Decarbonization of Aluminium Production Process Using Hydrogen Enhanced Natural Gas Fuel

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ABSTRACT

Aluminum is a significant industrial metal with numerous uses and is considered essential to the global economies. The primary raw material for producing aluminum is bauxite, which must be mined and refined into alumina using the Bayer Process. It is then transformed into aluminum ingots in a smelter plant before being semi-fabricated using rolling and extrusion. In 2021, about 3% of the world's 9.4 Gt of direct industrial CO_2 emissions was reported to have come from aluminum. To achieve the planned net zero emissions by 2050, the aluminum industry must create and implement innovative technologies to cut emissions. There are two main sources of CO2 emissions in aluminum production process the first one is the furnaces and the second one is the chemical reaction that's form in the carbon electrode (electrolysis). The use of hydrogen enhanced natural gas (HENG) as fuel for the industrial furnaces used in the aluminium industry is proposed. In this paper, the techno-economic analysis of this alternative fuel is investigated using Aspen process simulation software. A preliminary result obtained from the first set of simulation showed that HENG will be an excellent alternative as fuel for industrial furnace. One of the major advantages of using HENG is that it is easier and faster to implement because it will not require a major change or modification in the combustion system of the furnace currently used in the industry.

Introduction

Bauxite is the most often used raw material for making aluminum. The main component of the mineral is aluminum oxide, which is combined with a few other minerals. About 4-5 tons of bauxites are converted into 2 tons of alumina, from which about 1 tons of aluminum can be produced.

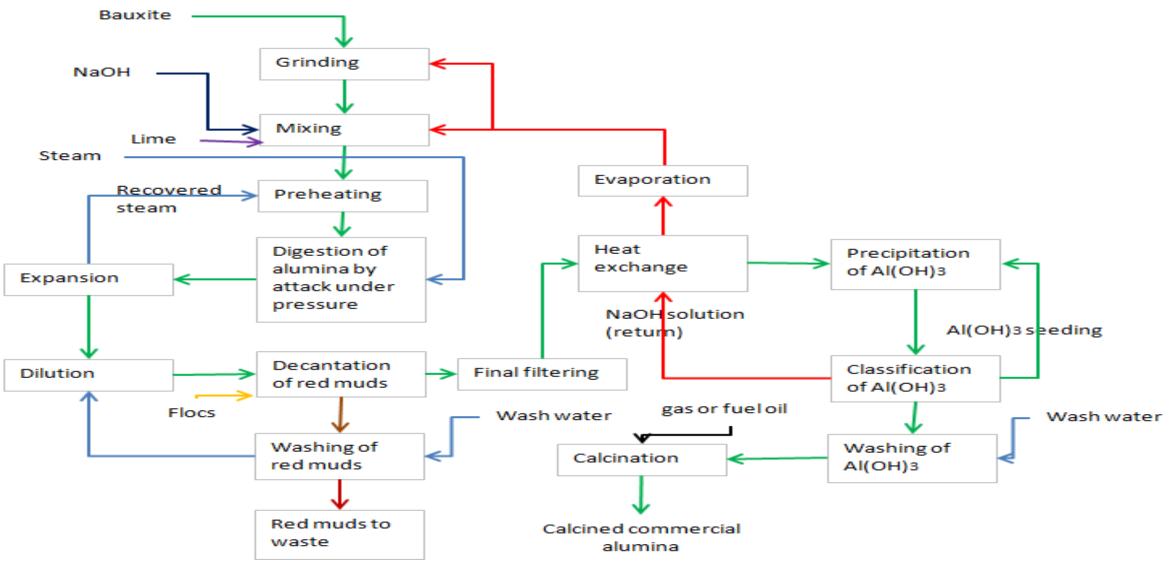


Figure 1. Block Diagram of Unit Operations (Wallis, 2016)

