Energy recovery of metallic aluminium in MSWI bottom ash

Different approaches to hydrogen production from MSWI bottom ash: A case study

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Abstract

Most of the wastes in Sweden end up in incinerator plants. These trashes are full of metals, especially aluminium, which will not oxidize, they can’t always be recycled and they will instead oxidize in water and leak hydrogen gas to its surrounding. Estimations calculate it could be an average potential of around 40-50 kWh/ton of burnt trash. Ignoring the imported trash, the national recovery potential of Sweden’s 4.3 million tonnes of trash would then be equal to 170-220 GWh/year due to non-recyclable metals, which are currently going to temporary landfills. The requirements to harness this potential are technically simple, and can be achieved by a quick separation of the recyclables and the non-recyclables. This report will review the factors which increase the rate of reaction and study different ways of extracting the energy, by electrolysis, thermal treatment and mechanical mixing. This was done by taking small samples from the MSWI, owned by Umeå Energi AB, and putting them in small containers. While using the different methods, electrolysis, thermal treatment and mechanical mixing, the amount of developed H₂ gas over time was measured. The result shows that the best methods are mechanical mixing together with thermal treatment, where mechanical mixing seems to give the biggest effect of them two. The electrolysis did not work as intended, where there could be issues with the conductivity of the ash-mixture.
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1. Introduction

Due to the high amount of trashes produced in the modern day European society, the EU legislation for landfills was changed in 1999. The amount of trash that goes to MSWI (Municipality Solid Waste Incinerators) for energetic recovery in Sweden has since increased by almost two times. Also recycling and composting increased by about the same. In many other EU countries, the energetic recovery, recycling and composting has increased even more (1).

Most of the metals that are present in the waste can be recovered and recycled, even though they are mixed with the rest products of the combustion. The best way to recover the metals that are not recyclable is to use energetic recovery by producing hydrogen (H₂), which partly already happens to some the thinnest aluminium (Al) sheets in the combustion chamber. Al is one of the most abundant metals in the ash. Left as it is, this metallic Al also becomes a problem in many cases. For example by causing explosions when coming out of the MSWI or by expanding when the ashes are used as a filler material in concrete, which will weakening it by causing cracks.

The CEN standard 13431:2004 assumes that all Al particles smaller or thinner than 50 μm is completely oxidized in the MSWI, thereby recovered in the form of energy. Previous work shows that this most likely is a false assumption, depending on several factors and should therefore be reconsidered and updated (2).

1.1. Hydrogen production today

If H₂ is used as a vehicle fuel, in a combustion engine or a fuel cell, it has no direct emissions, only water. Used in fuel cell systems, it can have a high efficiency, a theoretical efficiency at around 85%. Internal combustion engines (ICEs) have a theoretical maximum of around 58%. The practical efficiency in fuel cells vs ICEs that can be used in cars, is about 35-40 vs 20-25, using the same fuels (3).

Today’s H₂ is produced mainly by steam cracking natural gas, which consists of around 97-99% fossil methane (CH₄), and a small part from the electrolysis of water. H₂ is not common as a vehicle fuel today, partly because it has high cost of equipment, partly because of the inefficiency of production, but also it’s relatively hard to store and distribute. Having H₂ produced as a rest product could help crossing some of the large-scale barriers. H₂, at atmospheric pressure, has about 10 kJ/l, which is due to its low density. Therefore, a lot of focus and research today lies in improving the storage, by increasing the density and pressure of the H₂.

1.2. Umeå Energi AB

Umeå Energi AB is the municipality owned district heating and electricity company in Umeå, which is in the north region of Sweden. Umeå has several heating plants, but the two main plants are two Combined Heat and Power (CHP) plants in Dåvamyrén, a swamp about 10 km outside of the centre of the city of Umeå. The picture of these two plants can be seen on the front page of this dissertation, with the green Dåva 1 to the left and Dåva 2 to the right. Dåva 1 is a grate MSWI plant with a total effect of 65 MW, of which 10 MW is electricity. Dåva 2 is a fluidized bed plant, burning wood chips and peat, with a total power of 105 MW, of which 30 MW is electricity.

A grate plant (also called Stoker-type or roster) uses pistons to move the burning material through the combustion chamber. These types of plants are very good for trash with a high variety of sizes and content, and you can easily change the duration in which the trash stays inside of the combustion chamber.

A fluidized bed plant uses a sand bed, from which the air flows through the bottom, which in turn makes the sand bed act like a fluid. This fluid-like behaviour increases the mixing of the solid fuel,
which in turn makes it easier to build smaller plants. The sand also helps to reduce certain emissions, like S.

When it was new, Dåva 1 had one of the most modern gas cleaning systems that existed, cleaning out almost all acids and particles from the gases. It has a feeding capacity of around 20 tons/h of waste, giving an average of around 3 tons/h of bottom ash, which is sent to a temporary landfill, before being used as concrete filler material.

Previous research showed that the bottom ash in Dåva 1 was able to produce as much as 18 l H₂/kg bottom ash and 5 l H₂/kg fly ash, if extracted with high-pH solutions (4). In original pH, it produced only around 2 l H₂/kg ash. Of course, this is dependent on the trash input, reaction time, etc., but it’s a value which will be used in the discussions and conclusions.

Today Umeå Energi use oil to start the powerplant after it has stopped. It would be beneficial for Umeå Energi economy and for their environmental goals to use internal sources of stored energy for this.

### 1.3. Accidents in MSWI from hydrogen production

In 2003 there was an explosion in the basement of Umeå Energi AB’s MSWI Dåva 1, where the ashes come out. The walls of the ash storage house were pushed out, but luckily no one got seriously injured. The only thing they could do at that time was to increase the ventilation in the tunnel where the bottom ashes come out. After consulting with several experts, they concluded that this explosion was caused by H₂ being released from the warm and moist bottom ash, while it was being transported out to the storage house (5). Similar events have been reported in other MSWIs, from both bottom ashes and fly ashes in grate incinerators and fluidized bed incinerators.

