Enhancing Reaction System for Hydrolysis on Aluminum

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Abstract

A range extender in a battery electric vehicle supplements the existing drive system as an add-on module. Range extenders can comprise of any combination of conventional fuel, battery or fuel cell driven modules. The idea of a sub-system changes with the type of range extender. In this work, hydrogen generation is studied, a fuel is used to power the range extender via a fuel cell.

The thesis presents the work in progress for development of the sub-system for a range extender based on on-board production of hydrogen for automobiles. Several aspects of chemistry play equally pivotal role in control, hassle-free operation and safety of the system. After-treatment of the fuel by-products is the notorious issue that limits the reusing the reactor effecting the range extender. Along with this, reducing the reaction time with minimal usage of fuel is investigated. Both of these pressing issues are resolved correspondingly to an extent with the addition of several chemicals.

In addition, with the help of characterization techniques, a robust circular economy outlook of the range extender system has been initiated.
Sammanfattning

En distansförlängare i ett eldrivet fordon kompletterar det befintliga drivsystemet som en tilläggsmodul. Distansförlängaren kan vara olika kombinationer av konventionella bränsle-, batteri- och bränsleceldrivna moduler. Utformningen av de övriga delarna av undersystemet beror på vilken distansförlängare som används.


Dessutom har en robust cirkulärekonomisk syn på distansförlängaren utvecklats med hjälp av olika karakteriseringstekniker.
Acknowledgements

I must start by expressing gratitude to Pouya Moud, my supervisor, for not only giving me an opportunity to work with such an awe-inspiring project, but also for the freedom and constructive criticism. I also learned invaluable leadership aspects which I aspire to use further down in my career. The reviews given by Jonas Lindberg and Prof. Klas Engvall, my examiner, have greatly shaped the perspectives through which I looked at the project.

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I also thank Prof. Ethymios Kantarelis of the Process Technology group for helping me with the X-Ray Diffractometry, Post Doctoral scholar Fei Ye of the Department of Material and Nanophysics for training me to use the electron microscopy equipment.

Sincerely,
Akhil.
Foreword

From an engineering stand point, establishing hydrogen fuel infrastructure for cars is challenging given its multifaceted and dynamic perspective. Of them arguably, the most discussed one is the storage of hydrogen without inflicting on the performance of the car. Usage of compressed gas in cars has noticeably caused acceptability issues, concerns of safety. A possible remedy is to produce hydrogen on demand in the car from abundant resources.

This work looks at one such chemistry to be potentially used to power the range extender for automobiles. But, to make such an idea sustainable, the innate demand for lower use of resources during the process and fulfilling consumer demands are critical. Thus, these challenges demand a robust understanding of the fundamental aspects.

Due to the scope of monetary benefits and IP rights from this work, several aspects are not revealed to protect the interests of the firm involved. Upon further interest, the headquarters of myFC AB in Stockholm, Sweden shall be contacted.
# Contents

1 From the Literature ................................. 4  
   1.1 Introduction ................................. 4  
   1.2 Understanding the Chemistry ................. 5  
   1.3 The complexity of precipitation ............ 6  
   1.4 Sodium hydroxide regeneration ............. 8  
   1.5 Preliminary Work ............................ 8  

2 Methodology .................................... 10  

3 Method Development ............................. 13  
   3.1 Reactor Design ............................. 14  
      3.1.1 Reactor Design - Version 1 .......... 14  
      3.1.2 Reactor Design - Version 2 .......... 14  
   3.2 Benchmarking the Experiments .............. 15  
   3.3 Reaction Subsystem Design and Maintenance 17  

4 Precipitate Removal and Safety of the Reactor 18  
   4.1 Chemical Treatment of the precipitate ....... 18  
   4.2 Characterization ............................ 20  
      4.2.1 X-Ray Diffraction - XRD .......... 20  
      4.2.2 Scanning Electron Microscopy - SEM 21  

5 Tuning the reaction ............................. 22  
   5.1 pH Control ................................. 23  
      5.1.1 Weak Acid ............................ 24  
      5.1.2 Alcohol ............................... 25  
      5.1.3 Strong Acid ........................... 26  
   5.2 Separating Precipitate from the Reaction Mixture 26  
      5.2.1 Surfactants ........................... 26  
   5.3 Induced Disruption of Alumina .............. 27  
      5.3.1 Sodium Chloride ...................... 27  
   5.4 Precipitation Ratio ........................ 28  

6 Extended Discussion ............................ 29  

7 Conclusions .................................... 30
List of Figures

1.1 The reaction mixture ................................................. 5
1.2 Factors affecting the precipitation ................................. 7
1.3 H₂ profile - 5M NaOH .............................................. 8
1.4 H₂ profile - 4M NaOH .............................................. 8
1.5 H₂ profile - 2.5M NaOH .......................................... 9
1.6 H₂ profile - 1.5M NaOH .......................................... 9

2.1 The reaction scheme [10] ........................................... 11
2.2 Bronkhörst hydrogen flow controller ............................. 11
2.3 NTC Thermistor ................................................... 11
2.4 Schematic of the reactor setup .................................. 12

3.1 Schematic of the setup ............................................. 13
3.2 Preliminary Reactor - Top view .................................. 14
3.3 Improved Reactor - Top view .................................... 14
3.4 Reactor schematic for surfactant experiments ................ 14
3.5 Flow rate profile - Base experiment ............................ 15
3.6 Precipitation ratios with reference to the base experiment flow rates .......................... 16
3.7 Transformation of precipitate in alkaline media .............. 17

