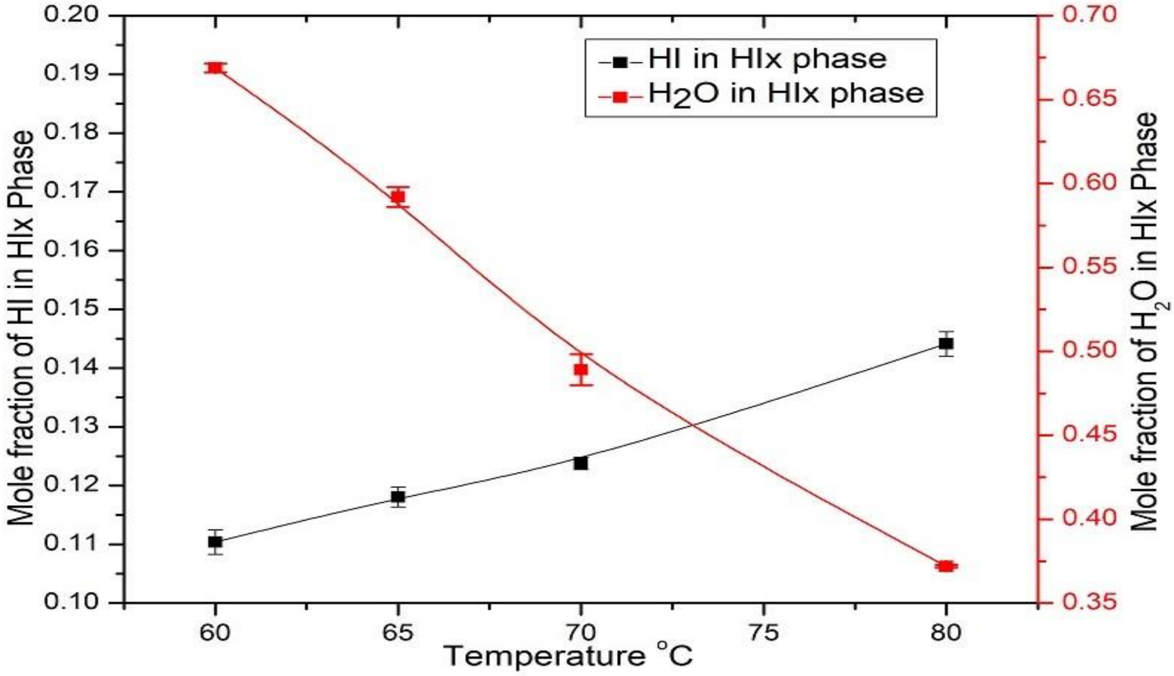


Fig. 5-7 Variation of HI, H_2O in HIx Phase with temperature at P=2 bar(g), SO_2=0.12g/s, O_2=0.008g/s, HIx= 2.3 l/h, mole feed ratio-HI/I_2/H_2O:1/2.2/7

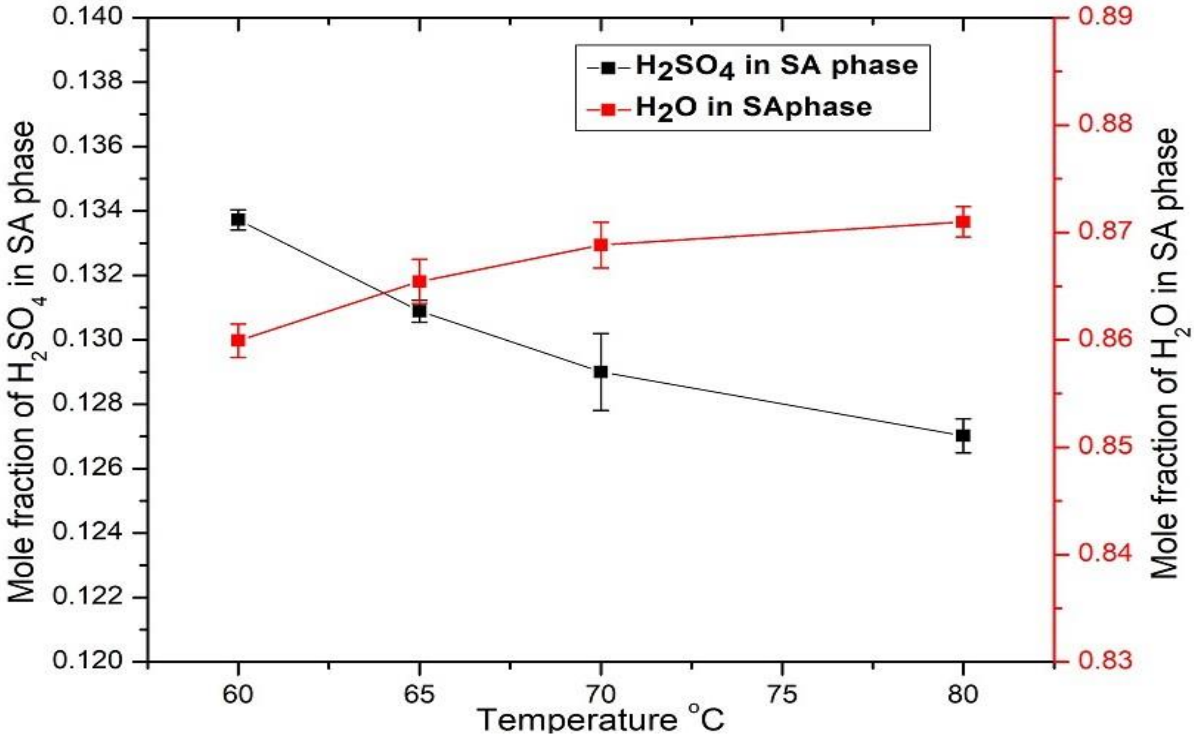


Fig. 5-8 Variation of H_2SO_4, H_2O in sulfuric acid phase with temperature at P=2 bar(g), SO_2=0.12g/s, O_2=0.008g/s, HIx= 2.3 l/h, mole feed ratio-HI/I_2/H_2O:1/2.2/7

Fig. 5.7 shows that as the temperature increases mole fraction of HI in the HIx phase increases and H_2SO_4 in sulfuric acid decreases as shown in fig. 5.8. It is because water content for a given I_2 concentration decreases in the HIx phase and increases in the sulfuric acid phase with temperature. This trend indicates that water prefers to move towards the sulfuric acid phase at higher temperatures. As the temperature increases the degree of hydration reaction (equation 5.1) in the HIx phase decreases [143] which lead to excess water to move from the HIx phase to the sulfuric acid phase thus decreasing the mole fraction of H_2O in the HIx phase and increasing the mole fraction of H_2O in sulfuric acid phase, this can be seen in fig 5.7 and fig 5.8 respectively. An increase in a mole fraction of HI in the HIx phase leads to higher concentrations of HI in the inlet of HI decomposer and minimizes the unconverted recycling flow rates.

5.2.3 Effect of SO_2 feed flow rate

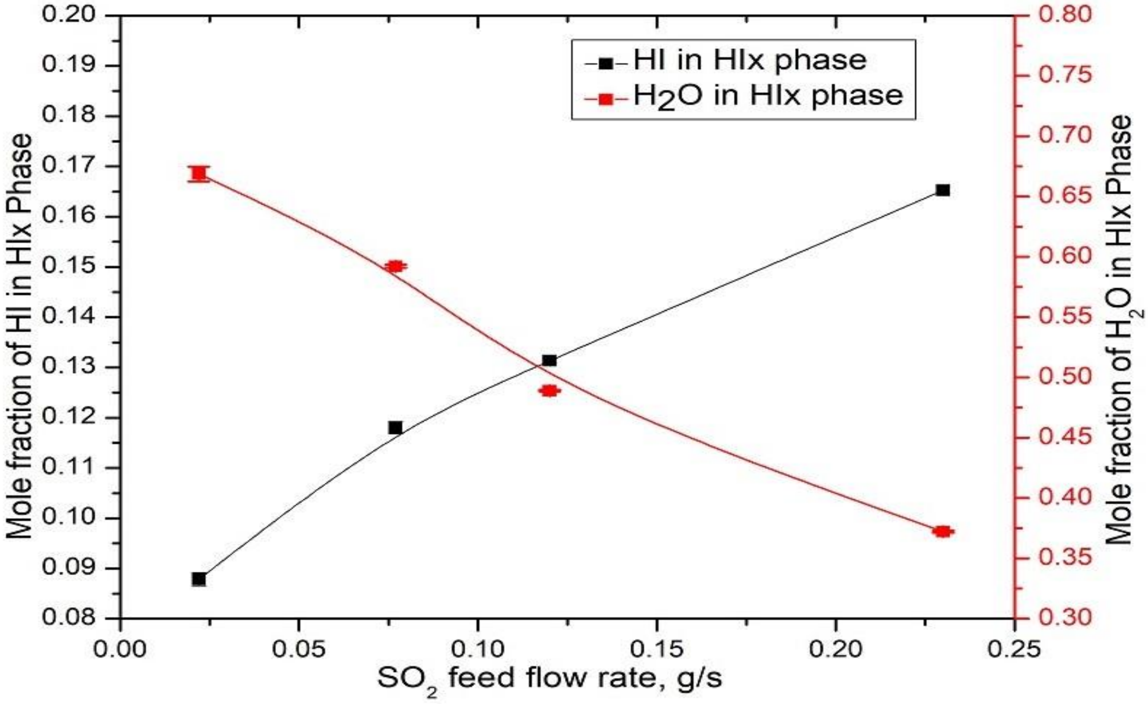


Fig. 5-9 Variation of HI, H_2O in HIx Phase with SO_2 feed rate at T=70 °C, P=2 bar (g), O_2=0.008g/s, HIx= 2.5 l/h, mole feed ratio-HI/I_2/H_2O:1/2.2/7