Some even more serious accidents have occurred with fly ash bunkers in Japan (6). Both of the accidents resulted in serious injuries, one of them including one death. One of the plants was a fluidized bed incinerator and the other a grate incinerator. Both accidents were caused by H₂ production in the fly ash bunkers. In both cases it was found that the fly ashes were rich in metallic Al. The grate incinerator had a high level of Al in its fly ashes, around 9%.

### 1.4. Aim of project

The project started with the purpose to increase the efficiency of MSWI’s and to reduce the amount of external energy that the plants need, by using an internal source of stored energy for starting the plants. This would be both an economic and ecologic profit for the company, and possibly other companies that own MSWI’s. Another advantage for treating the ashes was found after the project was started. This was to reduce the explosive risk which comes along transporting and storing ashes from MSWI’s (Read 1.3)

### 1.5. Scope of project

To complete the task, the work had to be limited for one semester of studies, 20 weeks of studies. Instead of looking at the possibility to build a treatment plant at Umeå Energi with known data, it was decided to look for the H₂ productivity, using electrolysis. Which variables to control and measure was decided by studying previous methods and results on the subject and discussing with employees at Umeå Energi and my supervisor at Umeå University. After this, the experiments was to be done using a simple and small experimental setup.

After a few attempts with electrolysis, it was decided to try some new methods. So the scope was changed to use thermal and mechanical treatments, instead of using electrolysis,
2. Theory and literature review

The main aim is, and should always be, to recycle as much metallic Al as possible, preferably starting already in the homes, since it has the smallest economic and environmental impact. However, in certain cases, it's not possible. Some products have very thin Al sheets integrated with layers of paper and plastic. Other times, the communities do not have a proper recycling system or they might simply do not care enough. When these trashes reach the incineration plants, some of the non-recyclable metals will oxidize, but not all.

By knowing and understanding the limitations of the recycling of metals in bottom ashes, we can quickly decide which part of the waste can go into metallic recycling and what part should go into energetic recovery. By that the efficiency of the metals lifecycle increases. To understand a field which has not been deeply researched, we start by understanding the processes in the ideal cases, for example H₂ production from pure Al metals. After that come the reports about MSWI bottom and fly ash and its recycling and H₂ production potentials.

2.1. Reaction

To recover the energy, which today is usually lost in the ashes at the landfill, the Al rich ashes can be left in water, where it will oxidize by splitting the water. See equation [1], [2] and [3], where [3] is the overall reaction.

\[ \text{Al} + 3 \text{H}_2\text{O} + \text{NaOH} \rightarrow \text{NaAl(OH)}_4 + \frac{3}{2} \text{H}_2 \]  
\[ \text{NaAl(OH)}_4 \rightarrow \text{Al(OH)}_3 + \text{NaOH} \]  
\[ \text{Al} + 3 \text{H}_2\text{O} \rightarrow \text{Al(OH)}_3 + \frac{3}{2} \text{H}_2 \]

[1] and [2] gives the overall reaction:

Important to note is that this is under NaOH rich, alkaline conditions, since the bottom ashes always have a high pH. Under neutral or acidic conditions, the reaction products will look differently. This has not been considered in this review, considering the alkaline nature of the bottom and fly ash.

2.2. Temperature dependence

There has been some research about using Al as energy storage. This research has covered the temperature and pH dependency of the reaction, see equation [3]. In the report of Parmuzinaa, et al. the H₂ production rate was looked into for Al mixed with Ga (70%) and In (30%) and also Al mixed with Ga (60%), In (25%), Sn (10%) and Zn (5%) at different temperatures. Only by increasing the temperature from 20°C to 40°C, the rate of production was increased by up to 100%. If the temperature is increased from 40°C to 60°C, the rate of production goes up by 200% and from 60°C to 80°C by another 100% (7).

Hiraki et al. also researched the rate of reaction. By checking the reaction of pure Al in a NaOH solution, with a pH above 12, at 291, 313, 323 and 333 K, they found that the activation energy of the reaction under those conditions was about 68 kJ/mol (8).

In temperatures higher than 280°C, the reaction changes to have different products. First it favours the production of AlO(OH) instead of aluminium hydroxide, Al(OH)₃. After that, over 480°C the more favourable product is instead Al₂O₃, completely jumping over the hydrated stages. (9) These oxides can also work as an additive that improves the H₂ production of metallic Al, see more in Figure 1 and under Additive dependence further down.

Considering that some of the work is done with pure Al, with known additives or increased pH, the temperature dependency of raw BA from MSWIs could be different.
2.3. pH dependence

By changing the pH of Al and the water mixture, it has been found that at a pH above 10-11, H₂ production from Al skyrocketed, see Figure 1 (10). This is due to the increased availability of OH-groups in the first reaction, see equation [1] above.

As one can see, the pH dependency is high. Problems could therefore occur for small amounts mixed with other residue, mainly other salts and acids, such as HCl acid, that could interact and neutralize the hydroxides. In a high purity system, the hydroxides could easily be replenished, since they are not consumed in the reaction or neutralized by any other substance (see equation [3]).

At the same time, this is also one of the limitations of the reaction; the reaction temporarily uses the NaOH, and thereby lowering the pH and the rate of reaction. This tendency can be seen in Figure 2, as the reaction starts, the pH drops, until the reaction is done, where it slowly regenerates. Luckily it’s just a relatively small decrease (8).

Figure 1. Hydrogen produced in 1h as a function of pH (10).

Figure 2. Time temperature and pH of the NaOH aqueous solution, the accumulated volume and the generation rate of H₂ (8).
In MSWI bottom ash, the pH is luckily already slightly alkaline. Because of this, the reaction gives a very clean H₂, especially since the gaseous traces would get neutralized in the alkaline solution (11). For a commercialized production of H₂ from bottom ash, it’s needed to keep the mix alkaline; thereby making sure that the H₂ does not need to be cleaned after production. Acid solutions in MSWI bottom ash produce a lot more CO₂, NH₄ and H₂S, among other things (6).

The pH level also has an extra importance, for the electrolysis. The high-pH solution of the ashes should reduce the electric resistance of the solution and therefore increase efficiency of the system.