In the Hall-Héroult process, aluminum is typically extracted from its oxide, alumina, during the smelting process. An alumina refinery uses the Bayer process to separate alumina from the bauxite ore. An aluminum smelter takes a significant amount of electric power because this is an electrolytic process. Smelters are typically situated close to major power plants, frequently hydroelectric ones, to keep costs down and lower their overall carbon impact. Since many smelters use alumina that is imported, smelters are frequently situated close to ports. The main way that primary aluminum is produced is by the Hall-Héroult electrolysis method. A steel shell and a number of insulating refractory material linings make up an electrolytic cell. The top lining of the cell is in contact with the molten metal and the cathode blocks are secured within by ramming paste. Large sintered blocks of carbon are also used to make the prebaked anode, which is floating in the electrolyte. A huge number of cells (pots), where the electrolysis occurs, make up an aluminum smelter. A huge number of cells (pots), where the electrolysis occurs, make up an aluminum smelter. Aluminum makers are continually refining their creation cycles to expand quality while limiting expenses and the ecological impression. Decrease cells have previously been planned that work at 400 and 500 KA amperage, more established age decrease cells are being modernized. Perhaps of the most state of the art innovation aluminum makers is dealing with today is the idle anode process. A special progressive interaction can permit aluminum makers to quit utilizing carbon anodes through and through. The dormant anode might possibly be utilized endlessly, yet what the latent anode-based decrease process discharges into the environment isn't carbon dioxide, yet unadulterated oxygen. One dormant anode call can create as much oxygen as 70 hectares of timberland. As of now, the idle anode process is being created stealthily and going through modern preliminaries yet who knows, perhaps soon it will transform the aluminum business into the lungs of our planet. Methods for measuring greenhouse gas emissions from the aluminum industry can be loosely categorized into three groups based on several generic data sources. Although it is challenging to execute, the aggregation of plant-specific data yields extremely accurate information. When the plant-specific data is not available, the calculation is based on the energy consumption broken down by sector from national metric statistics (EPA, 2008; Pardo et al., 2012). Comparing estimation using sector statistics to the earlier method reveals how GHG emissions are influenced by the energy structure of the industry. Another common technique is decoupling the relationship between mass flows and emission intensities by using industry-level emission coefficients to estimate emissions based on each subprocess's outputs (Liu et al., 2011, Das and Kandpal, 1998).

Methodology

The main industrial procedure for smelting aluminum is called the Hall-Héroult process. It entails dissolving aluminum oxide (alumina), which is most frequently derived from bauxite, the primary ore of aluminum, using the Bayer process, in molten cryolite, and electrolyzing the molten salt bath, usually in a cell that has been specifically designed for the purpose. The 940–980 °C Hall–Héroult process, used on an industrial scale, yields 99.5–99.8% pure aluminum. Since recycled aluminum doesn't require electrolysis, it skips this step. By emitting carbon dioxide and fluorocarbons during the electrolytic reaction and utilizing a significant amount of electrical energy, this process contributes to climate change. Electrolysis of an aqueous aluminum salt cannot create elemental aluminum because elemental aluminum is easily oxidized by hydronium ions. Aluminum oxide cannot be electrolyzed because it has a melting point of 2072 °C, whereas a molten aluminum salt can. Alumina, Al2O3, is mixed in molten synthetic cryolite, Na3AlF6, in the Hall-Héroult process to lower its melting point and facilitate electrolysis. Typically, coke is used as the carbon source (fossil fuel).