4.1 Comparison between Treated and Untreated precipitation samples ............................................. 19
4.2 Neutralization profile of the reactor with different acid concentrations after the reaction .................................................. 19
4.3 Emergency termination of the reaction .......................... 19
4.4 Acid treated samples - XRD ....................................... 20
4.5 Acid treated Al(OH)₃ - 651X ....................................... 21
4.6 Acid treated Al(OH)₃ - 5660X ..................................... 21

5.1 Flow profiles for different form-factors of aluminum ......... 22
5.2 Flow rate and Temperature profile for 325 Mesh Al powder .................................................. 23
5.3 Solubility curve of Al(OH)₃ [26] ................................. 23
5.4 Suggested mechanism for pH control ........................... 24
5.5 Effect of different ratios of weak acid on hydrogen flow rate .................................................. 25
5.6 Effect of different volumes of alcohol on hydrogen flow rate .................................................. 25
5.7 Effect of different volumes of strong on hydrogen flow rate .................................................. 26
5.8 Effect of different surfactants on hydrogen flow rate ........ 27
5.9 Effect of different ratios of salt on hydrogen evolution .......... 27
5.10 Effect of different additives on precipitation ratios ............ 28
List of Tables

1.1 Components of the reaction .............................................. 5
3.1 Operating conditions for base experiments .......................... 16
4.1 Induction time for different concentrations of acid .............. 18
Chapter 1

From the Literature

1.1 Introduction

Production of hydrogen from non-fossil resources and utilizing it into a commercial application has always been an engineering challenge [1]. The transient demand of the fuel and reliability of system when employed in domestic applications are the primary factors attributed to the challenge. A sheet of aluminum, when left in the ambience, corrodes into its oxide form of hydrated alumina \( \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O} \) [2]. Upon disrupting the layer of alumina, exposing the pure aluminum metal to water, the desired reaction of hydrogen evolution begins. Although the phenomenon of alumina formation on aluminum has been taken advantage of, in various material applications like construction of buildings, the presence of adherent oxide layer impedes the hydrogen production.

Therefore, continuous hydrolysis of water on aluminum demands a way of disrupting the layer of alumina continuously until all the metal is consumed. The disruption of alumina has been extensively studied with various promoters converging more towards mechano-chemical solutions for promoting hydrogen production. The most common classes of chemical additives used over aluminium are salts, oxides and hydroxides. Also, usage of several molten aluminum alloys like Al-Li [3, 4] and Al-Ga [5, 6] are also found in the literature with better hydrogen flow rates when compared at a certain temperature. This higher flow rates from the alloys can be attributed to the absence of adherent oxide layer in the molten form [2].

The salts disrupt the alumina layer by initializing a form of local corrosion called pitting [7]. It has been found that the flow rate of hydrogen thus obtained is over 1000 ml per gram of aluminum used at 60 °C with the usage of either NaCl or KCl [8, 9] at a weight ratio of 1 with Al. The first patent [8] filed over using salts for hydrogen evolution suggests strong temperature dependence. This can be extended to validate the theory of disrupting alumina layer by pitting corrosion as pitting accelerates at higher temperatures. Conversely, the hydroxides work by reacting with the oxide layer allowing water to react with Al to produce hydrogen, and decompose back into their original chemical form. This makes hydroxides the only class of chemicals that strictly work on \( \text{Al}_2\text{O}_3 \) by means of chemical reactions. With the addition of NaOH, the spontaneity of the hydrogen evolution changes. Although not at standard thermodynamic conditions, by IUPAC’s norm, the validity of NaOH as a catalyst has not been tested. On the other hand, the oxides demand intense mechanical activation [10] like ball milling before disrupting the alumina layer and act similar to the salts by inducing pitting.

This work is limited to the use of sodium hydroxide (chemical formula: NaOH) for hydrolysis. The main reasons behind using sodium hydroxide as a promoter of the reaction is due to the cost and availability. Other supplementary reasons include better control of the disruption of alumina, quick stalling of the reaction in case of a thermal run away, and customizability of the hydrogen flow profile. In addition, employing a liquid promoter has advantages with handling and in situ preparation. Thus, the reaction mixture for this study contains three components, aluminum, sodium hydroxide and water while the desired component is hydrogen and a precipitate as a side product.
1.2 Understanding the Chemistry

The aluminum hydrolysis reaction in the presence of NaOH gives sodium aluminate (NaAl(OH)$_4$) as a by-product. The sodium aluminate further decomposes into aluminum hydroxide and regenerates NaOH to support the preliminary aluminum hydrolysis. An open report from Department of Energy of United States [10] suggests that the possible reactions of aluminum reacting with water in presence of NaOH. They are:

$$2\ Al + 2\ NaOH + 2\ H_2O \rightarrow Na_2Al_2O_4 + 3\ H_2$$  \hspace{1cm} (1.1)

and,

$$2\ Al + 6\ NaOH + xH_2O \rightarrow Na_6Al_2O_6 + xH_2O + 3\ H_2$$  \hspace{1cm} (1.2)

and,

$$2\ Al + 2\ NaOH + 6\ H_2O \rightarrow 2\ NaAl(OH)_4 + 3\ H_2$$  \hspace{1cm} (1.3)

The first two reactions yield sodium meta aluminates, as multiples of NaAlO$_2$. It is merely suggestive that the concentration of NaOH, specific surface area of aluminum and the operating temperature are the factors determining hydrogen flow rate [11]. The meta aluminate products are insoluble in alcohol, highly soluble in water and possess an orthorhombic structure. Thus using lower concentrations of alcohol in the reaction mixture can help in dissolving the meta aluminates, as well as help in seedless precipitation of Al(OH)$_3$ as Lee et al. [12] suggest. But, the reaction 1.3, further referred to as the first reaction, gives a hydrated sodium aluminate which can be decomposed into NaOH and Al(OH)$_3$ as:

$$2\ Na[Al(OH)_4] \leftrightarrow 2\ NaOH + 2\ Al(OH)_3$$  \hspace{1cm} (1.4)