2.4. Additive dependence
As it can be seen in Figure 1 and in the work of Parmuzinaa et al. and Li et al., the additive effects can be huge (7) (12). Some additives, like Ga, In, Sn and Zn, can help to activate the metallic Al, by preventing the build of an oxidized layer. This prevention is thought to be because of an embrittlement and softening of the Al rich alloy. When the oxide is formed, it crumbles apart much easier, leaving the rest of the Al free to react with the surrounding medium (13).

Additives can be ground down into the Al to catalyse the oxidation of the Al. These materials include Al, Ca and Mg hydroxides and silicates as well as carbon powder (10).

Other additives, like Na₆Sn(OH)₉, are for the prevention of corrosion and H₂ production, mainly for battery applications, where corrosion and H₂ production is a parasitic effect and unwanted.

Additives like NaH₂PO₄, Na₂SO₄, NaF and NaHCO₃ have been looked into when using saline solutions for aluminium batteries. The reason to use these additives are to decrease the water use by reducing the gelation and preventing build-up of Al(OH)₃ on the Al particle surface, which would significantly reduce the conductivity of the Al anode (12).

2.5. Electrolysis and aluminium batteries
There were no studies found on the electrolysis of Al in the purpose of producing H₂, most likely since the process is spontaneous by nature. A common process is electrolytic anodization, which is used to cover an Al product with Al oxide, by applying a voltage over the Al product, which acts like an anode. It’s used for colouring, to prevent Al products to rust and to produce Al₂O₃ based capacitors. This produces some H₂ as a by-product, though this is unwanted, since it can create bubbles which could crack the oxide surface. The biggest difference between the anodization process and the production of H₂ is that in the anodization process, acid solutions are commonly used to promote Al₂O₃ formation, instead of alkaline solutions which promote Al(OH)₄ and H₂ formation.

Aluminium batteries are also interesting to look in the point of electrolysis, if one would ignore that it’s producing current, instead of using it. Also for batteries, the prevention of H₂ production is crucial. In despite of these differences, some experiments have been done on using Al pellet as source, called flow batteries. This means that there has to be an anode current collector in the media, which will connect to the loose Al pieces, making them into the working anode. From this, some ideas and conclusions can be drawn to use. Here Zaromb et al. used nickel as an anode current collector (14). Other current collectors that can withstand the electrolysis, as well as the alkaline conditions, include acid-proof stainless steel, platinum or palladium-plated steel, cermets, perovskites, etc.

This research was based on trying to use electrolysis of bottom ash for the production of H₂, since it has not been looked into before and also because it could be a simple way of implementing this process in an existing MSWI plant without adding any extra additives, than what already exist in the bottom ash.
2.6. Metallic aluminium in MSWI ashes
When the bottom ash comes out of the MSWI, it’s cooled down in a water bath. After this water bath, the ashes are transported for separation etc. As the ashes come out of the water bath, they are still moist and warm. The metallic Al will then oxidize by splitting the water, producing \( \text{H}_2 \). This \( \text{H}_2 \) will be produced during the transport towards the storage house and therefore the \( \text{H}_2 \) can and has caused explosions in enclosed spaces, see Accidents in MSWI from hydrogen production.

After a few days or weeks, the bottom ash is shipped to a cleaning facility, where it goes through metal separation. The Eddy Current Separation method is the most common method of separating out non-ferrous metals, such as Al. By having the material being transported on a conveyor belt, through a high-speed rotating magnetic field, the non-ferrous metals will create a current, creating an opposing magnetic field. Therefore a repulsion force will throw the non-ferrous metals off the end of the conveyor belt. See Figure 3. Meanwhile non-metallic residue just falls off. The problem comes if the non-ferrous metals are too small and/or covered by other non-metallic objects. Then they become too heavy or small, and therefore they are barely affected by the magnetic field and fall down together with the non-metal residue (15).

![Figure 3. Principle of Eddy Current Separation (16).](image)

About 30-50% of the Al that comes into the incinerator might not be recovered nor recycled from the bottom ash. They are too small for the Eddy current separation even though about 50% of this Al is metallic, which means that is still a potential of recovering it as energy (2) (15).

The non-metallic ashes are mostly oxides and salts etc., like sand. This can be used for filling material, mixed into concrete, asphalt, etc. The problem appears when there are still non-oxidized metals, most commonly metallic Al, left in the ashes. When used in mixes like these, the Al will expand, slowly, for a quite long time. This causes cracks in the material over time, reducing its strength and durability among many things. It will also continue to produce \( \text{H}_2 \), so if these ashes are used, or stored, in closed spaces, there is a big risk for explosions, even months after it comes out of the MSWI, depending on if it has been treated or not. For this reason, it’s crucial that these ashes are treated and tested before commercial use (17) (18) (19).

In Sweden, Alm et al. researched the maximum production of bottom and fly ash, including the Umeå Dåva plant. There it was found that the maximum production, at the time, was 18 l \( \text{H}_2 \)/kg bottom ash (4). This is 6 times as much as the maximum that was found in this report. It was also found that the fly ashes could produce up to 5 l \( \text{H}_2 \)/kg fly ash.

2.7. Age dependency of the ashes
Grate incinerators seem to have a relatively high amount of metallic Al, both in both bottom and fly ashes, meanwhile fluid bed incinerators have most of its metallic aluminium in the fly ashes. Most of the aluminium in the bottom ashes of fluid bed incinerators forms silicates, due to the vast presence of silica, from the sand (4).
Figure 4. Gas generation of almost fresh and aged ash at natural pH of the ash (l gas/kg ash) over 60 days. Filter ash material from Händelö, boiler 14 (4).

The time between the test and exiting the MSWI is also very important as seen in Figure 4. Most ashes lie outside for days or weeks before entering a separation plant. This means that most of the smaller metallic particles have already oxidized. This can also be seen by going through the reports, where the maximum production ranges between 0-70 l H₂/kg ash, probably also depending on a wide range of factors, the amount of recycling in homes, type of incinerator and equipment, legal demands on the power plants, etc., which is different in different areas and countries. It’s also correlated with the time it had been lying outside. After 60 days, up to 90% of the Al could be oxidized (4).