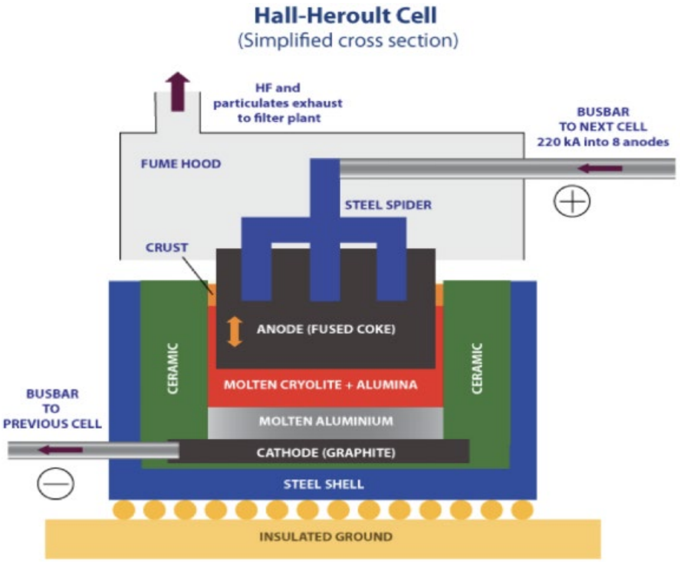


Figure 2. Hall-Heroult Cell (Wikipedia,2016)

In the Hall–Héroult process the following simplified reactions take place at the carbon electrodes:

Cathode	Anode	Overall
$Al^{3+} + 3\,\underline{e^-} \rightarrow Al$	$O^{2-} + C \rightarrow \underline{CO} + 2\,e^-$	$Al_2O_3 + 3\,C \rightarrow 2\,Al + 3\,CO$

In reality, much more $\underline{CO_2}$ is formed at the anode than CO:

$2\,O^{2-} + C \rightarrow \underline{CO_2} + 4\,e^-$

$2\,Al_2O_3 + 3\,C \rightarrow 4\,Al + 3\,CO_2$

Cryolite has a relatively low melting point, and is used as an electrolyte because it dissociates more easily than alumina and conducts electricity at higher voltages. Cryolite also has a lower density than aluminum at the temperatures required for the electrolysis of alumina to make it cryolite. The melting point of aluminum in an electrolysis cell is between 940 and 980 °C, and the density of the electrolyte should be less than 2.1 g/ml. Aluminum fluoride (AlF3) is added so that the cryolite ratio is 2–3 to further reduce the melting point. In addition to AlF3, other additives like lithium fluoride may be added to alter different properties (melting point, density, conductivity etc.) of the electrolyte. A low voltage (under 5 V) direct current that flows through the mixture at a rate of 100–300 kA electrolyzes it. This results in the deposition of liquid aluminum metal at the cathode, while the oxygen from the alumina reacts with the carbon at the anode to mostly form carbon dioxide. To prevent the molten material inside the cells from solidifying, companies run them 24 hours a day. Electrical resistance is used to maintain the cell's internal temperature. As the aluminum is taken out of the cells, alumina is added. Coke is added to the electrolytic mixture to stop the anode from being oxidized by the oxygen evolved. Most of the electrodes in cells are made of coke that has undergone high-temperature purification. Tar or pitch resin are employed as binders. Remains from the petroleum sector make up most of the materials utilized in anodes. The Söderberg and prebaked anode technologies are the two main anode technologies used in the Hall-Héroult process. Prebake anodes require less pitch than Söderberg anodes because they must be more stable. Prebake technology significantly reduces the anode impact risk (see below), but it is more expensive to produce and labor-intensive to utilize, making it less suitable for all cell types. Once utilized, each prebaked anode in a cell needs to be taken out and replaced. During electrolysis, cathodes also deteriorate, but much more gradually than anodes. Anode effect occurs when a layer of too many gas bubbles gathers at the bottom of the anode. The anode effect lowers the cell's energy efficiency and aluminum output. Additionally, it promotes the synthesis of the powerful greenhouse gases hexafluoroethane (C2F6).