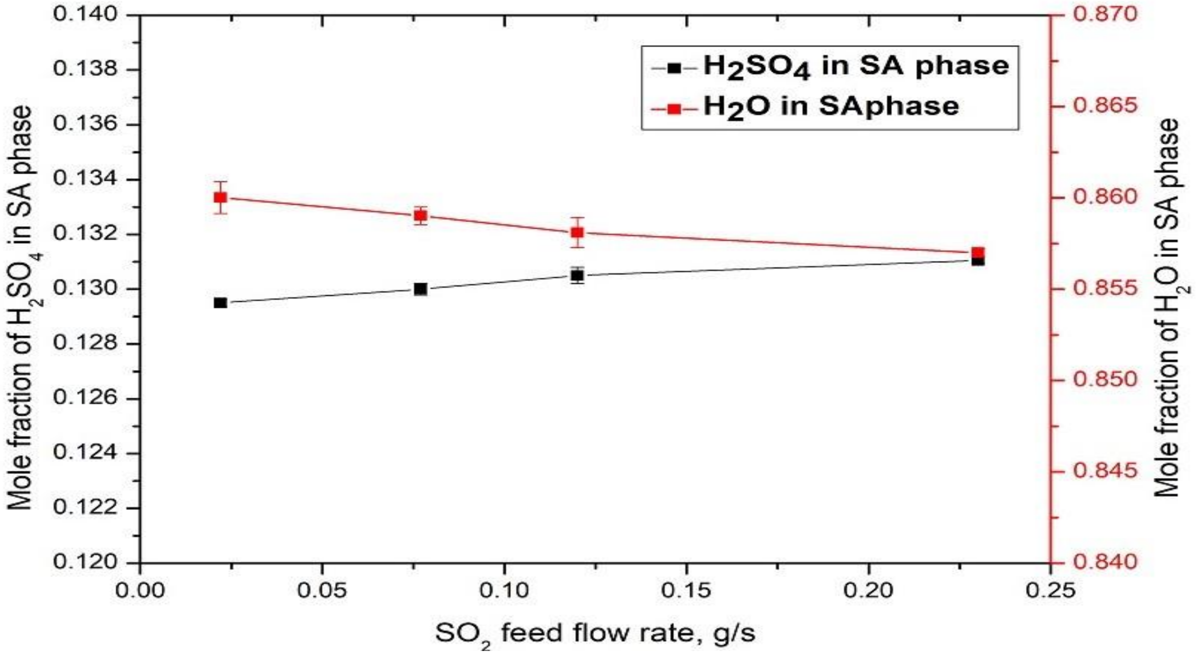


Fig. 5-10 Variation of H_2SO_4, H_2O in sulfuric acid phase with SO_2 feed rate at T=70 °C, P=2 bar(g), O_2=0.008g/s, HIx= 2.5 l/h, mole feed ratio-HI/I_2/H_2O:1/2.2/7

Fig. 5.9 shows that increase of SO_2 feed flow rate results in an increase of a mole fraction of HI in the HIx phase. An increase in the SO_2 feed flow rate increases the extent of reaction which results in an increase in both HI and H_2SO_4 in the product phases, which can be seen from fig 5.9 and 5.10. An increase in the extent of reaction leads to a reduction in the amount of excess water in the feed for distribution in the product phases. The decrease of water content in the HIx phase is significant as a major amount of water tends to move towards the HIx phase which can be seen from fig 5.9. Another reason for water tending towards HIx phase is because of hydration reaction with iodine in the presence of iodide species. The increase in gas flow rate improves the mass transfer characteristics of the system by decreasing the film thickness thereby improving the yield of overall reaction. Reduction in water content in the HIx phase is better in the HI section as it reduces the pumping power requirement in the process cycle.

5.2.4 Effect of HIx feed flow rate

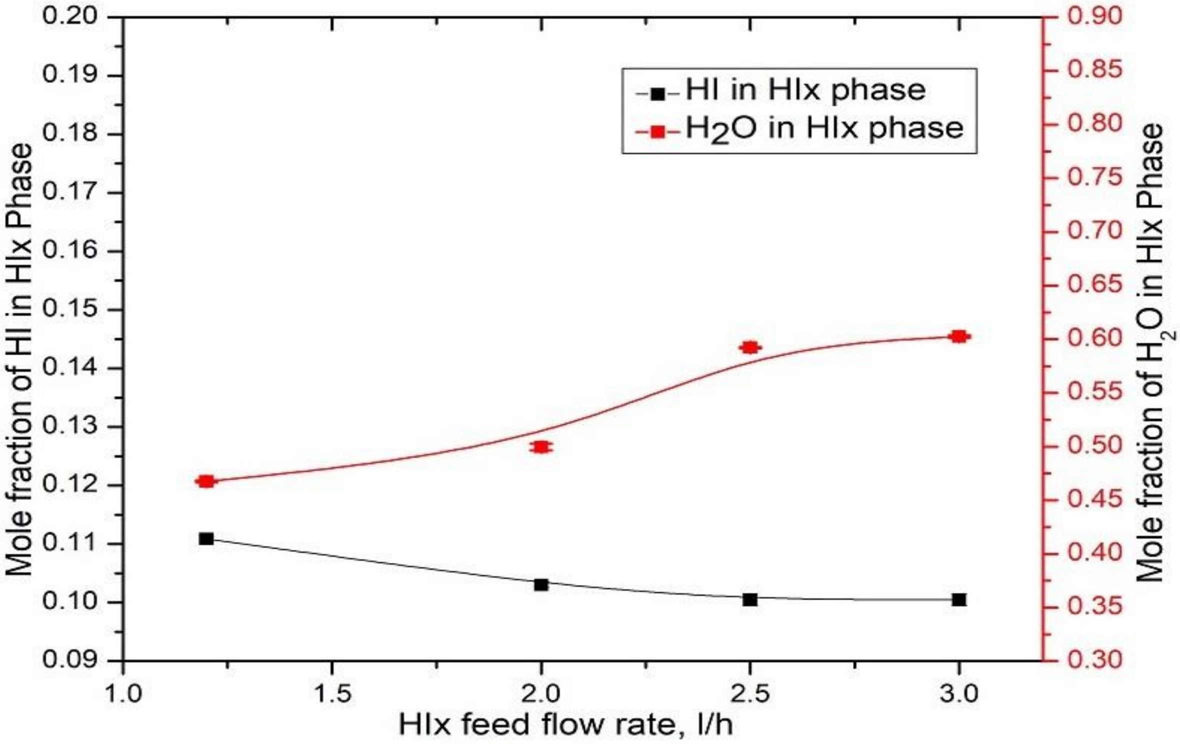


Fig. 5-11 Variation of HI, H_2O in HIx Phase with HIx feed rate at T=80 ^oC, P=4 bar (g), SO_2=0.12g/s, O_2=0.008g/s

Fig. 5.11 shows that an increase in the HIx flow rate decreases the conversion of SO_2 because of a reduction in residence time of liquid reactants in the reactor. This results in a reduction of HI concentration and increased water concentration in the HIx phase. Because of hydration reaction in HIx phase, there is also increase in water concentration in HIx phase. The further increase in HIx flowrate beyond 3 lph has not resulted in a significant increase in HI and H_2O concentration. The increase of H_2O mole fraction in the HIx phase is significant as a major amount of excess feed H_2O tends to move towards the HIx phase because of complexation reaction in presence of iodide species as shown in fig. 5.11. An increase in water content in the HIx phase increases the pumping power requirement in the process cycle.

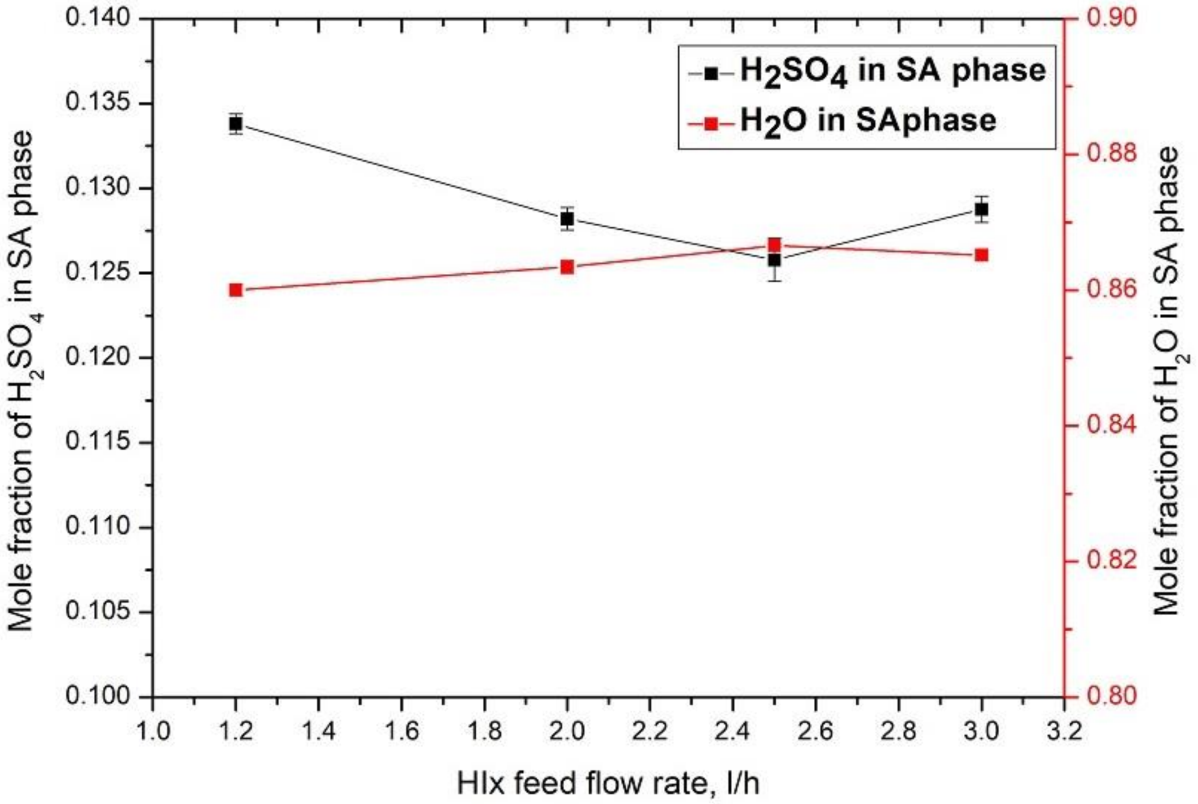


Fig. 5-12 Variation of H_2SO_4 and H_2O in sulfuric acid phase with HIx feed rate at T=80 ^{o}C, P=4 bar (g), SO_2=0.12g/s, O_2=0.008g/s