By understanding what will oxidize, why and how fast, we can separate the ashes in recyclable and non-recyclable fractions very early and thereby increase the energetic recovering rate. This is specifically important, since it’s the smaller particles that are non-recyclable and it also has a much faster rate of reaction. An example, if Tetra pak cartons are sent to the paper recycling, the aluminium and plastic layers will be separated and reused at a relatively high percentage (20). If they are burnt instead, there might be some parts that are not oxidized and not recycled, due to its layered design. It’s these cartons that are assumed to be oxidized according to the CEN standard 1343 1:2004, which has shown not always to be the case (2).

In his thesis, Iliyas et al. experimented with producing H₂ from bottom ashes with just mixing water and 2 week old bottom ashes, from a MSWI in Lund, in the south of Sweden (11). This proved to be a difficult task, with a production of only around 2 l H₂/kg ash, over 150 days in room temperature. The rate of production was also compared to its water content, showing that the higher amount of water would produce more H₂, though the production stagnated at saturation. Testing the gas for traces of CO₂ or CH₄ was also done, but none was found. This was supporting the hypothesis that the H₂ produced in the reaction was due to the Al particles in the bottom ash and that the alkaline solution will neutralize some of the trace gases. Production of H₂ from ashes that had been in open-air conditions for over 2 years was also looked into. This produced no detectable H₂, most likely due to the neutralized pH and/or the extensive oxidization of the sample.

2.8. Particle size of MSWI bottom ash and fly ash
A similar work was done by Biganzoli et al. in two different plants in northern Italy (21). They looked specifically at the part of the bottom ash which does not get separated by the Eddy Current separator. The bottom ash was also older, around 4-6 weeks old. The possible H₂ production of this ash was between 6-11 l H₂/kg fine ash, meaning particles smaller than 4 mm, which in itself only was about 8% of the total ash weight. It could be that the amount of Al entering the incinerator is higher, than in the previous mentioned case.
The particle size has a great impact in the recoverability rate of both bottom ash and fly ash. Bigger metallic particles, as mentioned earlier, can easily be recovered through Eddy Current Separation and the smaller particles cannot. In this subject, interesting results was found, both by Tang et al. (22) and Berkhout et al. (15) for bottom ashes and Mizutani et al. (6) for fly ashes. The results show that around 50% of all the ashes are smaller than 5 mm in bottom ashes, and smaller than 125 µm for fly ashes.

When it comes to aluminium content, Berkhout et al. (15) also found that about 10% of the total metallic aluminium is in the smaller particles, and none of it is recycled with common processes. He also found that about 50% of the aluminium between 5-20 mm was not recovered either, which shows that there is an even bigger potential than just the fine ash. Admittedly, this probably varies a lot from region to region, depending on type of trash and how much is being recycled at home among other things.

For fly ashes, Mizutani et al. (6) found that the fly ashes from both grate incinerators and fluidized bed incinerators had high contents of Al, but most metallic Al was found in the fly ash of fluidized bed incinerators. In his samples, from a lot of different plants, he found a production of up to 70 l H₂/kg ash in some samples. Such extreme cases might just be a coincidence, since the average was of around 30 l H₂/kg fly ash. It's still a big potential, about 0.1 kWh/kg fly ash. In grate incinerators, the level was kept at around 0-15 l H₂/kg ash, which is also a rather big potential.

When it comes to the rate of reaction, the fly ash and smaller bottom ash particles will have a higher rate of reaction than the bigger particles, partly since they have a higher surface-volume area. They are also better to have as a filler material in concrete, since it most likely has less metallic particles, which would cause problems.

This is important, since at the same time it's the smaller particle that has a potential for energetic recovery, they cannot be recycled in the most common processes. So by taking use of the ashes straight after they come out of the MSWI, minimizing open-air oxidization and increasing the rate of production, there is a possibility for a higher production of H₂ and reducing risk at the same time.

### 2.9. Other sources of waste aluminium

Metallic Al can also be found as waste in the production and recycling of Al. When the Al is produced, its oxide is melted down and converted. It then forms a crust on top with the rest products, commonly called salt dross, white dross or black dross, depending on its properties and content. White dross has in some cases a lot of metallic Al and can then be sent to Al recycling plants for extra treatment. The dross is rich in Al₂O₃, but also AlN, AlC, AlS, NaCl, KCl, MgO and a lot of other elements (23). The leftover dross could be full of metallic Al, it has been found to have between 1% and 70% metallic Al, together with a lot of salts etc. The whiter the dross, the more metallic Al has been found (24). This means that it’s one of the most concentrated losses of metallic Al. Of course it’s once again better if it can be recycled, but considered that a lot of it cannot, it should be considered to produce H₂ from it, before putting it in a landfill.

One of the issues with energetic recovery of the dross would be that it’s not only H₂ which is produced. Water oxidizing with AlN, AlC and AlS, which commonly can be found in the dross, gives a lot of gases such as NH₃, CH₄ and H₂S, especially if the dross is acidic or not alkaline enough (25). Thereby the gas would be in need of a proper cleaning process to be used industrially and commercially.

### 2.10. Gas separation

The gas produced from MSWI ash should be relatively clean, considering that the product, H₂, comes from metals and the ashes are most commonly alkaline, neutralizing CO₂ and similar gaseous substances. There is still a possibility of trace gases, especially in the case of dross leftovers. Therefore it’s also interesting to go through a variety of gas separation techniques.
The most commonly used is pressure swing adsorption (PSA). In principle, a material adsorbs different gases at different pressures, so by swinging the pressure of a gas over such material, different gases will be adsorbed and released. In the PSA process, the bigger molecules get trapped due to surface interactions meanwhile the smaller ones just pass right by. The materials used are different for different applications and gas compositions, but for H$_2$ separation, Zeolite (Alumina silicates), activated carbon and silica gel were looked into by Golden et al. (26). Because of the material dependency, most commercial cleaning processes use several stages for higher efficiency.