Aluminum manufactured through the Hall-Héroult technique, along with magnesium accidentally, became a common commodity rather than a valuable metal because to cheaper electric power. The only way of smelting aluminum that is now employed in the industry is the Hall-Héroult process, which is used all over the world. As a result, inventors like Hugo Junkers and Howard Lund were able to produce aluminum fishing boats and other products using aluminum and aluminum-magnesium alloys, producing thousands of metal airplanes. According to estimates from 2012, each ton of aluminum produced results in 12.7 tons of CO2 emissions. There are two main sources of CO2 in aluminum production process: 1) The cell's bottom is where the molten aluminum sinks and is tapped off. The positive electrodes progressively disappear because the oxygen in the air combines with the carbon in those electrodes to produce carbon dioxide. The positive electrodes must therefore be changed regularly as a result. This raises the price of the procedure. When carbon (or consumable) anodes are employed, the reaction releases the oxygen that was previously trapped in the alumina, but it also immediately creates carbon dioxide (CO2). For every ton of aluminum used in the process, more than 400 kg of carbon anodes are consumed. Utilizing inert (or non-consumable) anodes prevents the production of CO2 such that the only byproduct is pure oxygen. Inert anode technology has the potential to significantly improve the energy, cost, productivity, and environmental aspects of the aluminum sector globally if it is effectively developed and implemented. The method should yield even higher advantages when paired with other improvements in electrolytic cell design, like wettable cathodes. Conventional carbon anodes are only good for a short time since they are "consumed" by the smelting process. Emissions of greenhouse gases (GHGs) result from the carbon anode's oxidation (or consumption). Inert anodes, also known as "non-consumable anodes," prevent oxidation and hence restrict the production of GHGs. However, a completely inert anode is unlikely to be found because the electroactive surface of an inert anode in the Hall-Herault smelting process must be an oxide with semiconducting properties, and all oxide materials have a finite solubility in the fluoride electrolyte (which is highly corrosive).

The Anode Gases CO_2 and CO

The general chemical equations state that when alumina reacts, molten aluminum and the gases CO2 and CO are produced:

$$\tfrac{1}{2}\,Al_2O_3\ (\text{dissolved}) + \tfrac{3}{4}\,C\ (s) = Al\ (l) + \tfrac{3}{4}\,CO_2\ (g) \qquad (1)$$

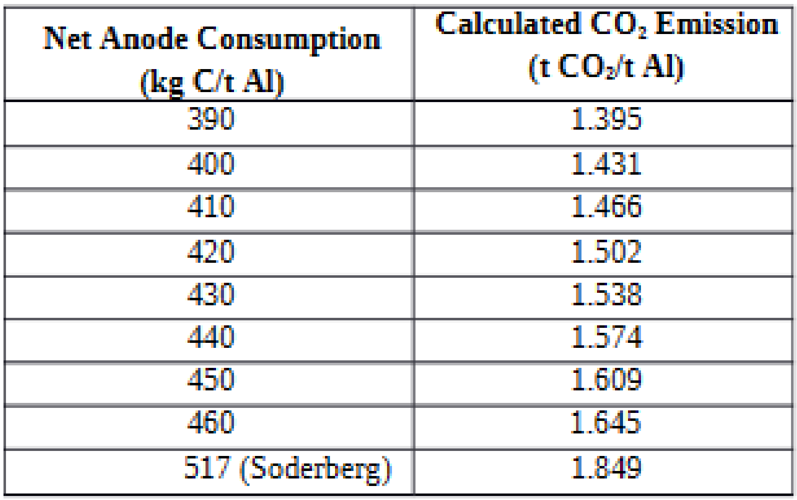
And:

$$\tfrac{1}{2}\,Al_2O_3\ (\text{dissolved}) + 3/2\ C\ (s) = Al\ (l) + 3/2\ CO\ (g) \qquad (2)$$

Due to co-evolution with carbon monoxide, aluminum cannot be produced using CO2 as the lone anode product. There is always some direct electrochemical creation as well as significant amounts of indirect reaction since we cannot begin producing carbon dioxide until the electrode is sufficiently polarized to raise the electrode potential above that of carbon monoxide formation. We receive a variety of products, with CO2 predominating. Unavoidable secondary reactions in the cell result in excess CO, but all processes must be evaluated as a whole and not just one of many that take place. In the flame of the cell gases, almost all the CO is oxidized in a nearly spontaneous reaction with air's oxygen mixture. At low temperatures, CO2 is preferred in the CO, O2, and CO2 thermodynamic equilibrium. The industry average for CO utilizing the highest-grade anodes is roughly 20%, and the lowest quantity of CO ever discovered in an anode gas sample in the cell is around 12%. All CO that is produced electrochemically and chemically within the cell eventually reports as CO2 in the environment. Carbon monoxide is known not to be a direct cause of global warming because of its short lifetime in the atmosphere, which is typically between one and two months. However, because it combines with CO2 and methane in the atmosphere, it has unintended consequences.