The reaction 1.4 is further referred to as the second reaction in this document. The main challenge in controlling the production of hydrogen lies in the understanding of the second reaction at a fundamental level as the equilibrium is not exclusive. With the second reaction, the rate of regeneration of NaOH is explained, which in turn explains the hydrogen generated by the first reaction 1.3, allowing for better control. The list of the all the components in the reaction are presented in the table below:

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical Formula</th>
<th>Stance in the reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>Raw material</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>NaOH</td>
<td>Raw material</td>
</tr>
<tr>
<td>Water</td>
<td>H$_2$O</td>
<td>Raw material</td>
</tr>
<tr>
<td>Aluminum hydroxide</td>
<td>Al(OH)$_3$</td>
<td>End product</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>H$_2$</td>
<td>Desired end product</td>
</tr>
<tr>
<td>Sodium aluminate</td>
<td>NaAl(OH)$_4$</td>
<td>By-product in equilibrium</td>
</tr>
<tr>
<td>Sodium meta aluminate</td>
<td>NaAlO$_2$</td>
<td>By-product to decompose</td>
</tr>
</tbody>
</table>

Table 1.1: Components of the reaction
1.3 The complexity of precipitation

Precipitation is a crucial phenomenon in the reaction that might be correlated to hydrogen flow rates. From the literature, it is understood that a multitude of parameters influence the precipitation of Al(OH)$_3$ from the sodium aluminate solution. But, it is to be noted that a few parameters are independent, and a combination of them can either enhance or deteriorate the precipitation. For instance, use of magnetic field and additives are independent of each other as they work differently. The effect of these multivariate combinations is unknown.

Further, the literature on precipitation directly suggests the usage of methanol, which catalyzes the removal of the water molecules more effectively from the hydrated aluminate ion. The usage of methanol improves the precipitation ratio also in a shorter time for the mole ratio of NaOH to Al of 1.36 with a 20% (v/v) concentration of methanol [13]. A patent [14] suggests that the concentration of the additive alters the composition and morphology of the crystals. While the size and morphology, as not the primary concerns, disregarding them could cause trouble in the overall utilization of the range extender.

The effect of agitation rate, mode of feeding and temperature are studied extensively by Zhang et al. [13]. The results on the precipitation study with changing temperature suggest that the precipitation ratio decreases with increasing temperature when using methanol. This decrease of precipitation ratio with increasing temperature is in agreement with the behaviour of seeded precipitation. The increase agitation rate also suggests the increase of precipitation ratio. Though the rate of feeding did not show significant difference in the yield and morphology of Al(OH)$_3$, the feeding caustic solution into methanol caused 3% improvement in precipitation rate, compared to both simultaneous feeding and feeding methanol into caustic solution. These fluctuations confirms the hypothesis the precipitation ratio of Al(OH)$_3$ is a complex function of experimental conditions, purity [14] and nature of the materials involved [15, 16].

Recent research is inclined towards adding several additives as the seeded process is extremely tedious and inefficient. This improvement in efficiency can be attributed to the additive characteristics of interface adsorption, colloidal formation and decrease of surface tension, thus intensifying the precipitation [17]. The favoured candidates include most anionic surfactants [18] choline [14], polyethylene glycol, Tween 80, SDBS and combinations of the later [17]. The statistical design for a set of parameters executed by Ying Zhang et al. [17] suggest that the amount of additives added does not have a significant effect on the improvement of precipitation rate, but greatly influence the particle size distribution. A combination of Tween 80 and SDBS are added to the aluminate solution containing 50 g per liter concentration of caustic. To achieve the best precipitation ratio reported, 0.5% (w/w) of additives are added with reference to the parent liquor to achieve 96.71% precipitation.

Ultrasound and magnetic field are also found to marginally improve the precipitation efficiency [19, 20]. Although both the methods are intended to fine-tune the particle size distribution and morphology of the particles, improvement in precipitation efficiency of 2-6% can be achieved independently over a reaction time of 4 hours. All the above factors are combined and represented in the figure 1.2 below.
Figure 1.2: Factors affecting the precipitation
1.4 Sodium hydroxide regeneration

It is to be noted that the primary goal of the available research is not to improve the precipitation of Al(OH)$_3$, but to NaOH regeneration. Also, improved precipitation of Al(OH)$_3$ does not necessarily regenerate NaOH. This can be explained by a simple reaction extrapolated from the research of Li et al. [21]. Above a pH of 10, the aluminate ion decomposes as:

\[
[\text{Al(OH)}_4^-] \rightleftharpoons \text{Al(OH)}_3 + \text{OH}^- \quad (1.5)
\]

Upon carbonation with NaHCO$_3$,

\[
\text{NaHCO}_3 \rightleftharpoons \text{Na}^+ + \text{HCO}_3^- \quad (1.6)
\]

\[
\text{HCO}_3^- + \text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \quad (1.7)
\]

This leaves Al(OH)$_3$, H$_2$O and 2 Na$^+$ ions and a CO$_3^{2-}$ ion which would most likely form Na$_2$CO$_3$. This is also validated from the article where a white precipitate [21] is observed. This is similar with usage of Methanol by Zhang et al. [13]. There is a very high probability of formation of alkoxides [22] by the following reaction scheme without leaving enough NaOH for the disruption.

\[
\text{CH}_3\text{OH} + \text{NaOH} \rightarrow \text{CH}_3\text{ONa} + \text{H}_2\text{O} \quad (1.8)
\]

This leaves an extremely narrow window of using additives in a particular mode and increasing the operating temperature for the given promoter. In other words, only to play with the chemical equilibrium. Also, a combination of a salt and NaOH can be used to improve the hydrogen flow rate.