One very interesting solution is membrane filters. They can be much cheaper, especially for smaller applications, much more cost and energy efficient, depending on what gases need to be separated. As in all gas separation techniques, the bigger the difference in molecule size, the easier it is to separate them out. Because of this reason, it’s very promising for H$_2$ separation, as it’s the smallest atom in the periodic table and all gases are bigger than H$_2$.

In principle, the gas flows past the membrane with a low pressure on the other side. Because the membrane let the smaller molecules through, like H$_2$, but not the bigger molecules, only the H$_2$ comes out the other side and can then be transported to storage. Similar materials as in the PSA are used, with a different purpose. Instead of having the bigger molecules adsorbed, the surface interaction causes an overall repelling effect on the bigger molecules, letting the smaller molecules go through. They have also looked more into ion exchange membranes, with metals like for example palladium, which will allow H$_2$ molecules break down into ions, diffuse through the metal and come out on the other side, see Figure 5. These could be extremely efficient, but of course at a higher price (27).

Figure 5. Seven-step diffusion mechanism in dense metal phases: (1) movement of the raw gas (mixture of H$_2$ and undesired) to the feed stream surface of the membrane; (2) dissociation of chemisorbed H$_2$ into hydrogen ions (H$^+$) and electrons (e$^-$); (3) adsorption of H$^+$ ions into the membrane bulk; (4) diffusion of the H$^+$ ions and electrons through the membrane; (5) desorption of H$^+$ ions from the membrane bulk to the product stream surface of the membrane; (6) reassociation of the H$^+$ ions and the electrons into discrete molecules of H$_2$; and, finally, (7) diffusion of the H$_2$ from the product surface of the membrane (27).

These more advanced methods should only be used if really necessary. If there are some impurities like H$_2$S or other molecules with a high dipole moment, a simple cleaning system as a scrubber could prove to be more than enough. In a scrubber, you spray the gas with water, which means that it will absorb acids and high dipole molecules. After that you dry it to get the water out.

In the case of bottom ash, ideally, the gas will be clean of almost all impurities, due to the alkaline nature of the ashes which neutralize anions like carbonates, sulphites, chlorides etc. The pressure build-up can instead aid in increasing the density of the H$_2$ in the storage tank. The most probable gas impurity would be N$_2$, which will in itself, in small amounts, cause no harm what so ever. In more than a few percentages N$_2$ would cause a decrease of combustion and thermal efficiency.
3. Experimental setup and method

The setup was done rather simply, partly due to shortage of time and partly purely for simplicity itself. By having an electrode resting on the bottom of an Erlenmeyer flask, with the ash on top of the anode current collector, Al should be aided in the oxidation and release a hydrogen ion, see equation [3]. The hydrogen ions will form H₂ gas at the cathode, where it will exit the Erlenmeyer flask through a tube, into a measuring cylinder. Picture example is with a test tube instead of an Erlenmeyer flask (see Figure 6). The setup is generally called a Eudiometer.

![Figure 6. Basis of the measurement setup, called a Eudiometer. Picture from Wikipedia.](image)

3.1. Samples

The ash was taken from Umeå Energi’s MSWI, Dåva 1. The collection was done one day over several hours, to get a bigger variety in the mix of ashes. It was then brought to Umeå University, where it setup was located. The experiments were done over several weeks, so one assumption was that, over time, the production would decrease.

When it comes to the concentration, a higher amount of moisture content has shown to produce more H₂ from bottom ashes, up to 80% gravimetric content of water. (11) Though the H₂ production was also checked with an over saturated sample, at above 100%. This also means that, since the only pH-additive comes from the ashes themselves, a higher concentration of water might lower the pH of the solution. Therefore the H₂ production was compared as a function of water content as well as its pH as a function of water content.

Since the size of the particles matters for its recyclability, it was interesting to see how much the smaller particles produced in comparison to the bigger particles. Bigger particles can be recycled; meanwhile the smaller particles can, in most cases, only be energetically recovered. Also, previous studies have shown that particles smaller than 5 mm produce a big part of the total H₂ production (See Particle size of MSWI bottom ash and fly ash).

3.2. Electrolysis

To be able to stir the ash and water mix, so that the Al pieces would touch the anode current collector, magnetic stirring could disturb the electrolysis process and possibly also the metallic pieces. Therefore a shaking table was used instead of magnetic stirrers, which would be the simpler choice.

Instead of using distilled water, as most experimental research would, regular tap water was used. The reason for this is to make the experiments as similar to realistic conditions as possible, since it’s what would be used in a larger scale.

Since the Al pieces are small and mixed into the ashes, an anode current collector is needed, working the same principle as an anode current collector work in a flow battery, by delivering the current to the
small Al particles, while the anode is not consumed itself. Nickel and acid-proof stainless steel are cheap and easy-to-get current collectors that can resist corrosion and surface deposits from the ashes.

As a cathode, a material with a large surface area-to-volume ratio is ideal, to increase the connection to the solution. Graphite, a thoroughly tested, cheap and easy-to-get material was chosen for this. Since it has a relatively large porosity, its surface area-to-volume ratio is also rather large. Though, it could also cause problems by reacting with the H₂ and form CH₄.

The voltage matters as well, the higher voltage the reaction is given, the faster the process should become. Therefore the experiment tried with voltages ranging from 0,1 to 1,5 volt, since above this it’s likely that water splitting occur by itself, without the metallic oxidization.

3.3. Thermal treatment
Since a lot of issues appeared with the electrolysis of the ashes, it was interesting to see how much was actually possible to produce. So the next experiments were to see how much could be produced by heating it up, keeping it at different temperatures and different concentrations. In this setup, the electrodes were removed and a hot plate was used instead, keeping the rest of the previous setup.

Unfortunately, it was only possible to keep the plate’s temperature constant, not the actual solution. It was kept at 80 degrees through most of the experiments, to get as much data as possible, to reduce deviations as much as possible.