Fig. 5.12 shows that an increase in the HIx flow rate decreases the conversion of SO_2 because of a reduction in residence time of reactants in the reactor. This results in reduction of H_2SO_4 concentrations and increased water concentration in the product phases. After the HIx feed flow rate of 2.5 lph there is a marginal increase in H_2SO_4 concentration in the sulfuric acid phase. As HIx flow rate is increased, the consumption of feed iodine also decreases. This augments iodine concentration in product solution. Higher iodine concentration improves the phase separation because of triodide formation and complexation reaction (equation 5.1 & 5.2) in HIx phase. H_2SO_4 from HIx phase migrates to sulfuric acid phase thereby increasing its concentration.

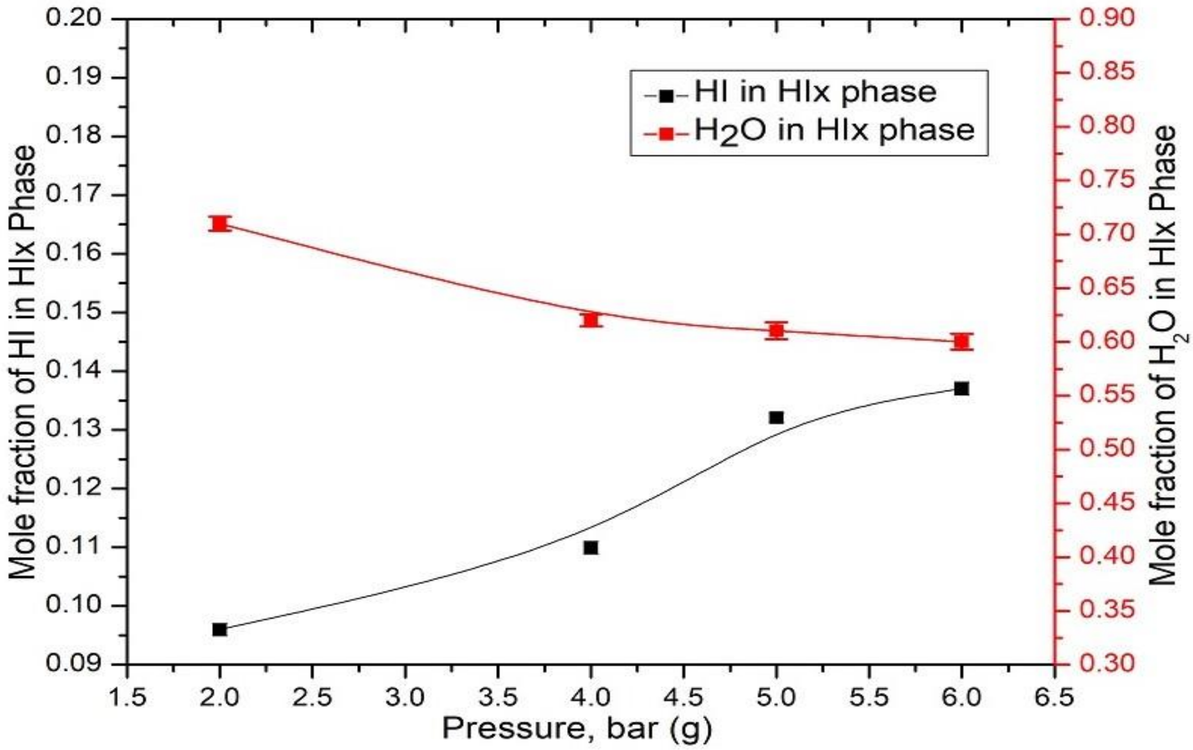


Fig. 5-13 Variation of HI, H_2O in HIx phase with pressure at T=70 °C, SO_2=0.12g/s, O_2=0.008g/s, HIx= 3 lph, flow rates, mole feed ratio-HI/I_2/H_2O:1/2.6/7.

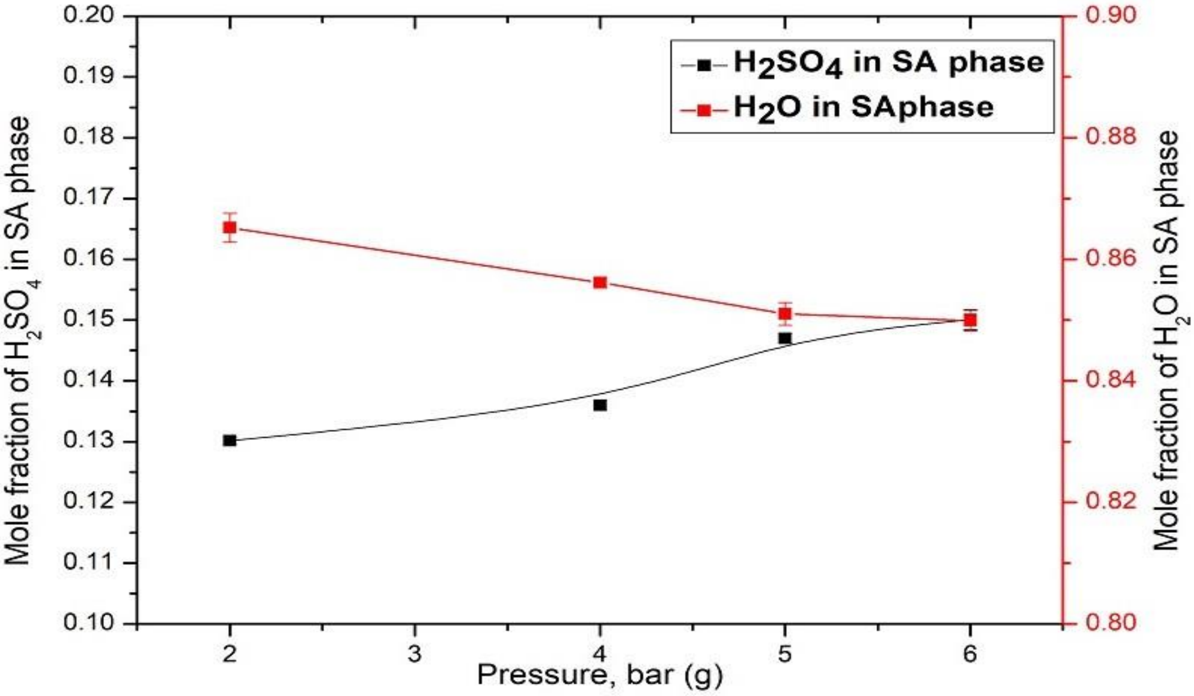


Fig. 5-14 Variation of H_2SO_4, H_2O in sulfuric acid phase with pressure at T=70 °C, SO_2=0.12g/s, O_2=0.008g/s, HIx= 3 lph, flow rates, mole feed ratio-HI/I_2/H_2O:1/2.6/7.

Fig. 5.13 shows that increase in pressure results in an increase of a mole fraction of HI in the HIx phase. This is because at higher pressure the solubility of SO_2 in HIx increases which leads to a higher yield of HI. The increase in solubility enhances the reaction rates in the liquid film. Further increase in pressure does not enhance the HI concentration this is because SO_2 gas solubility does not greatly enhance beyond 6 bar (g) pressure in aqueous medium. An increase in pressure results in a decrease of H_2O in the HIx phase this is because at higher pressures consumption of H_2O in the feed solution increases, which results in a decrease of excess feed H_2O available for distribution between the phases. Fig. 5.14 shows that increase in pressure results in an increase of a mole fraction of H_2SO_4 in the sulfuric acid phase. This is also because of an increase in the solubility of SO_2 in feed HIx. Similar to the concentration of HI in the HIx phase, a further increase in pressure does not enhance the H_2SO_4 concentration this is because of SO_2 saturation in feed HIx. An increase in pressure results in a decrease of H_2O in the sulfuric phase this is because at higher pressures consumption of H_2O in the feed solution increases, which results in a decrease of excess H_2O available for distribution between phases. A higher concentration of HI and H_2SO_4 leads to a reduction in recycling flow rates and hence pumping power in sections 2 and 3 of the I-S process.

Bunsen reaction has been studied in a co-current reactor by varying the operating conditions such as temperature, pressure, feed flow rates, and concentrations.