1.5 Preliminary Work

The previous work performed by a different research team at myFC at different concentrations [23] of NaOH show differences in the hydrogen evolution profiles. From the hydrogen evolution profiles, it can be observed that significant precipitation of the Al(OH)$_3$ begins right before the hydrogen evolution plateaus suggesting that the second reaction is crucial. In this work, the formed precipitate during the reaction is left undisturbed to further the precipitation. This idea of removing the water molecules from the hydration sphere of aluminate ion is validated by the literature [13].

The experiments were carried out spanning from 5M of stoichiometric excess of NaOH towards a stoichiometric deficiency of 1.5 M NaOH. With the experiments in stoichiometric excess quantities, the flow rate profile resembles the concentration profile of a component in a batch reactor. The concentration exponentially decreases following an initial peak as the equilibrium decomposition reaction does not take place. The peak in the profile of 4M NaOH appears to be sharp, thus suggesting a possible thermal event rather than an actual reaction event.

Figure 1.3: H$_2$ profile - 5M NaOH

Figure 1.4: H$_2$ profile - 4M NaOH
However, the steady state flow rate of hydrogen seems to appear when the stoichiometric quantity of NaOH is decreased. Also, it can be observed that by decreasing the supply of NaOH, the reaction run time also extends from 240 minutes to 275 minutes respectively while the plateau region flow rate seems to be around 5 ml/min.

Figure 1.5: H₂ profile - 2.5M NaOH

Figure 1.6: H₂ profile - 1.5M NaOH
Chapter 2

Methodology

To understand the fundamental aspects of a reaction, it is important to know how each component of the reaction exists in the system and how they interact with each other on a macro scale. A solid sheet of aluminum in contact with liquid caustic gives hydrogen and precipitate. Although the precipitate is Al(OH)$_3$, it does not suspend into the alkali solution, instead forms as a hard solid and settles to the bottom of the reactor. This freshly formed precipitate has a dark greyish colour on the surface with a lighter hue beneath the first layer. And, the precipitate is resilient to mechanical scraping complicating the removal of precipitate which further has an impact on re-using the reactor. Thus, this work intends to answer two major questions:

- Can the precipitate be removed as required?
- How to achieve a higher flow rate of hydrogen and shorten the reaction time?

While the first question demands a robust solution, the second seeks for an optimum. Also, it is to be noted that the questions are mutually dependent on each other to some extent. If the reaction is carried out continuously, the solution to the removal of precipitate and the desired Hydrogen profile is strictly mutually dependant i.e., the precipitate must be removed as soon as the corresponding change in hydrogen flow rate profile is observed. As it is evident, the continuous mode of operation demands a lot of auxiliary systems to pump all the reaction components and is operationally expensive. A way out of this corner is to run the reaction in batch mode with a mass of Aluminum and water present in the reactor, induce NaOH to start the reaction and treat the system as a semi-batch system as Hydrogen flows out of the reactor as soon as it is produced.

From the fundamentals of reactor design, a material balance equation for a component can be described as:

$$\text{Inlet} - \text{Outlet} + \text{Generation and/or Consumption} = \text{Accumulation} \quad (2.1)$$

Thus, an $i^{th}$ component in such a semi-batch system is described as,

$$F_{i,\text{in}} - F_{i,\text{out}} + r_i.V = \frac{dN_i}{dt} \quad (2.2)$$

Then, a material balance equation for the hydrogen from the equation 2.2 can be written as:

$$- F_{H_2} + \int_0^V r_{H_2} dV = 0 \quad (2.3)$$

From the kinetic rate law, the reaction rate can be described as:

$$r_{H_2} = k.c_{\text{NaOH}}.A_{Al} \quad (2.4)$$

Replacing the rate of reaction in the equation 2.3 with the above equation, the dependency of the molar flow rate of hydrogen can be derived.

$$F_{H_2} = k.c_{\text{NaOH}}.A_{Al} \quad (2.5)$$

where, $c_{\text{NaOH}}$ is the concentration of NaOH, and $A_{Al}$ is the specific surface area of aluminum.
Equation 2.5 serves as a linchpin to understand the dependencies of hydrogen flow rates. However, the reaction scheme is quite complex for this reaction. This intricacy unfolds from quantifying the rate constant \( k \) described in the equation 2.5. The reaction mixture gives out two classes of products, namely, sodium meta aluminates and sodium aluminates [10]. The class of sodium meta aluminates have at least three identified components with unknown quantity and varying rate of decomposition. Further, the chemical equilibrium established between NaAl(OH)\(_4\), NaOH and Al(OH)\(_3\) hardens the knot. A reaction scheme for this reaction is represented in the figure 2.1. The isolation of each equilibrium constant and combining rate constants of all the above discussed reactions is very tedious and often unnecessary.

![Figure 2.1: The reaction scheme [10]](image)

Thus, the experiments are carried out further with sole emphasis on precipitate removal and improving NaOH regeneration rate to achieve higher Hydrogen flow rates in a shorter time. The literature available does not directly aim towards improving hydrogen flow rates, instead targets on to production of aluminum hydroxide [13, 20] to be used in the Bayer process. Thus, almost all of the cited literature is an extrapolation from the Bayer process related research on to improving the reactor sub-system design.