To see the cheapest and possible way of producing H₂, the focus changed to adding mixing together with the heating, so therefore magnetic stirring was added. Due to the changes in approach, the amount of data is a bit low, but enough to see a plausible potential.

4. Results

The result is varied due to the heterogeneity and setup-problems faced. The data lacks in confidence, partly due to a lack of time and keeping it simple. It can be seen as good guidelines for where and how to continue looking for information regarding energetic recovery of bottom ashes.

4.1. Electrolysis
The result of the electrolysis was, unfortunately but not surprisingly, non-existent. It was not possible to have a noticeable production of H₂ with the electrolysis method. Not even by pressing the ashes on top of the anode current collector, changing from a small nickel anode to a big acid-proof stainless steel anode, intense and no mixing, there was no noticeable production. Variations to the voltage had no effect, until at around 2 V, where the water was split at the anode current collector instead of by the oxidation of Al particles. After trying with the most probable methods to make it produce something, and it didn’t work, it was decided to continue with other methods.

4.2. Thermal treatment
Once thermal treatment was started, some H₂ production finally started (see Figure 7). The plate was kept at 80 degrees throughout these experiments. No significant difference could be noticed on the effect of concentration, except maybe that a lower water concentration gives a lower production, but it’s hard to say for sure from just the single data series acquired, specially taking in the inhomogeneity and aging factors of the ashes.
Figure 7. Production of hydrogen when only using heating, plate kept at 80°C. ◆ and ▲ are two different tests as much water as ash, by weight, meanwhile ▼ has 33% and ● 150% water of the ash by weight. The lines -- is a trendline with its confidence band of all the values. See Appendix.

Considering that all the ashes just lay down in the bottom of the flask and separating from the water, and also the low rate of reaction, it was obvious that the concentration level was not of high importance, at least without mixing. It could make a difference, but with only a few experiments like this, it’s not significant enough to be noticeable.

4.3. Mixing
When using mixing as well as heating, the production really started off, as seen in Figure 8, starting with serie ▲. Unfortunately, the magnetic stirrer that was used caused some problems, jumping out of place and kept wiggling in one position, stopping to mix properly, especially if using more than 100g of ash in the 500 ml Erlenmeyer flask. This can also be seen in the data, where several series have a lower production in the middle, due to no mixing. Since it was in the night and no data was collected, the mixing could only be started in the morning after and the rate of reaction was once again increased after the first data point in the morning.

Figure 8. Production of hydrogen when using heating and mixing, plate kept at 80°C. ▲, with 400%, and ●, with 450% water as ash by weight, are two different tests with a mix of size. The series ◆ with 200%, ▲ with 300% and ■ with 400% water of the ash by weight and only with particles smaller than 5 mm. The lines is a trendline with its confidence band. See Appendix.
Even though some problems were encountered, the potential is still promising. The last series ■ had a serious problem, the system had leaked during the night. Though, it’s unknown from when and how much it leaked and it seemed like it didn’t affect the result much more than having no mixing, as happened for series ◆ and ◆.

Also an unfortunate accident happened in series ●, sometime between 24 and 48 hours, the sample had produced 4 l H₂/kg as, but some foam had built up on top of the ash-water mix, blocking the gas evacuation tube, making the pressure build up and the lid popped off, throwing foam all over. Most likely these results are from a solid piece of metal, suddenly producing a lot of H₂ at once.

Our data gives clear trends on how to pursue a project for producing H₂ from bottom ash, but it is also clear that more measurements at different conditions and at larger scale is important in order to improve the confidence. The statistical variance is noteworthy in some cases, by for example considering that for some measurements at temperatures as low as 50°C and mixing, the production was as high as 4.2 l H₂/kg ash over 20 hours. See Figure 9.

![Figure 9. Production of hydrogen when using heating and mixing, plate kept at 50°C. ▲ and ■, with 400%, and ●, with 450% water as ash by weight. See Appendix.](image)

It’s very hard to see a pattern, at least it’s not similar as how it’s thought to, logarithmic or a negative-powered exponential, nor is it close to how the other experiments looked. Most likely there were some small metal pieces in the samples that, during mixing, broke down and started producing a significant amount of H₂. The foam productions in these cases are also relatively high, plugging the pipe. Because of this, the experiment had to be stopped straight away when noticed. Luckily, the lid didn’t pop off, throwing foam everywhere, as the first time.

4.4. Ageing

To properly see the effect of aging, the first thermal treatment experiments were tried again after a few weeks, just to see the difference of H₂ production over time. The result was, surprisingly, no difference in production from the first week and the fifth week. Though, once again it’s using only one sample, so the statistical accuracy relatively low. See Figure 10.
4.5. pH measurements
One of the more interesting results that were obtained came from the pH measurements. The pH level doesn’t change with 50-1000% distilled water and ash mixes; it was constant at 12.6-12.7. This buffer effect probably comes from having a lot of alkaline salts in the ashes, which is dissolved only as the mix is diluted with more water. Interestingly, using tap water gave similar results. According to the local water treatment plant, the water has a pH of around 8, a dGH (10 mg/l) of 2.8 and an alkalinity of 45 mg/l.

Instead, after the experiments, the pH had lowered slightly. From a pH starting with around 12.6, to around 12.0-12.3 after the experiments. This could be a limiting factor as well as an indicator that the ashes have some organic material, changing NaOH to NaHCO₃, or that the of reaction is severely limited by equation [1], leaving the Al as NaAl(OH)₄ lowering the pH and by extension lowering the reaction rate.

One problem with this is that the pH meter used was a regular glass electrode, which possibly does not measure correct at a pH over 10.5, since some of the assumptions made do not always apply. Therefore a litmus test was also used, to make sure the range was around the correct value, which it was, showing something around 12-13 in pH. Because of this, these pH results should be taken with a pinch of salt.

4.6. Particle size dependency
In Figure 8 compared with Figure 9 one can also see the difference in particles smaller than 5 mm and the homogenous mix. It might not always seem like it’s a big difference, but maybe sometimes there were bigger metal particles in the homogenous mix, producing a lot more. One thing to keep in mind here is also that the ashes are a few weeks, meaning the smaller particles should have a smaller production due to air-oxidization.