It is found that increasing operating temperature has increased the mole fraction of HI in the HIx phase to 0.144 and decreased the mole fraction of H_2SO_4 in the sulfuric acid phase to 0.129. An increase in the SO_2 feed flow rate has improved the mole fraction of HI in the HIx phase to 0.165. An increase in the HIx feed flow rate has decreased the mole fraction of HI in the HIx phase to 0.1 and H_2SO_4 in the sulfuric acid phase to 0.129. An increase in pressure has increased both HI and H_2SO_4 mole fractions in both the HIx phase and sulfuric acid phase to 0.137 and 0.15 respectively. Highest mole fraction of H_2SO_4 in sulfuric acid phase i.e. 0.15 is obtained at operating conditions T=70 °C, P=6 bar (g), SO_2=0.12g/s, O_2=0.008g/s, HIx= 3 lph, flow rates, mole feed ratio-HI/I_2/H_2O:1/2.6/7. Highest mole fraction of HI in HIx phase i.e 0.165 is obtained at T=70 °C, P=2 bar (g), SO_2 = 0.24 g/s, O_2=0.008g/s, HIx= 2.5 l/h, mole feed ratio-HI/I_2/H_2O:1/2.2/7. To obtain the concentrated acid phases higher pressure operation is desirable.

5.3 Results of studies on reaction kinetics of Bunsen reaction

Experiments have been performed with H_2O-SO_2 and HI-I_2-H_2O-SO_2 system at stirring speeds between 0-360 rpm. Varying temperatures of reaction from 30°C to 50 °C and pressures up to 0.5 bar (g). The experimental setup is described in detail in section 4.3 of chapter 4.

All the experiments are repeated 3 times. The error of the experimentations is ± 3.1 %. The t-values are calculated for all the experiments and the confidence interval is found to be more than 99.9 % in all the experiments. Hence the experiments are considered to be statistically significant.

5.3.1 Effect of stirring speed on absorption rates

An increase in stirring speed has increased the rate of absorption. The rate of pressure decrease has marginally changed when the stirring speed is increased from 0 rpm to 180 rpm. But the rate of pressure decrease has changed drastically from 240 rpm onwards and stabilized near 360 rpm. This indicates that the resistance to transport is not governed by mass transfer. The increase in stirring speed has decreased the film thickness δ, thereby decreasing the resistance to mass transfer. The fig.5.15 is used to obtain the mass transfer coefficient using the regression fitting parameter for equation 4.16 is obtained.

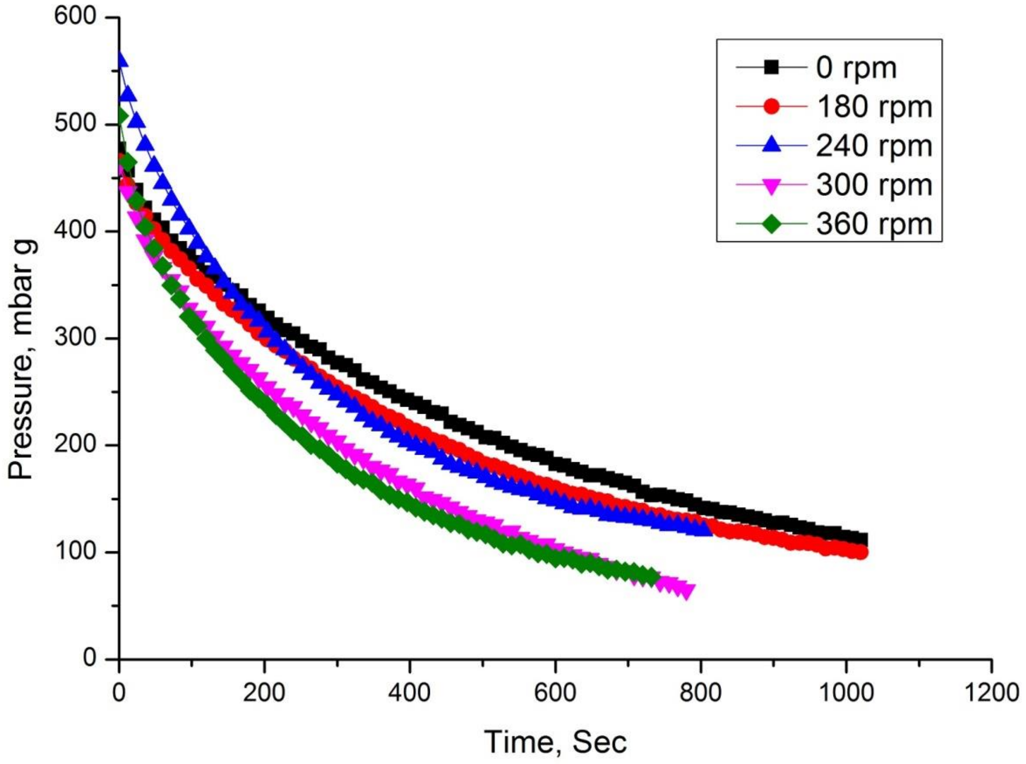


Fig. 5-15 Rate of pressure variation profiles at various agitation speeds and 30 ^{o}C for H_2O-SO_2 system

5.3.2 Effect of temperature on absorption rates

Fig. 5.16 represents the SO_2 pressure decrease rate at different temperatures. As the temperature is increased there is a reduction in the rate of decrease in pressure. This is because an increase in temperature leads to a decrease in solubility which in turn decreases the absorption rates.

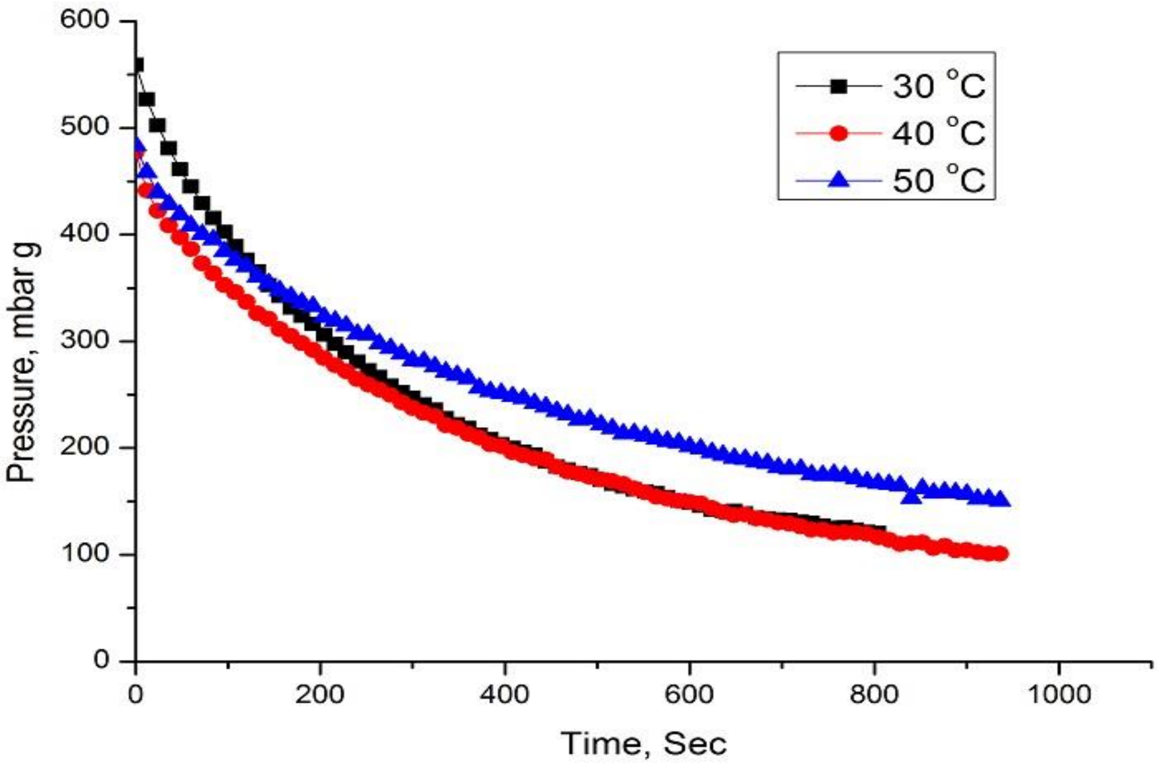


Fig. 5-16 Rate of pressure variation profiles at different temperatures and agitation speed of 240rpm for H_2O-SO_2 system

The rate of decrease of pressure is reduced at a higher temperature because of the decrease in SO_2 solubility in water with an increase in temperature

5.3.3 Effect of stirring speed on liquid side mass transfer coefficient

Equation (4.16) is used to evaluate the mass transfer coefficient in which the only unknown parameter k_{AL} by regression. Mass transfer coefficients obtained are plotted in fig. 5.17. This can also be seen from R^2 values given in table 5.6. From the plot, the significant conclusion can be obtained that after 300 rpm the stirring effect is not enhancing the mass transfer coefficient. Hence the effect of mass transfer can be neglected from 300 rpm in kinetic rate experiments using the HI-I_2-H_2O-SO_2 system. The film thickness δ, has reached a constant value at higher stirring speeds resulting in asymptotically increase of mass transfer coefficient.