All the reactions are performed at a constant temperature of 50\(^\circ\)C in a water bath unless mentioned. The NTC thermistors are used to measure the temperature along with Bronkhört hydrogen flow controllers. The reaction vessel is made of polypropylene and is made leak proof. Custom built LabView programs are used for flow and temperature monitoring since the reaction time extends from 4 to 5 hours. Aluminum sheets are selected from a single batch from a single supplier to eliminate slight variations in the trace metal quantities. The water bath is controlled with a feed forward loop, built into the heater ensuring the constant temperature as shown in the figure.

![Figure 2.2: Bronkhört hydrogen flow controller](image)  
![Figure 2.3: NTC Thermistor](image)

The aluminum is cut into sheets and run in test experiments to determine the form factor to be used. Instead of using a single sheet, splitting a sheet into half and slightly bending one of
them is observed to not mask any of the available surface area. Thus, all the experiments are carried out in batch mode using dual aluminum sheets.

Figure 2.4: Schematic of the reactor setup
Chapter 3

Method Development

Custom lab scale reactors were designed for the experiments. In lab scale, a reaction volume of 30 ml is constantly used for most experiments to maintain uniformity with the stoichiometric ratios. A polypropylene pill vial is selected as the reactor instead of glass vessels as the highly alkaline environment tends to etch the silicates in the glass to form silicon hydroxide [24]. Polypropylene supplemented with the use of right sealants, the reaction vessel can be made leak-free. To remove the moisture from the gas, a knock out drum along with a desiccating chamber are used. The schematic of the setup is shown in the figure 3.1.
3.1 Reactor Design

As mentioned, over a pill vial, a single hole is made on the top of the screw cap and a suitable pipe gland is fitted. Through the gland, the thermistor wire to data acquisition hardware is laid, followed by a hard tubing around the wire and the gland is sealed. Epoxy based glue is used to seal all the possible hydrogen leaks. Impromptu tests were carried out with the reaction mixture and to assure the absence of leaks.

3.1.1 Reactor Design - Version 1

With time, the leaks started to appear with the preliminary design. The primary issue is the hydrogen leaks after using the reactor for a few runs. A hydrogen sniffer is used to detect any leaks around any joint, later surfactant was used to locate the leak and is corrected. In the existing design, the wires for the temperature NTC sensor were laid through the outlet pipe making the wires concentric to the gas outlet pipe. Using epoxy based sealant to prevent leaks around this concentric wires has proved to be inefficient, especially when the pressure builds up inside the reactor. The setup is vulnerable to adjustments after the reaction starts. Hence, this design must be improvised into minimizing the leaks allowing robustness and reliability of the reactor.

The temperature probe is laid out into the data acquisition hardware through another bore made on the top of the cap and sealed with a clear silicon based sealant. This improved design presented in figure 3.3, when used with a single layer of sealant tape around the thread, has helped minimizing the leaks. But, it is to be noted that silicone based sealants has higher fixating time of approximately up to 4 hours.

3.1.2 Reactor Design - Version 2

For the use of surfactants, there is significant foam generated due to the turbulence created by the evolving hydrogen gas inside the reaction mixture. A set of impromptu experiments are conducted with a measuring jar at the same reacting temperature as the rest of the experiments. The volume of the reaction mixture is noted and the reactions are allowed to run with the select surfactants. The level of foam for each experiment is manually observed and the highest volume mark is noted. It is found that the foaming is inversely proportional to the diameter of the reaction vessel, while directly dependant on the volume of the reaction mixture.
For the available standard diameters of the graduated cylinders, the volume of peak foaming is observed to lie within 3 to 4.5 times the reaction volume. To avoid damage of the flow meters in hazardous situations, reactor selected is 5 times the reaction volume. In other words, only a maximum of 20% of the reactor volume must be used when surfactants are used. Hence, for 30 ml reaction volume, the volume of the reactor must be at least 150 ml. These experiments are suggested when there is a change of reactor design. For example, depending in the type of impeller, the peak foaming volume might change.

### 3.2 Benchmarking the Experiments

While the primary objective of the study is to generate a sludge that is easy to pump, generating the required hydrogen profile is also a crucial aspect. To observe the probable enhancements of the chemistry, a set of experiments were determined to act as a reference. Thus, a set of experiments revealing different parameters are performed. The first of them is to gauge hydrogen flow profile at desired concentration of NaOH and operating conditions with a fixed weight and form factor of aluminum. Later, the precipitation ratio of Al(OH)$_3$ is measured with reference to the stoichiometric weight of Al(OH)$_3$. Precipitation experiments are made to eliminate any possible external effect that might have effected the Hydrogen flow rate like heat of dissolution.

![Figure 3.5: Flow rate profile - Base experiment](image)

It is important to realize that the temperature curve displayed in black in the figure 3.5 is a trace of the smoothed flow rate profile in red. This is due to the fact that the only heat generation occurs along the reaction as Hydrogen is produced. In other words, the enthalpy of Hydrogen production exclusively contributes to the temperature rise in the system.
Figure 3.6: Precipitation ratios with reference to the base experiment flow rates

The precipitation ratio is defined as the weight of Al(OH)$_3$ at a point during the reaction to the weight of stoichiometric Al(OH)$_3$ at the end of the reaction.

\[
\text{Precipitation Ratio} = \frac{\text{Weight of precipitate at a time during the reaction}}{\text{Stoichiometric weight of the precipitate at the end of the reaction}} \tag{3.1}
\]

The relationship of flow rate and precipitation ratio can act as a crucial visualization to understand the dynamics of precipitation with reference to the formation of Al(OH)$_3$ as represented in the figure 3.6 below. Thus, the stoichiometric parameters for all the experiments further on are:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Operating temperature</td>
<td>50°C</td>
</tr>
<tr>
<td>NaOH concentration</td>
<td>0.75 M</td>
</tr>
<tr>
<td>Aluminum weight</td>
<td>1.62 g</td>
</tr>
<tr>
<td>Stoichiometric quantity of NaOH</td>
<td>37.4%</td>
</tr>
<tr>
<td>Expected precipitate</td>
<td>4.68 g</td>
</tr>
</tbody>
</table>

Table 3.1: Operating conditions for base experiments

The change of precipitate during the reaction is important for the understanding of the properties of the precipitate. Thus, XRD is carried out on precipitates at different times during the reaction to understand the structure of the precipitate.
As the XRD patterns reveal, the Gibbsite peak starts to appear gradually during the reaction when the precipitate is left in alkaline conditions.