4.7. Maximum production
Maximum production of H₂ is most likely dependent on the size as well as reaction time, age, content, etc., even though no significant result has been seen in this report. As said before, there were three cases with a high production, one with over 3 l H₂/kg ash over 20 hours and two cases with over 4 l H₂/kg ash, once over 96 hours and once over 20 hours. A realistic estimation is still around 3 l H₂/kg ash, partly due to the highest production still isn’t the maximum of that sample and most of the samples are made with ashes that are a few weeks old, among other factors.
5. Conclusions

The result obtained shows very positive tendencies and potential, but more data is needed. In despite, the result should be a very good guideline for future research and pilots.

5.1. Electrolysis

After a few tries with the electrolysis, it was understood that it was a dead end. Probably this is due to several effects, contributed by for example, the ashes insulating the anode and causing a high resistance and a double layer effect over the anode and over the cathode. It might be an interesting method for pure Al, but probably not the most efficient way.

5.2. Thermal treatment

When starting the thermal treatments, the production was a bit slower than expected. Possibly, when still, bubbles of H₂ and a layer of Al(OH)₄ are forming and getting stuck on top of the metallic particles. This insulates the particles from water and NaOH, disabling them from producing any more H₂ until the layers are removed.

When using mixing, the difference between the temperatures 80 and 50°C was looked into. No significant difference could be found, only a very small difference, probably because of the increased production by mixing and that the variations from mixing are bigger than what the difference in temperatures give.

Already when starting with these experiments, the ashes were starting to age a bit, between 1-2 weeks old. For this reason, considering the knowledge from previous work, these results could be considered a low estimation; maybe in comparison to not even letting the ashes come in contact with the air.

5.3. Mixing

By this point, the ashes were over 3 weeks old, except for the first series ▲, which was only 2 weeks old at the time of testing. This might be one of the reasons why it’s standing out above the rest. Another reason why it’s standing out could also be because no problems were encountered during that specific run, meanwhile for the other runs it was usually something causing a problem.

This seems to be the best method to increase the rate of reaction. Which is not surprising, when you stop to think about it, if the ashes and particles are constantly hitting each other, they will be exposed to more NaOH, since the layer of Al(OH)₄ and gas will be removed as it forms on the particles.

Though, as seen in the results, it’s hard to say what the maximum production is. Since there were so few data points, it’s unclear how the production looks over time, but the factors probably include speed of mixing, temperature, particle size, amount of air is in the system, as well as previously mentioned factors. An experiment with many samples and automatic feed and measurement would give a better idea of the rate of reaction and how it changes over time as well as the maximum potential.

5.4. Aging

The ashes were also aging during the experiments. They were in a closed bucket, allowed to leak out if pressure would increase and still in room temperature, opened mostly every day. The first experiments took 1-2 weeks to do, but since there weren’t any production from those, it’s impossible to make a comparison. Figure 7 and Figure 8, where the first experiment, ♦ respectively ▲, was done over a week earlier than the others and have slightly higher production. Of course, they could also be random coincidence, considering that some of the last experiments on lower temperatures with mixing had a production of 3 and 4 l of H₂/kg ash over 20 hours, a lot higher than any other sample over the same time.
Surprisingly there was no significant difference in the samples after they had been standing for several weeks. This might just be a sample with a higher metallic content. Other factors might also be in effect, like low oxygen availability during storage and low initial moisture.

5.5. Concentration
The difference between concentrations cannot be said to be significant. It seems to be most important to cover all the ashes with water and to fully saturate them. If it’s over saturated, it will be easier to mix and it will have a higher production because of that. Maybe lower water concentrations also matter in the sense that the water does not interact enough with the ashes.

Concentration could also change the buffer ability of the ashes, even though no difference in production could be found by different concentration. There might be come factors that take each other out, like increased water concentration means higher mobility, but smaller buffer, among other things.

5.6. pH measurement
The pH measurements were rather interesting, giving a few hints. First of all, considering the constant pH level over such high dilutions, up to 10 times more water than ash, the ash is most likely full of NaOH salts and other alkaline salts.

Secondly, the pH was reduced after the experiments. In the thermal treatment experiments, the pH dropped from around 12.6-12.7 to around 12.0-12.3. The question is if the change is truly this big, or if it’s bigger, considering that it was out of range of the measurement equipment used. Even though the litmus paper test confirms that the range is correct. This problem also applies to the first conclusion.

5.7. Particle size dependency
There was not a noticeable difference between the production of H$_2$ from the smaller ashes compared to the production from mixed ashes. Admittedly, the spoon used to measure the amount of ash in each test was fairly small, meaning that the bigger particles fell off. The mix might not have been as homogenous as it was supposed to be in any of the sample, due to a lack of bigger particles, which anyway could be recycled.

Using the data from other authors (see Introduction), about 50% of the mass from the bottom ashes are particles smaller than 5 mm and cannot be recycled. About 10% of the total metallic Al is in this part, about 5-10 g/kg ash, which would be giving about 3-6 l H$_2$/kg fine bottom ash. Considering that they also found that a lot of the Al in the bigger particles is not recycled, up to 50% of those might not be recycled either, there is a possibility to use that ash for an even higher production, after taking out as much metallic Al as possible.

5.8. Parasitic effect in the system
Since a new experiment was started mostly every day and since there was no lock for removing old and feeding new samples in the setup, there was new air in the system every time an experiment restarted.

If one assumes that all of the O$_2$ in the air reacted with as much H$_2$ as it could, this could prove a huge parasitic effect. Most of the volume left in the flask is determined by the amount of water used, since the ash has a density at around 2.5 times more than the water.

To take an example, when using around 300 ml water and 100g ash, it would be around 350 ml substance, the rest would be air. The flask, with its lid on, has space for around 600 ml. This means that there is 250 ml air in the system. It might look harmless for the experiments, but it’s 50 ml of O$_2$ which is being able to form water with 100 ml of H$_2$. This only means that the potential might even be higher than the result show, especially for the samples where less water was used and more air was introduced in the system. Probably not 100% of the O$_2$ will form water with the H$_2$, but a lot of it possibly could.
During the experiments, some H₂ might form with other particles in the ashes as well as being suspended in the water. All of these effects could change or disappear in a more closed system, like using a water lock when feeding the system with more ash.