According to Eqn. (1), for every mole of aluminum produced, 34 moles of CO2 are created. The electrolytic process theoretically produces 1.22 tons of CO2 for every ton of aluminum if we convert the moles back into weights. The amount of CO2 is more closely correlated with the net anode consumption and is based on the anode's quality. This is expressed in kg C/t Al and represents the net mass of carbon anodes consumed in the electrolysis cell. For aluminum electrolysis cells, calculated CO2 emissions are shown in Table I as a function of net anode consumption.

Table 1. CO_2 EMISSIONS (Wikipedia,2016)



Net Anode Consumption (kg C/t Al)	Calculated CO_2 Emission (t CO_2/t Al)
390	1.395
400	1.431
410	1.466
420	1.502
430	1.538
440	1.574
450	1.609
460	1.645
517 (Soderberg)	1.849

Between 390 and 460 kg of anodes are typically utilized for prebaked anode cell technologies for every ton of aluminum produced via a combination of the reactions described by equations (1) and (2), as well as excesses through current efficiency losses and secondary reactions and processes. Due to this, the electrolysis process emits between 1.4 and 1.6 t CO2/tAl.

What Kind of Fuel Does a Furnace Use in Oman?

Nowadays, furnaces typically use one of three energy sources: propane, electricity, or natural gas. The optimal type for your property will depend on a variety of variables. In this piece, we'll compare the three main options to aid in your decision. To make a wise final decision, you will need the assistance of home heating professionals. For answers to all your inquiries about furnace installation in Boerne, Texas, contact Cowboys Air Conditioning & Heating.

In furnaces for melting, holding and processing of aluminum, the following types of fossil fuels are used:

- natural gas
- fuel oil
- diesel fuel.

Natural Gas

In American houses, this is the furnace type that is most prevalent. They use municipally supplied natural gas that is piped into them. This supplies the fuel for the burners, which produce a hot combustion gas that warms the air circulated by the ventilation system. Because gas is a less expensive fuel than other fuels, gas furnaces are the most efficient furnace models and have lower operating costs than other kinds. Additionally, they have a high temperature range. However, not every home can install one because they need an existing gas line.

Propane

Similar to natural gas heaters, propane furnaces run on a propane supply that is stored in a tank. Because propane does not burn as efficiently or cleanly as natural gas and is available in restricted quantities rather than flowing directly into a home, propane furnaces are less common nowadays. However, propane furnaces are much more effective as backup systems for hybrid heat pumps and have lower combustion risks.