3.3 Reaction Subsystem Design and Maintenance

From figure 3.1, it can be seen that the reactor vessel, knockout drum and the desiccator have to be connected in a robust way to avoid hydrogen leaks while being feasible for maintenance. Commercially available soft tubing from one supplier is consistently used to connect all three of them together with the mass flow meter. However, soft tubing has a set of challenges with hydrogen permeability and clogging from the precipitate. Since permeability of hydrogen through the tubing wall can be rendered as a systemic error, clogging is an issue that needs to be solved. An easy solution is to replace clogged tubes after a few experiments by validating visually. This is critical to avoid disruptions with the hydrogen leaks.

Employing a knockout drum and a desiccator before the Hydrogen gas enters the mass flow meter is consequential for the longevity of precision of the mass flow measurements. If the moisture from the Hydrogen gas is not removed before measurement, the condensation inside the device can cause dead-zones and greatly affect the validity of displayed values. This denaturation of silica can be visually observed with a color change from opaque orange to clearer beads.

Another crucial aspect for the accuracy of results is the temperature measurement with the NTC thermistor. While the reaction proceeds, precipitate forms and deposits on the bottom of the reactor vessel and on the thermistor. With deposits on the sensor, the temperature readings will deviate from the true values. For this, the thermistors must be verified for true reading after a set of experiments using a solution of known temperature. If the difference of temperature from the true values is more than 2 °C, the thermistor must be replaced.
Chapter 4

Precipitate Removal and Safety of the Reactor

4.1 Chemical Treatment of the precipitate

Once the reaction completes, i.e., aluminum reacts with sodium hydroxide to give out hydrogen, the precipitate aluminum hydroxide is formed as a by-product. The by-product is grey in color with a sponge-like surface. However, the texture of the precipitate poses a challenge to the reaction system. With the precipitate being very hard, pumping out the precipitate is nearly impossible. Even mechanical scraping does not help in mobilizing the precipitate. Extrapolating this to a system perspective, the precipitate builds up over time in the reactor and clogs all possible piping. Thus, the removal of sludge is inevitably a challenge that needs to be solved. It is also observed from previous research that the precipitate [23], when left in the alkali solution gradually changes into a white color which behaves like an emulsion. Overtime, the precipitate also settles to the bottom of the reactor. In the present work, the sludge is chemically removed using a strong acid after the reaction ends.

After all the aluminum is exhausted, the reaction ends. Then, the alkaline solution is removed from the reactor which is a dilute solution of NaOH. Then, the precipitate is treated with a strong acid of different concentrations ranging from 0.01N to 12.06N.

The time of formation of the white colored precipitate from the grey is observed to be dependent on concentration of the acid used and the area of contact with the precipitate. As soon as the acid is in contact with the grey precipitate, the area slowly fades into a white color. For a volume of 2.5 ml of acid, the following table illustrates the time taken for the fresh grey precipitate to turn into a white precipitate.

<table>
<thead>
<tr>
<th>Concentration range[N]</th>
<th>Rest period[min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01 - 1</td>
<td>greater than 30</td>
</tr>
<tr>
<td>2 - 6</td>
<td>approx. 6</td>
</tr>
<tr>
<td>6 - 12</td>
<td>less than 3</td>
</tr>
</tbody>
</table>

Table 4.1: Induction time for different concentrations of acid

The idea of rest period is stipulated according to the behaviour of acid that in contact with the precipitate. The second column in the above table 4.1 represents the time taken for visual confirmation of the color change.

This has a greatly enhanced the pumping ability of the sludge as displayed in the figure 4.1. On the right, the untreated sample is seen with precipitate sticking to the bottom of the vessel. But, on the left, the precipitate is cleared off and is made pumpable just by inverting the reactor vessel.
With further deliberation, it is also understood that this strong acid can be used to neutralize
the reaction mixture after the reaction ends, to ensure the safety. Thus, a test was conducted to
quench the reaction mixture after the reaction ends towards a safe pH. This test was carried
out with 3N and 5N concentrations of strong acid. As acid-base neutralization is intuitive, the
higher concentration of acid in lesser volume or lower concentration acid in higher volume is
required. The volume of acid required is represented with reference to the volume of reaction
mixture as shown in the figure 4.2

Figure 4.1: Comparison between Treated and Untreated precipitation samples

Figure 4.2: Neutralization profile of the reactor with different acid concentrations after the
reaction

However, in case of accidental situations such as a car crash, the usage of acid does the oppo-
site of increasing the flow rate instead of terminating the reaction. For this, two kinds of sugars
were tested to add in the reaction mixture to completely abate the reaction. The presumption of using sugars is that the aldehydes produced by reacting with NaOH would not react with Aluminum. Both the sugars, have successfully eliminated the hydrogen flow rate as soon as they are added.

4.2 Characterization

4.2.1 X-Ray Diffraction - XRD

To enable XRD analysis the precipitates are treated with 12N and 5N acid, washed with water and dried at 80°C for 3 hours to remove the water. The dried samples were analyzed using a X-Ray diffractometer between 5° - 75° of 2θ with a rate of 0.5° per minute. The obtained pattern is represented in the figure 4.4 below.