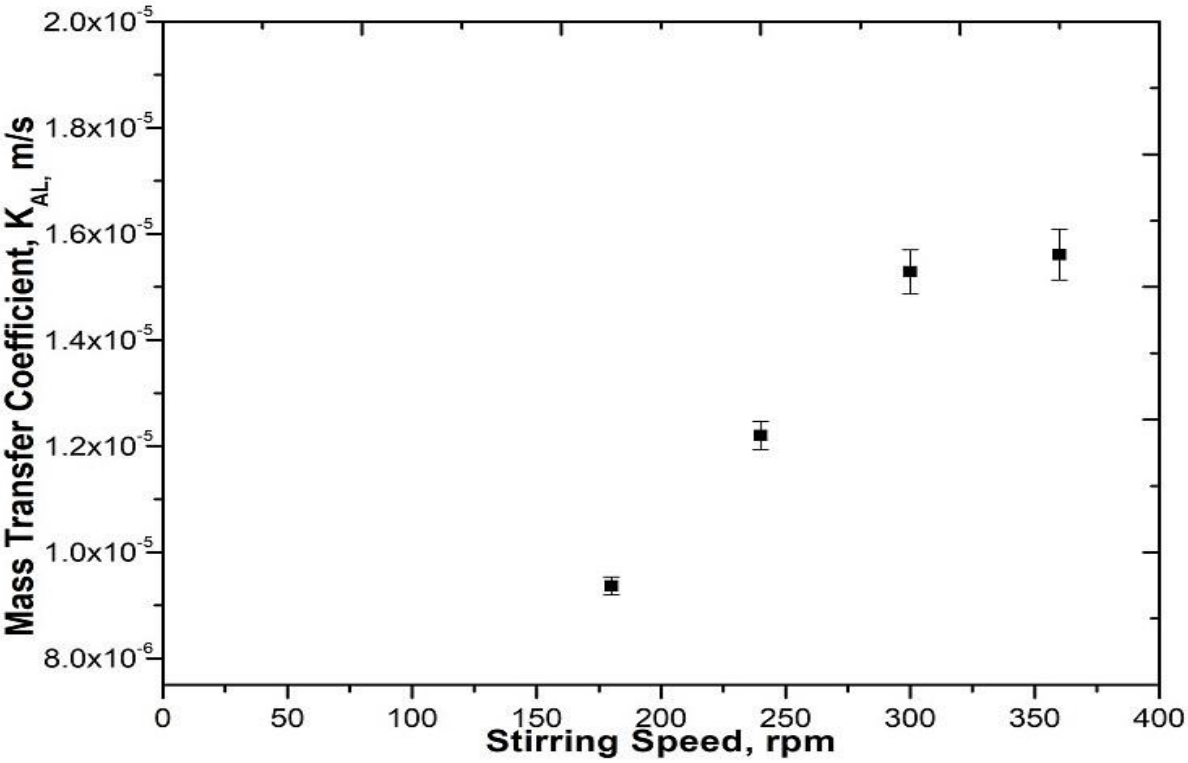


Fig. 5-17 Variation of mass transfer coefficient with agitation speed at 30 ^{o}C for H_2O-SO_2 system

Table 5-6 R^2 fitting values for different experiments to obtain mass transfer coefficient values

Experiment No.	Agitation speed	R^2 fitting value
1	180 RPM	0.9990
2	240 RPM	0.9989
3	300 RPM	0.9974
4	360 RPM	0.9948
5	240 RPM-40 ^{0}C	0.9958
6	240 RPM-50 ^{0}C	0.9958

The experimentally obtained mass transfer coefficient for the H_2O-SO_2 system has been compared with published literature correlation [169] as given in equation (5.1).

$$Sh = 0.7082\ Re^{0.66} Sc^{0.11} - - - (5.1)$$

The plot is shown in fig. 5.18. The experimentally predicted mass transfer coefficients are slightly higher than those obtained from equation (5.1). The average accuracy associated with equation (5.1) is ± 11.8 % as given in [169]. The equation (5.1) is applicable from 80-250 rpm. This could be the reason for the deviation from experimentally obtained values. At higher rpm, the stirring effects do not change the mass transfer as these two becomes independent hence there is a flat profile after 300 rpm in experimentally determined mass transfer coefficient as shown in fig. 5.18.

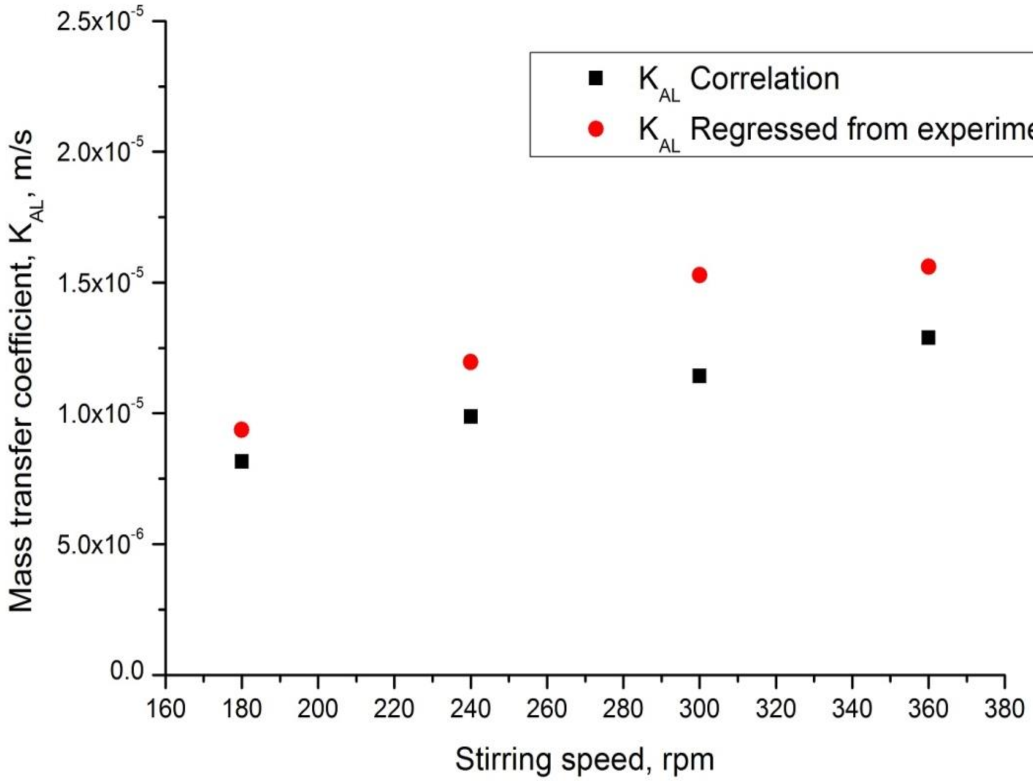


Fig. 5-18 Variation of mass transfer coefficient with agitation speed at 30 °C for H_2O-SO_2

Fig. 5.19 is the pressure profile with time for the HI-I_2-H_2O-SO_2 system at 30 °C and 300 rpm. The stirred vessel is charged with HIx and SO_2 is passed. The curve is fitted using equation (4.18) and obtained the rate constant as 1.8 second^{-1}.

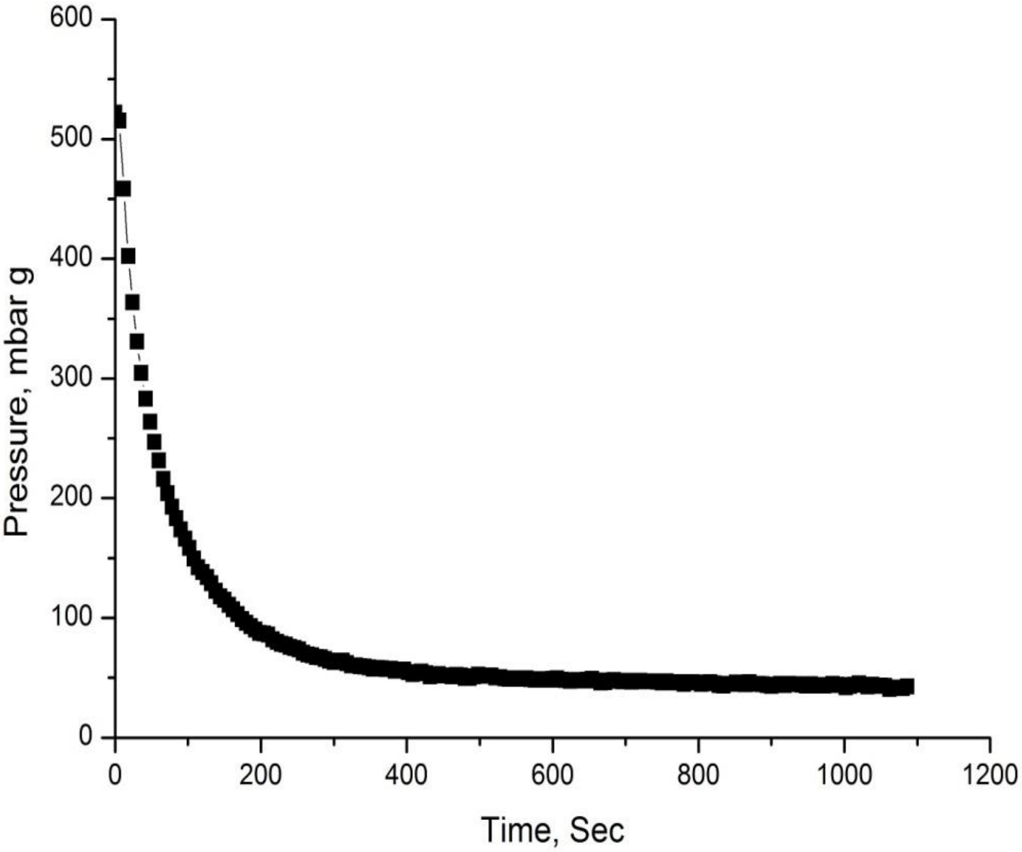


Fig. 5-19 Rate of pressure variation at 27 ^oC and 300 rpm system for $HI-I_2-H_2O-SO_2$ system

To ensure the chemical reaction regime is in the fast pseudo first-order regime, equations 4.8 and 4.11 needs to be satisfied. From the experimental analysis, k` is obtained as 1.8 $second^{-1}$. From equation (4.6) Hatta number is 3.7. From equation (4.7) E_{inf} is 18. Hence equations 4.8 and 4.11 are satisfied. The applicability of equation (4.12) is justified for the evaluation of the kinetic rate constant.