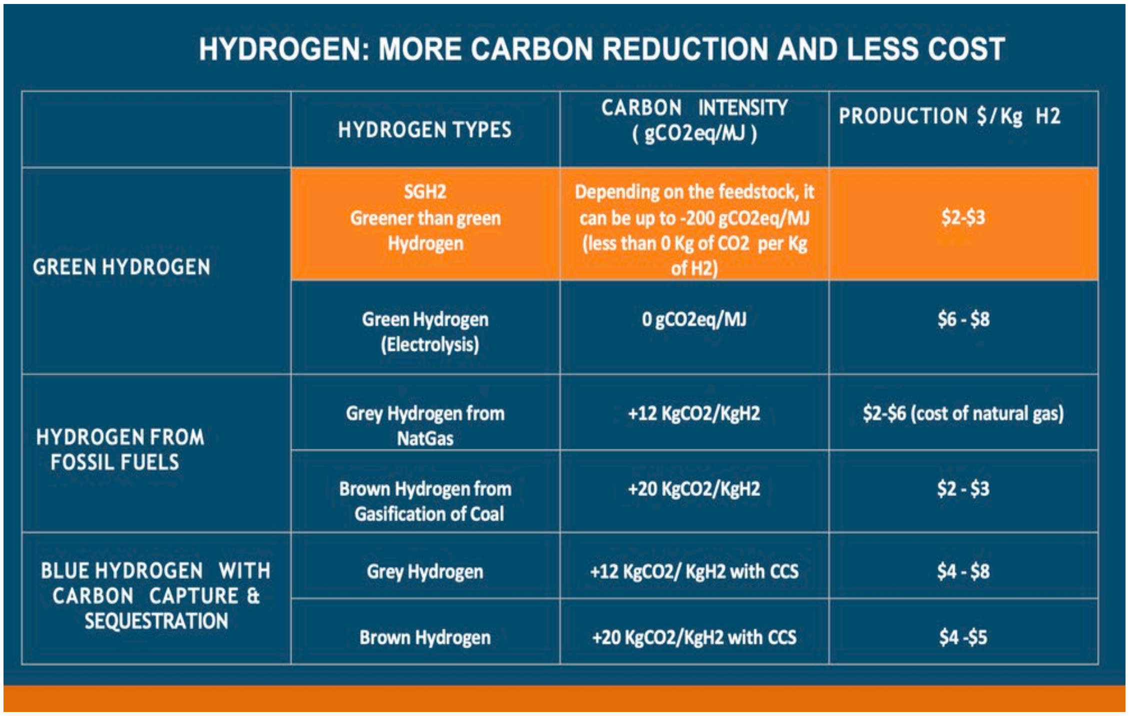
The ideal furnace for your house has not yet been chosen. Professional installers are needed to assess your home's heating requirements and discover the furnace that will keep you warm at the best price.

Natural Gas & Hydrogen Cost

The production costs are anticipated to be $2 per kilogram of green hydrogen (based on current US prices). In India, brown hydrogen costs $2 per kg and is created from cheap coal. Depending on supply, the cost of green hydrogen produced through electrolysis using renewable energy ranges from US$10 to US$15 per kg. Hydrogen may substitute for and decarbonize natural gas in all applications, beginning right away at up to a 20% blend and increasing that amount as pipes are updated. While one of California's top utilities plans to blend 20% of hydrogen into its natural gas power plants, other large industrial companies in Japan are already blending up to 90% hydrogen into their natural gas units that are currently in operation.

- Just 20% hydrogen added to natural gas pipelines in the UK would eliminate 2.5 million cars' worth of carbon dioxide yearly, or 6 million tons.
- A transition approach for decarbonizing natural gas grid assets that doesn't require significant infrastructure expenditures is hydrogen blending.

Table 2. (SG H2 ENERGY, 2023)