From the XRD data, it is clear that the obtained precipitate is a mixture of both Gibbsite
Bayerite from the characteristic peaks. The characteristic peaks of the Gibbsite are represented in the appendix.

4.2.2 Scanning Electron Microscopy - SEM

The obtained precipitates were examined for morphology and shape under a scanning electron microscope. The main reason to study the morphology is to understand if the precipitate generated from this reaction can be used directly in the aluminum processing. The micrographs reveal nearly spherical structures with plate-like deposits validating the structure represented by XRD. Monoclinic-prismatic structures on the Gibbsite globules can be observed in both the figures 4.5 and 4.6.

Figure 4.5: Acid treated Al(OH)$_3$ - 651X

Figure 4.6: Acid treated Al(OH)$_3$ - 5660X
Chapter 5

Tuning the reaction

The first set of experiments are carried out with different form factors of aluminum. Different shapes of aluminum translates into different available surface area and corresponding rate of change of area along with the reaction. With the aluminum sheets, the rate of change of available surface area almost stays constant. With the use of finer particles, the reaction would behave according to the *shrinking core* model and shall limited by other parameters like critical radius and solid-liquid contact [10]. Moreover, the deposition of Al(OH)$_3$ on the aluminum particles is also detrimental to hydrogen production. Here, it is to be noted that the method of preparation of the reacting aluminum plays a crucial role. The continuously cast aluminum sheets are often spray or water quenched while the aluminum pellets are often glycol quenched [25]. With the alkali medium, if the pellets are not cleaned of quenching media, the organic matter is causticized and can be observed as black soot particles inside the reactor vessel. Consequently, the soot tends to deposit on the reacting aluminum particles blocking the available surface area leading to lower hydrogen flow rates.

![Flow profiles for different form-factors of aluminum](image.png)

Figure 5.1: Flow profiles for different form-factors of aluminum

Figure 5.1 represents different form-factors of aluminum used to observe corresponding hydrogen flow rate profiles. Also, the figure provides a compelling evidence of Al(OH)$_3$ deposition on aluminum particles through the sloping plateau region. In addition, the area under the black curve proves that the hydrogen yield is below 90%. Identically, when 325 mesh aluminum powder is used, as shown in the figure 5.2, similar yield of hydrogen, in terms of volume is reached as the reaction is extremely rapid.
5.1 pH Control

The solubility of Al(OH)$_3$ is crucial in shifting the equilibrium of the second reaction 1.4. If Al(OH)$_3$ is at its best solubility, the equilibrium exists by changing Al(OH)$_3$ to NaAl(OH)$_4$. In this process, NaOH is also consumed delaying the Hydrogen output. Thus, the solubility curve of Al(OH)$_3$ is one of the critical trends to observe if the hydrogen yield is to be changed. Weak acids are the perfect class of chemicals to lower the pH to a required value.

The equation for temperature compensation of pH can be written as:

$$pH_{\text{compensated}} = 7 + (pH_{\text{measured}} - 7) \frac{T}{T_0}$$  \hspace{1cm} (5.1)

For 0.75M NaOH at 25°C, the theoretical $pH$ value is 13.875. This is compensated to a working temperature of 50°C by using the equation 5.1 to yield a value of 10.44 $pH$ units. With a slight decrease of $pH$, the solubility of Al(OH)$_3$ can be greatly minimized at 50°C. Thus, weak acids are added in the plateau region to keep the Al(OH)$_3$ dissolved and force the equilibrium of the reaction to regenerate more NaOH.
It is baffling that the removal of NaOH from the system by adding acid is increasing the flow rate of Hydrogen. For this, a probable mechanism is proposed in this work. Although this mechanism is strictly for this application, scientific analysis through the elementary steps of the reaction is necessary to provide a robust proof or denial.

![Figure 5.4: Suggested mechanism for pH control](image)

The addition of an acid reduces the pH. This reaction of reducing the pH causes heat effects like Heat of neutralization and heat of dissolution to kick in causing the temperature to rise. The raise of temperature alters the equilibrium constant to change forcing the equilibrium concentration of \( \text{NaAl(OH)}_4 \) to increase. This increase of equilibrium concentration of \( \text{NaAl(OH)}_4 \) establishes higher equilibrium concentration of NaOH. Thus, the relatively higher concentration of sodium hydroxide yields better hydrogen flow rates.

According to the Le Chatelier’s principle [27], when an equilibrium reaction’s conditions are changed, the position of equilibrium shifts to counteract the change to reestablish the equilibrium. Applying this principle to equation 1.4, if NaOH is removed, the equilibrium shifts to the right of the reaction. Then, higher quantities of NaOH is produced while the amount of \( \text{Al(OH)}_3 \) produced is reduced.

### 5.1.1 Weak Acid

The weak acid only removes excess \( \text{OH}^- \) ions from the reaction mixture, but keeps NaOH intact. Instead of adding weak acid in the reaction mixture, neutralization is carried out only after the plateau is reached to force the equilibrium to generate more NaOH. To supplement, different ratios of weak acid are tested.
Figure 5.5: Effect of different ratios of weak acid on hydrogen flow rate

Here, 25% (w/w) of weak acid represents 25% in weight of weak acid per required stoichiometric value of NaOH. As the picture represents, 25%(w/w) weak acid has best shift. But, due to the excess of Na+ ions left out by the formation of tetraborate ion, the Na+ ions forces the Al(OH)$_3$ to form NaAl(OH)$_4$ after some time. Thus, the shift caused by weak acid seems to come back to the steady state flow rate of $\sim 5$ml/min.