The experimental setup of the stirred cell reactor has been installed and tested, to evaluate the mass transfer coefficient and reaction kinetic rate constant for the Bunsen reaction. Experiments to evaluate the mass transfer coefficient in the water-sulfur dioxide system is carried out by varying stirring speed and temperature and obtained the same in the range of $8.7X10^{-6}$ m/s to $1.5X10^{-5}$ m/s at different stirring speeds. To evaluate the kinetic rate constant for the Bunsen reaction experiments are to be carried out such that mass transfer should be independent of stirring rates. Different methods are identified to evaluate the mass transfer coefficient. Mass transfer coefficient values initially increased with stirring speeds of up to 300 rpm and remained almost constant at higher rpm's, implying that the stirring speeds of more than 300 rpm do not greatly enhance the mass transfer rate. Beyond 300 rpm absorption of SO_2 into the HIx medium is governed by kinetics and evaluation of the fitting parameter gives the value of the kinetic rate constant and obtained the same as 1.8 second^{-1} at 30 ^{o}C. Hatta number and infinite enhancement factor are evaluated from the experimentally obtained kinetic rate constant as 3.7 and 18 respectively. Evaluated Hatta number and infinite enhancement factor satisfies the condition of fast pseudo first-order reaction regime for which equation (4.12) can be used to obtain kinetic parameters. Zhu Q. et al. (2013) has reported reaction rate constant parameters (frequency factor and activation energy). From the rate constant equation in the study, the rate constant is obtained as 0.13 second^{-1} at 30 ^{o}C. The rate constant value is lower than that is obtained in the thesis. This is probably because the study by Zhu Q. et al has considered higher water content in the initial solution and further the level of agitation is less i.e the stirring rate is 100 rpm. The stirring rate may not be adequate to overcome the mass transfer resistances in this gas-liquid Bunsen reaction.

Zhang Y. et al. (2014) has qualitatively studied kinetics. Quantitative estimation of rate constant is not carried out in the study.

Zhou. et al. (2017 a&b) initially has studied reaction kinetics without iodine content. Followed by Bunsen reaction in the subsequent study. The rate constant obtained in the study is 1.9 second^{-1}, this is close to the value obtained in this thesis. However, the study did not calculate the Hatta number and infinite Enhancement factor. These two factors are required to identify the regime of gas-liquid reaction. As discussed earlier, the regime of operation has to be in fast pseudo-first order to obtained intrinsic rate constant parameter.

Ying Z. et al. (2016) has studied the kinetics of Electro-chemical based Bunsen reaction. The study has obtained rate equation parameters for anode and cathode reactions and the kinetics data obtained cannot be directly compared to conventional gas-liquid reaction.

Ying Z. et al. (2018) has studied the Bunsen reaction by considering recycle HI stream as one of the components in the reaction mixture. The rate constant obtained in the study is 0.32 second^{-1}. The water concentration is high in the study. The water concentration has the role in dilution of the solvent in which reaction occurs. The dilution causes decrease in effective collusion between the active species. Probably this could be reason for lesser value of rate constant which is obtained from the study. Further the study did not identify the regime in which the gas-liquid reaction is operating. In order to calculate reaction kinetic parameters from concentration measurements, it is required to drive the reaction in fast pseudo first order regime. The thesis has targeted to achieve this regime of gas-liquid reaction.

5.4 Results of studies on side reaction and settling rates of Bunsen reaction products

Experiments have been performed to carry outside reactions as described in chapter 4. Samples were collected and analysed. The results are given in table no.5.7 and 5.8. The experimental setup is described in detail in section 4.4 of chapter 4.

All the experiments are repeated 4 times. The error of experiments is ± 2.1 %. The t-values are calculated for all the experiments and the confidence interval is found to be more than 99.9 % in all the experiments. Hence the experiments are considered to be statistically significant.

Table 5-7 Concentrations of I^-, $H^{+,}$ and I_2 for experimentation No. 1

Time (min)	I^- Concentration (moles/litre)	H^+ Concentration (moles/litre)	I_2 Concentration (moles/litre)
0	4.38	4.75	4.46
10	3.84	4.41	4.67

30	3.56	3.93	4.81
40	3.32	3.71	4.99

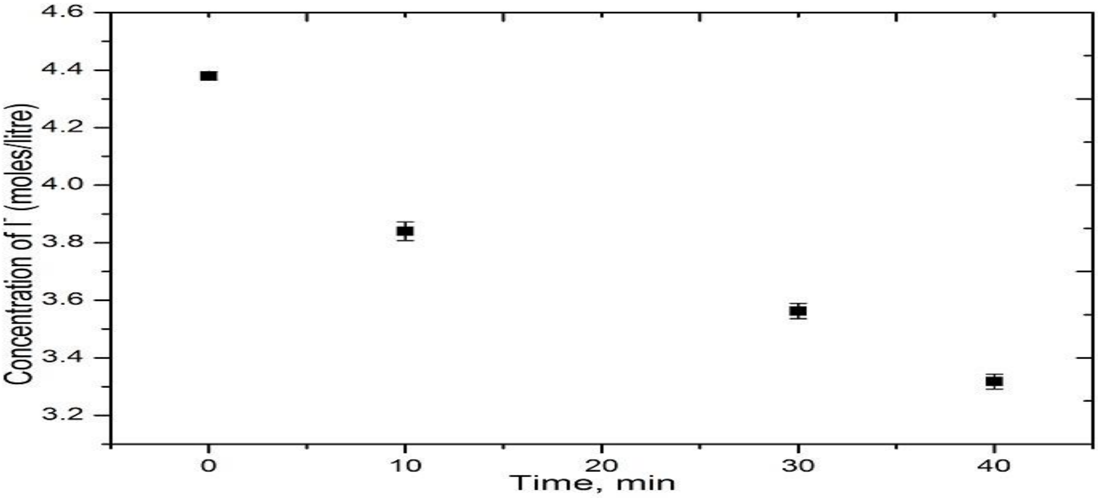


Fig. 5-20 Variation of I^- concentration with time at I_2/HI ratio of 1 and temperature of 80 °C

Figure 5.20 shows the variation of concentration of I^- with time. The concentration of I^- is decreasing with time. Initially, there is a sharp decrease which describes that the consumption of HI is rapid which indicates that reactions 1.2 and 1.3 are dominant than reaction Bunsen reaction.

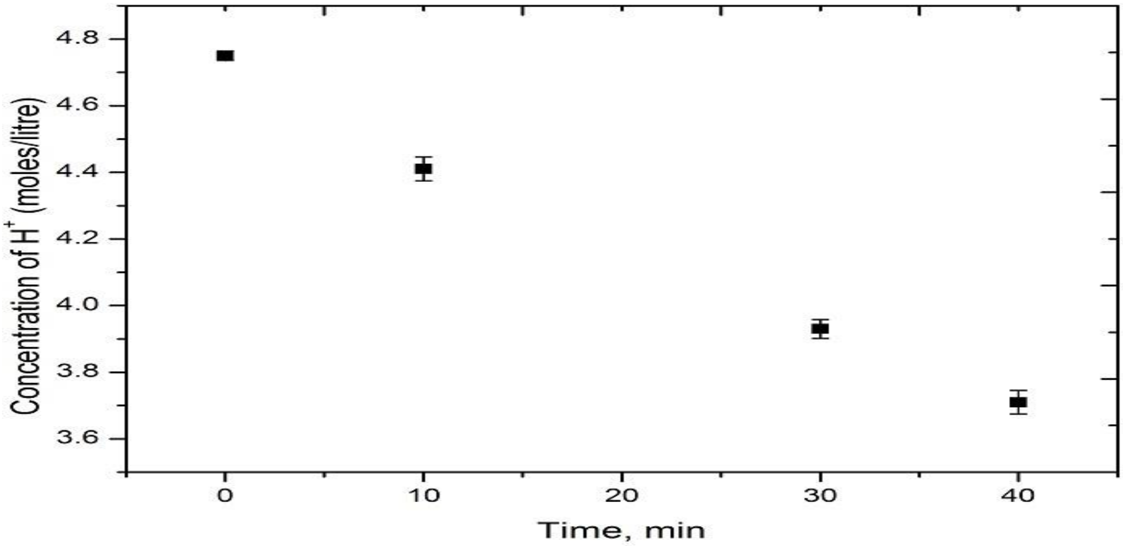


Fig. 5-21 Variation of H^+ concentration with time at I_2/HI ratio of 1 and temperature of 80 °C

From figure 5.21 it can be seen that the concentration of H^+ is decreasing with time. It suggests that both HI and H_2SO_4 are reacting to form one of the three reactions mentioned in chapter 4.