5.9. Theoretical calculations and maximum production

Assuming that the bottom ash from Umeå Energi’s Däva power plant has a potential of producing around 6 l of H₂/kg ash, and they have around 3 ton/hour of bottom ash, that means that they produce around 1.5 ton of small particles, which gives 3000 l H₂/hour and 26280000 l H₂/year. Of course, 6 l of H₂/kg ash might be a high or a low estimation, but that is not certain until a bigger study has been done. Also, 50% of the ashes being smaller than 5 mm might be an underestimation. Either way, a production of 6 l of H₂/kg ash would give around 72 MWh/year for Umeå Energi AB. This is enough fuel for driving people 144 000 km, as the Swedish average fuel consumption with an ICE car is 0.5 kWh/person-km (28). The average fuel consumption of a H₂ fuel cell car is around 30-50% of a ICE car per km, meaning between 0.15-0.25 kWh/person-km and would take one person between 288 000-480 000 km per year. (29)

On top of this, there is a potential for the rest of the ash after it has gone through metal separation and also there is a potential for using the fly ash to produce H₂. Adding these all together might add up close to the 1 GWh of gas that the landfill, especially since it’s given more time to oxidize there (30).

Using the 18 l H₂/kg ash which was found by Alm et al., using the same assumptions as above with usage of smaller particles, the potential is around 220 MWh/year instead (4). Considering the 1 GWh that is produced in the landfill, it doesn’t seem unlikely.

Probably the difference in H₂ production will vary a lot, depending on several different factors that might not even have been considered here. To find the true potential of the ashes, a long term study, with proper setup and consistency is needed. The most important result obtained here is that mixing could be the most important method to use to recover energy from ashes and that the potential could be everything from 1-20 l H₂/kg ash, depending on the reaction time, particle size, among other things.

Another thing that should be remembered is that these results and assumptions are only considering the bottom ash. Considering that bottom ash is usually somewhere between 25-40% of the total input of trash and the fly ash around 10-30%, and fly ash might have a higher potential per kg ash, there are huge, unexploited potentials which isn’t even looked into very deeply in these assumptions above.

This means it’s very likely that for every ton of trash burnt in Sweden, there is a possible potential of around 40-50 kWh/ton of trash. Ignoring the imported trash we also burn today, the national potential of Sweden’s 4.3 million tonnes of trash might be close to 170-220 GWh/year.

5.10. Suggestion and guidelines to a practical application or further research

If one would want to take up all the non-recyclable aluminium, there should be a separation mechanism of the smallest particles, very early after the ashes come out of the incinerator. This could, for Umeå Energi, either be by separating them in or right after the quencher. With a 5 mm particle filter, one could easily separate the smallest particles and send the rest for metallic and magnetic separation. This would also mean that there is a smaller explosion risk in the facility, possibly reducing the H₂ produced by half, probably more since it’s the smaller particles that have the highest rate of reaction and produce a high amount of H₂ in the beginning.

This solution would require some serious modification of current equipment; with for example a new outlet for the smaller particles. Another solution would be to filter it out in or after the shaker table or transportation belt. On the other hand, this would not reduce the explosion risk much. A faster transition from the incinerator to the metal separation system would also reduce the oxidization of bigger particles, which would also increase the amount of metals being recycled.
If the ashes would be crushed before left in the reaction chamber, it would release some metallic ash which could be trapped inside other melted material, as glass or uncombusted plastics, thereby increasing the rate of reaction. Also, if the ash is then left in water for a longer time then, there will be a significant increase of total H₂ production. For example, by using the return-heat from the district heating system at ~50°C instead of keeping it at ~80°C, there will be a slower reaction, which could be compensated for by increasing the size of the chamber, thereby increasing the time.

If there is a problem with trace gases, like N₂, H₂S, there is a possibility to use different separation techniques, where some examples include swing adsorption, and membrane filters, see Gas separation. Membrane filters are very interesting, mainly due to its low operating cost, efficiency when used for separating H₂ and its possibility to be used on smaller scales, but they’re not so commonly used yet.

Scrubbers also work to separate gases from acids and particles, if that would appear to be an issue. The study lacked a proper analyse of the gas, but even from a gas chromatography, the samples would probably prove to have an increased amount of nitrogen and maybe oxygen, since so much air was inside of the system at start. H₂S and other acids are most likely not so abundant, even if it would be scaled up, considering that the solution would keep alkaline in most cases.

To continue further research, it’s suggested to use several smaller samples or bigger, due to the heterogeneity of the samples. A bigger sample would most likely be easiest if mixing should be included. Out of 8 samples taken while mixing, there were 3 that had an extreme production of H₂, where one of them has no statistic value as of the rate of reaction due to a leakage. Also, an automatic measurement system would increase the data points and therefore a better understanding of the reaction is possible. A closed system with input and output of material through locks would also be highly recommended, to reduce the influence of air in the system.

No matter if further research would show a higher potential than we here, it will depend a lot on region and country as well as technical details. Therefore, if it would be commercialized, a proper study has to be done on the production of H₂ from the different ashes for the specific plant. Even in Sweden, we have a high variety of potential, as can be seen in research of Alm et al, which shows that it’s not only dependent on the input. (4).

6. Acknowledgements

I would like to thank Thomas Wågberg, for accepting to supervise this thesis after I came to him with my idea and helping me every step of the way. I would also like to thank Niklas Jakobsson and Umeå Energi AB for allowing me to come and take samples and for the help they have provided. Last but not least I have to thank my loved ones, family and friends, who have supported me throughout entire time, both by keeping me in balance and helping me to put pieces together when I’ve lacked ideas of how to proceed.
7. References


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8. Appendix

Raw data from the experiments.

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Heating and mixing 80°C (F means fine, smaller than 5 mm)

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Heating and mixing 50°C

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