5.1.2 Alcohol

Alcohol neutralizes NaOH by forming alkoxides. The depravation of NaOH similarly effects the reaction system just like weak acid.

Figure 5.6: Effect of different volumes of alcohol on hydrogen flow rate
5.1.3 Strong Acid

Strong acid neutralizes all the available NaOH if added in stoichiometric quantity without leaving any free ions. By the addition of strong acid, the system is deprived of NaOH and the equilibrium is forced to generate more NaOH than the equilibrium quantity.

![Graph showing the effect of different volumes of strong on hydrogen flow rate](image)

Figure 5.7: Effect of different volumes of strong on hydrogen flow rate

Using 3ml of 0.1N strong acid has significantly improved the hydrogen flow rate up to 10 ml/min without altering the profile of the plateau. As can be seen from the figure 5.7, the flow rate is almost constant until aluminum exhausts.

5.2 Separating Precipitate from the Reaction Mixture

Aluminum is a group 13 post-transition element with an electron configuration of [Ne]3s²3p¹. This electron configuration of aluminum suggests a valency of +3. However, even when three anions like OH⁻ are in the vicinity of Al³⁺, there is a residual positive charge present on the metal cation. This residual charge in presence of alkaline media attracts another anion to form [Al(OH)₄]⁻ followed by NaAl(OH)₄.

5.2.1 Surfactants

Two surfactants were tested to see their influence on the hydrogen flow rates. Although both of them peaked to a higher flow rate than the base experiment, the steady state flow rate showed no significant difference from the base experiment.
5.3 Induced Disruption of Alumina

5.3.1 Sodium Chloride

The objective of using salt is to start pitting on the alumina layer at the operating temperature to supplement the disruption. Salt is added in two ways to observe any advancement of flow rate profile. The first way is to add the salt to reaction mixture at room temperature and then heat up to operating temperature while the second way is to pickle the aluminum sheet in salt solution for 48 hours and then transfer into reaction mixture.

Despite the operating temperature being 50°C, addition of salt did not seem to have any positive effect on the hydrogen flow rates. The flow rate profiles for different ratios of salt is similar to the parent experiment as the figure 5.9 displays.

The invariability of the flow profile can be attributed to the initiation of pitting. Upon observation of the surface of aluminum just before the reaction, no pits are found. However, this reason may not be exclusive.
5.4 Precipitation Ratio

As understood from the figure 3.6, the precipitation can be observed with an linearly increasing profile with time. But, with the addition of other components, the equilibrium of the sodium aluminate decomposing into precipitate and NaOH is disturbed. As explained by Le Chatelier’s principle, the system tries to achieve the equilibrium again.

![Figure 5.10: Effect of different additives on precipitation ratios](image)

If higher amount of NaOH is removed, the system regenerates proportional amount of NaOH to compensate the deficiency. As a consequence of higher regeneration of NaOH, the production of Al(OH)$_3$ decreases. The figure 5.10 provides experimental evidence of this. The slope of the linear fit for weak acid experiments appears to slightly decrease when compared to the parent experiment. But with the use of strong acid, although the final precipitation ratios at the 300$^{th}$ minute are similar, the ratio is higher at the 200$^{th}$ minute.
Chapter 6

Extended Discussion

The flow profiles are not an exact match even when the experimental conditions are exactly the same. This hypothesized to the minor change in chemical properties caused by quenching of the aluminum sheets. This chemistry sustains on the residual charge that aluminum has to give steady flow rates. A minor proportion of impurity like chromium or tin can disrupt this subtle residual charge, leading to complex chemistries. This can ultimately lead to differences in the run time.

The emergency stop of the reaction using sugars is only a face of safety systems in the car. The safety system in a car is often more robust and includes a failure protection system. Often, the trigger mechanism includes system of sensors that are market specific and governed by regulations.

In the pH control phenomenon although heat effects change the reaction system’s behaviour, these effects are induced by altering the pH. Also, the mechanism discussed is strictly a hypothesis and needs rigid scientific study to confirm or deny this hypothesis.

On the other hand, the induced disruption of alumina by soaking in salt solution is a time dependant phenomenon which circumvents the scope of the study. Although the phenomenon of pitting is a promising and a well-studied way of disrupting oxide layer over metals, pickling in a salt solution for more than 48 hours is operationally expensive for a fuel system. Similarly, the experiments intended to hinder Al(OH)₃ generate a lot of foam forcing physical limitations on the system in lab scale. For both these set of experiments, the results are recorded for further analysis with changing reaction volume, design of reactor and interaction with other sub-systems.
Chapter 7

Conclusions

This work encompasses several discrete aspects of the range extender sub-system, starting with development of methods to carry out research in lab scale and understanding the limitations of such lab scale systems. Necessary suggestions are provided to further minimize the limitations of the built systems. Arguably, the most disruptive problem of the sub-system, sludge removal has been solved using chemistry for a mode of operation, which is most likely to be the systems mode of operation on a bigger scale. Safety perspectives of the reactor have been looked into and solutions for emergency stopping of the reaction and making the reactor safe after the reaction have been proposed.

While the effect of change of concentration is known, the behaviour of each component in the reaction, at least on an empirical scale has been found out through this work. These phenomena have been taken advantage of and a few methods for fine tuning the reaction for increased flowrate of Hydrogen are evaluated. The pH control of the reaction, while being locked onto lower amounts of NaOH has been identified as the optimum way for fine tuning the reaction given the multi-faceted advantages it possesses.

In addition, with the help of X-ray diffractometry and scanning electron microscopy, insights into circular economy that could be generated with the Al $\rightarrow$ Al(OH)$_3$ $\rightarrow$ Al loop have been initiated.
Bibliography