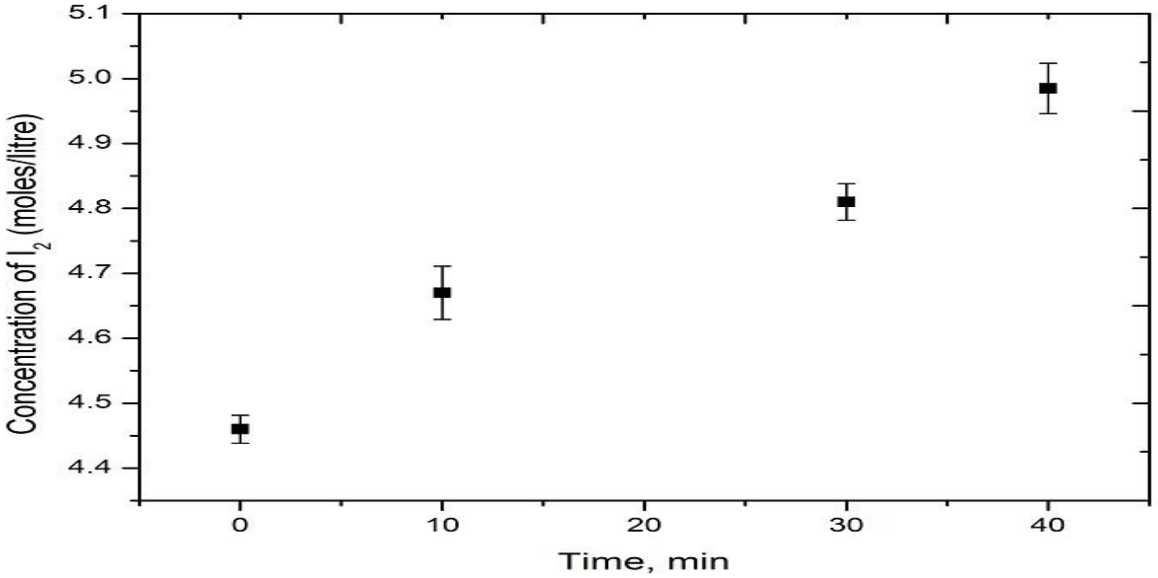


Fig. 5-22 Variation of I_2 concentration with time at I_2/HI ratio of 1 and temperature of 80 °C

Another experiment is carried out at 90 ^{0}C to study the effect of temperature on side reactions.

Table 5-8 Concentrations of I^-, HI and I_2 for experimentation No. 2

Time (min)	I^- Concentration (moles/litre)	H^+ Concentration (moles/litre)	I_2 Concentration (mes/litre)
0	3.53	3.84	4.72
10	3.54	3.82	4.75
30	3.12	3.18	4.87
50	2.37	2.68	4.89

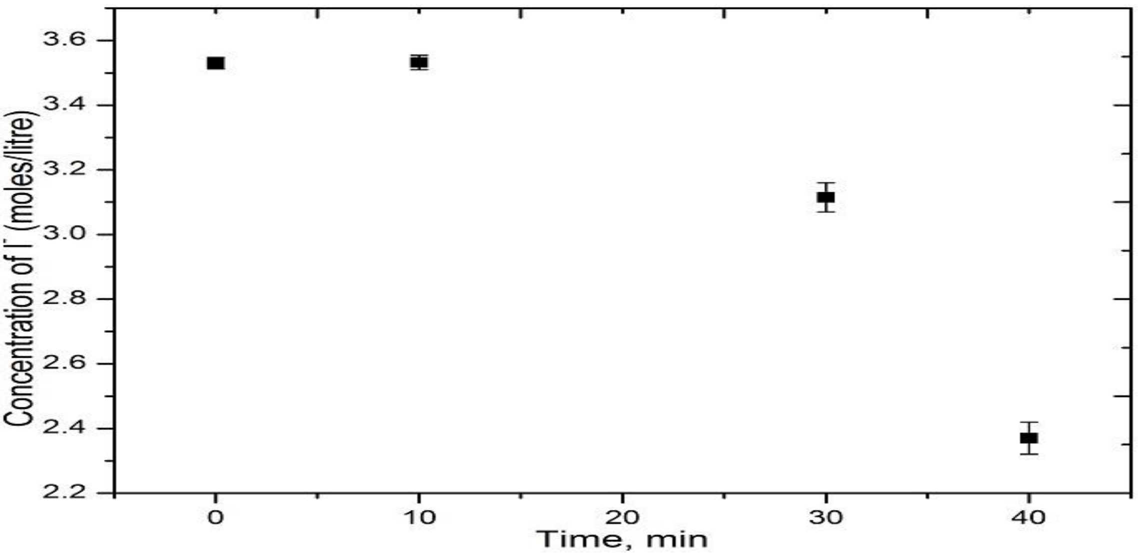


Fig. 5-23 Variation of I^- concentration vs time at temperature of 90 °C

Figure 5.23 shows that the concentration of I^- which depicts the concentration of HI is decreasing with time, initially there is a slight decrease, and later the steepness increases. At higher temperatures, the free Iodine availability decreases as it gets dissolved more at higher temperatures. Hence there is a possibility of side reactions.

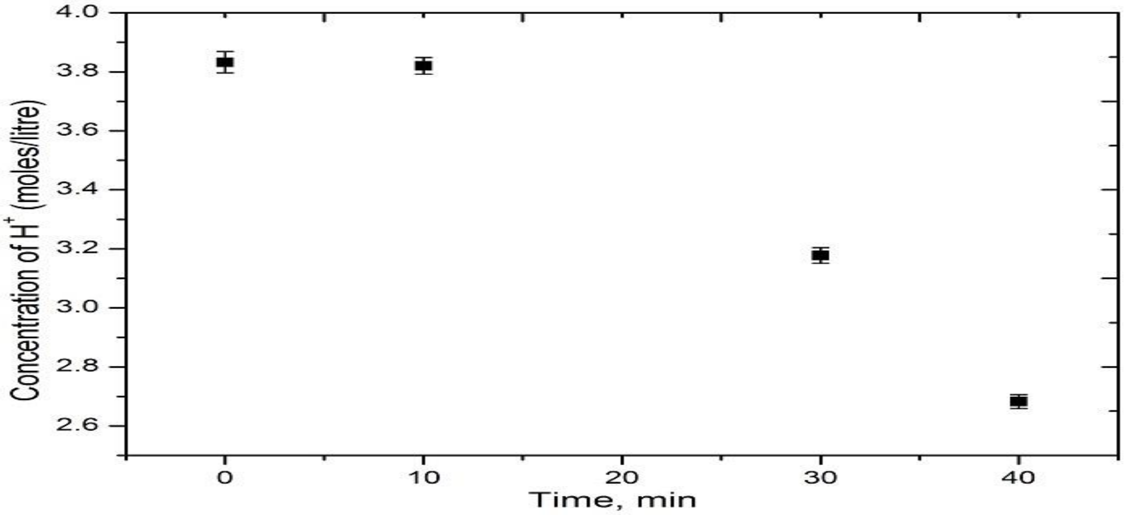


Fig. 5-24 Variation of H^+ concentration vs time at temperature of 90 °C

From figure 5.24 it can be seen that the concentration of H^+ is decreasing with time. It suggests that both HI and H_2SO_4 are reacting to form one of the three reactions mentioned in chapter 4.

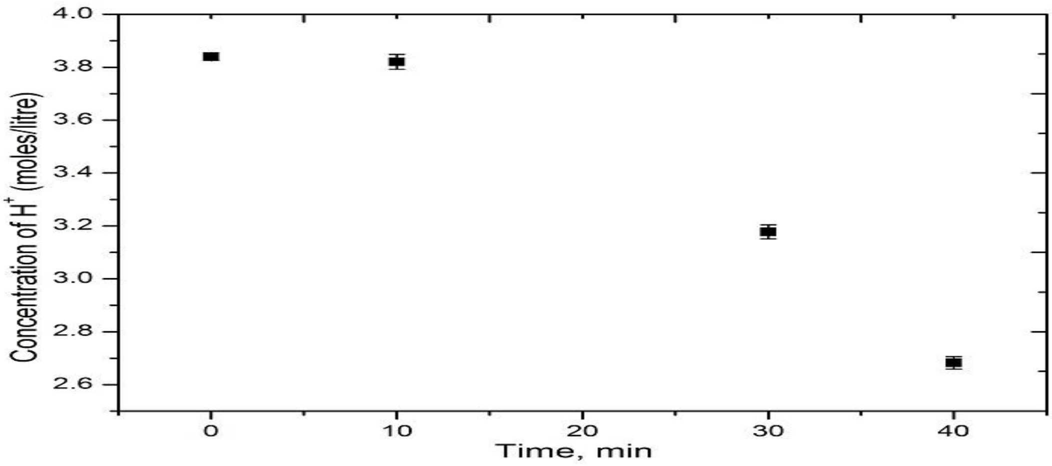


Fig. 5-25 Variation of I_2 concentration vs time at temperature of 90 °C

From figure 5.25 it can be seen that the concentration of I_2 is increasing with time.

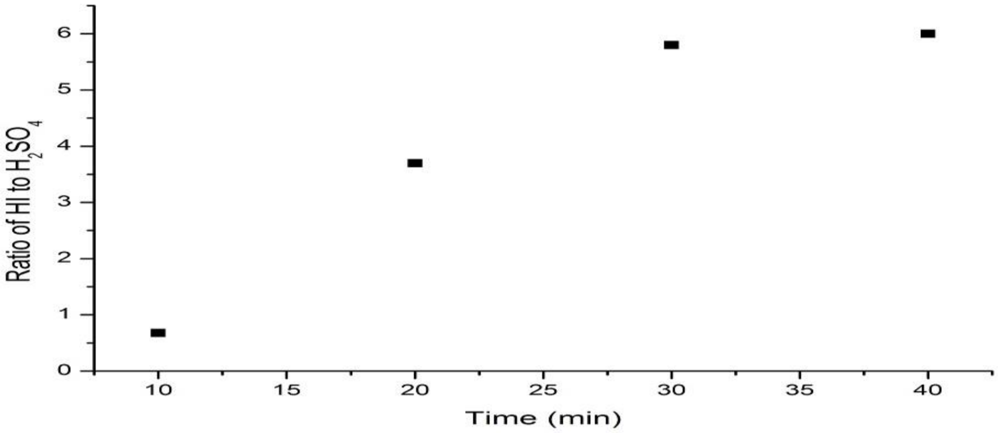


Fig. 5-26 Ratio of HI to H_2SO_4 with time at feed I_2/HI molar ratio of 1

From figure 5-26 it can be seen that the ratio of HI to H_2SO_4 is increasing with time which suggests that over a while side reaction occurrence increases. This suggests that over and above the temperature of 90 °C the occurrence of side reaction is dominant.

Table 5-9 Result of the two-phase separation at temperature 30 °C, pressure 1 atm

Exp. No	HIx			H_2SO_4 ml	Molar ratio	Observations	Remarks
	HI, ml	I_2 gm	HIx ml		$HI:I_2:H_2O:H_2SO_4$		
1	40	40	50	20	0.109:0.057:0.779:0.055	Layer observed after stirring for 5 mins	Settling time by

						and 3 min settling time (100ml Beaker)	varying feed composition
2	40	79	60	20	0.103:0.107:0.738:0.052	Layer observed immediately while mixing the acids (100ml Beaker)	
3	40	106	66	20	0.099:0.141:0.71:0.05	Layer observed immediately while mixing the acid (100ml Beaker)	
4	40	40	50	20	0.109:0.057:0.779:0.055	Layer not observed till 30 mins (100ml Beaker)	Settling time by varying surface area
5	60	60	75	25	0.109:0.057:0.779:0.055	layer observed after 15 min (150ml Beaker)	
6	85	84	106	43	0.109:0.057:0.779:0.055	Layer observed after 11 mins (250ml Beaker)	
7	75	112	112	43	0.109:0.086:0.75:0.054	Layer observed after 4 sec (150ml Beaker)	Settling time by varying feed composition at high I_2 concentrations
8	80	100	105	43	0.112:0.074:0.76:0.052	Layer observed after 7 sec (250ml Beaker)	

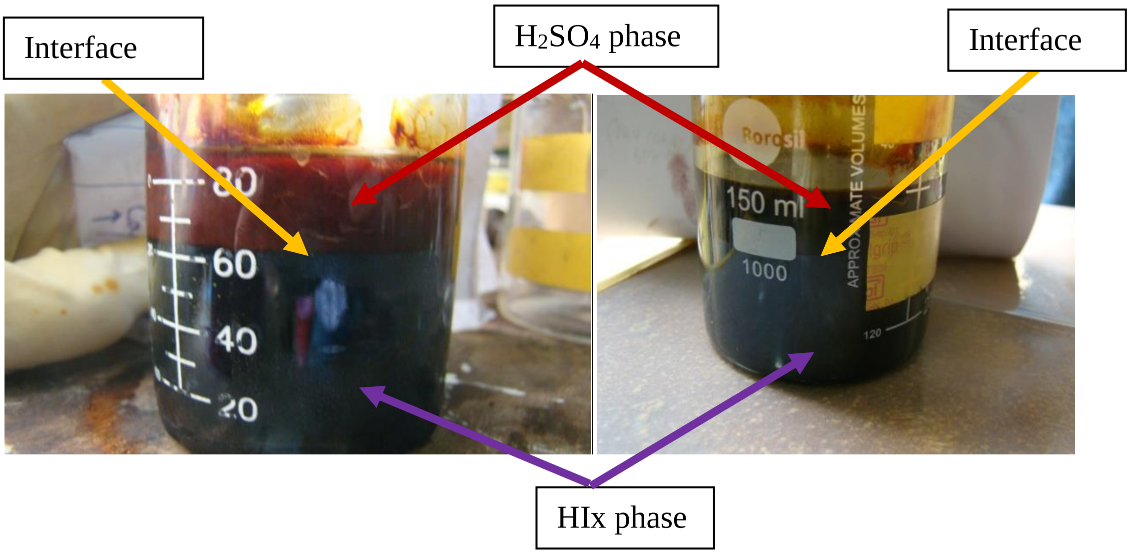


Fig. 5-27 Interface after separation of two phases

Figure 5-27 shows the phase separation that has occurred in two different sizes of beakers which differ in the cross-sectional area.

From table 5-9 it can be seen from the first three experiments where only the I_2/HI ratio is varied keeping the interface area for settling constant. The observation is that at the I_2/HI ratio of 0.52 phase separation occurred 3 minutes after agitation stopped whereas beyond the I_2/HI ratio of 1, interface appeared instantaneously after agitation stopped. This shows that the coalescence of H_2SO_4 drops is faster beyond the I_2/HI ratio of 1 because of increased immiscible nature with an increase in I_2 concentration.

Experiments 4-6 in table 5-9 are carried out by varying the cross-section area available for the settling of two phases. For 100 ml beaker with an I_2/HI ratio of 0.52 without agitation interface could not be observed till 30 minutes which signifies that at lower Iodine concentration, longer times are required for distinct interface visibility. As the cross-sectional area is increased interface appeared which promoted coalescence of H_2SO_4 drops. At higher Iodine concentrations settling cross-sectional area don't influence the interface visibility which can be inferred from experiments 7 and 8 in table 5-9.

Table 5-10 shows the typical calculation for error in phase separation experiment and calculation of t value to study statistical significance of the experiments. The confidence level of experiment is found to be greater than 99.9%.

Table 5-10: Typical calculation for t Value for Phase separation experiment

Temperature ^oC	Mole fraction of H_2SO_4 in HIx Phase-Runs 1-4				Mean	Standard Deviation	% error	T Value	Confidence level
50	0.00355	0.00381	0.00375	0.00369	0.0037	0.00011	3.0096	66	>99.9%

6 CONCLUSIONS AND RECOMMENDATIONS

The realization of hydrogen as an energy carrier relies on a practical method of producing hydrogen on a large scale with no emission of greenhouse gases. Thermochemical route hydrogen production is such a method to obtain hydrogen by splitting water through a series of reactions. The iodine-sulfur process is one of the capable water-splitting methods using iodine and sulfur dioxide as recycling agents. In the iodine sulfur cycle, all process fluids are recycled, and no greenhouse gases are emitted.

To realize continuous iodine sulfur operation, the Bunsen reaction must be operated at best-operating conditions to give maximum concentrations of product acids, good phase separation, and minimum or nil cross-contamination of two product phases, even at large scale operations. The thesis study is mainly focussed on the above discussed points. The salient highlights of the research study are as follows

1. The study on Bunsen reaction, phase separation, and side reactions are vividly described in the literature survey. The gap areas are identified to realize the objective of the study. An elaborate experimental facility with all safety features, instrumentation, and control is set up and commissioned to carry out Bunsen reaction at higher pressures of up to 6 bar (g).
2. Bunsen reaction has been carried out successfully up to 6 bar (g). The reaction has been carried out in a co-current reactor at various operating conditions such as temperature, pressure, feed flow rates, and concentrations.
3. At 80 ^{o}C, the mole fraction of HI in the HIx phase is higher and the mole fraction of H_2SO_4 in the sulfuric acid phase lower which is not desirable. SO_2 feed flow rate has improved the mole fraction of HI in the HIx phase and the HIx feed flow rate has decreased the mole fraction of HI in the HIx phase and H_2SO_4 in the sulfuric acid phase.

4. An increase in pressure of up to 6 bar (g) has increased both HI and H_2SO_4 mole fractions in both the HIx phase and sulfuric acid.
5. The study identified the condition of the highest mole fraction of H_2SO_4 in sulfuric acid phase i.e. 0.15 is obtained at operating conditions T=70 ^oC, P=6 bar (g), SO_2=0.12g/s, O_2=0.008g/s, HIx= 3 lph, flow rates, mole feed ratio-HI/I_2/H_2O:1/2.6/7. Highest mole fraction of HI in HIx phase i.e 0.165 is obtained at T=70 ^oC, P=2 bar (g), SO_2 = 0.24 g/s, O_2=0.008g/s, HIx= 2.5 l/h, mole feed ratio-HI/I_2/H_2O:1/2.2/7. To obtain the concentrated acid phases higher pressure operation is desirable.
6. To obtain a regime in which minimum cross-contamination of Bunsen reaction product phases experiments have been performed at various temperatures, pressures, and by varying SO_2 and HIx flow rates. It is found that at 4 bar g and 70 ^oC the purity levels in the sulfuric acid phase are highest at this the HIx and SO_2 flow rates are 1.8 l/h and 0.24 g/s respectively. And at 4 bar g and 60^oC the purity levels in the HIx phase are highest at this the HIx and SO_2 flow rates are 1.5 l/h and 0.12 g/s respectively.
7. Side reaction experiments have been carried out at different temperatures, I_2 concentration, and excess H_2O concentration. At a lower molar ratio of iodine to HI, the rate of consumption of both HI and sulfuric acid is higher. As the molar ratio of iodine to HI and temperature is increased the rate of consumption has decreased.

The salient conclusions are

1. To obtain the concentrated acid phases operation pressures of more than 4 bar (g) is required.
2. To obtain maximum purification of product phases in the studied regime, the reactor operation pressure shall be at 4 bar (g), temperature in the range of 60^oC – 70 ^oC with feed concentrations of HI/I_2/H_2O:1/2.8/7.7.

3. The study identifies the limiting conditions of operating parameters to obtain maximum concentrations of Bunsen reaction product phases with minimum cross-contamination of two phases.
4. To obtain reaction kinetics of the Bunsen reaction, a methodology is developed. The overall kinetic rate constant is evaluated and obtained as 1.8 second^{-1} at 300 K.
5. The study concluded that at higher ratios of I_2/HI and increased surface area the phase separation is immediate.

Recommended future studies are the following:

1. Bunsen reaction has to be carried out in a counter-current reactor under high pressures to ascertain the feasibility of reaction and phase separation in the same equipment.
2. Side reaction studies and settling rates have to be identified at higher pressures
3. Reaction kinetic rate constant parameters to be obtained for Bunsen reaction.

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