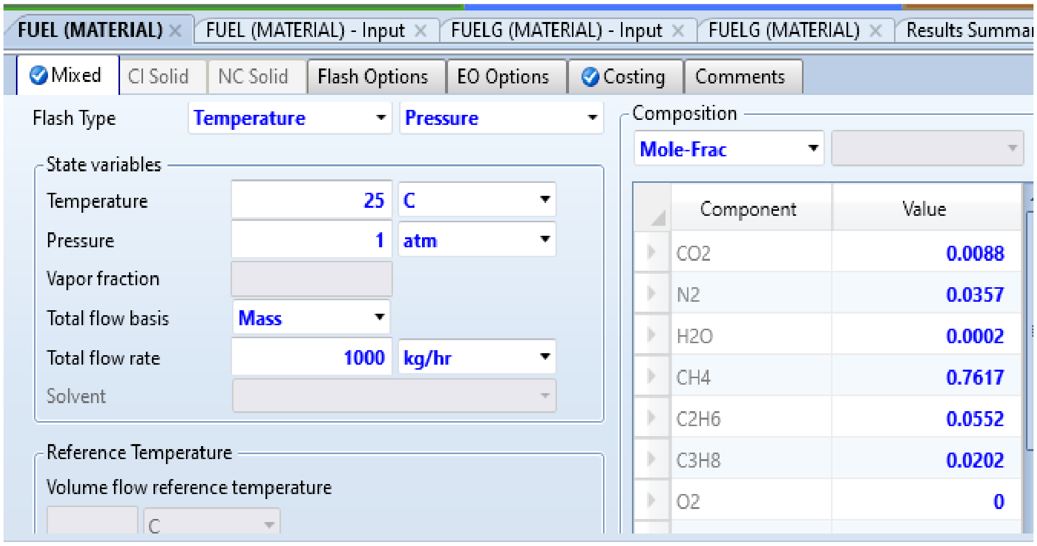


HYDROGEN: MORE CARBON REDUCTION AND LESS COST

	HYDROGEN TYPES	CARBON INTENSITY (gCO2eq/MJ)	PRODUCTION $/Kg H2
GREEN HYDROGEN	SGH2 Greener than green Hydrogen	Depending on the feedstock, it can be up to -200 gCO2eq/MJ (less than 0 Kg of CO2 per Kg of H2)	$2-$3
	Green Hydrogen (Electrolysis)	0 gCO2eq/MJ	$6 - $8
HYDROGEN FROM FOSSIL FUELS	Grey Hydrogen from NatGas	+12 KgCO2/KgH2	$2-$6 (cost of natural gas)
	Brown Hydrogen from Gasification of Coal	+20 KgCO2/KgH2	$2 - $3
BLUE HYDROGEN WITH CARBON CAPTURE & SEQUESTRATION	Grey Hydrogen	+12 KgCO2/ KgH2 with CCS	$4 - $8
	Brown Hydrogen	+20 KgCO2/KgH2 with CCS	$4 -$5

Process Description

Aluminum Smelting is a process to produce Aluminum and carbon dioxide. In this process, Aluminum is produced by electrolytic reduction of aluminum oxide that is dissolved in molten cryolite. Smelting process takes place at about 950◦C. The overall energy requirement for this process is met using natural gas as fuel. This modeling therefore a assumes that natural is combusted to cover the heat requirement of the process for both heating and smelting process (Energy Efficiency Best Practice and Division, 2000; Sadoway, 2001). The natural gas is feed into a conversion reactor which operate at 850 ◦C. It is assumed that the flue is vented to the atmosphere at 115 ◦C. Process Modeling and Simulation decarbonizing process model was developed for the flue gas from aluminum production process. There are different cases, which were considered for the simulation studies in Aspen Plus process simulation tool. The natural gas is the main feed for the first stage which is reactor. Component selection was done using the natural gas composition shown and air was used as a mixture of oxygen (21%) and nitrogen (79%). Aspen model of component selection is shown in figure 1.



Flash Type: Temperature, Pressure

State variables

Temperature	25	C
Pressure	1	atm
Vapor fraction		
Total flow basis	Mass	
Total flow rate	1000	kg/hr
Solvent		

Reference Temperature

Volume flow reference temperature: C

Composition: Mole-Frac

Component	Value
CO2	0.0088
N2	0.0357
H2O	0.0002
CH4	0.7617
C2H6	0.0552
C3H8	0.0202
O2	0

Figure 3. Component selection for natural gas

Table 3. Composition of Natural Gas

Constituent	Design Fuel Gas (mole%)
CO2	0.88
N2	3.57
H2O (Steam)	0.02
CH4	86.17
C2H6	5.52
C3H8	2.02
C4H10	1.20
C5H12	0.40
C6H14	0.19
C7H16	0.03
SUM:	100.00

The combustion reaction was modelled as reaction between the natural components and the oxygen. The modeling was done assuming a 100% conversion of the fuel (complete combustion). The Peng-Robinson was used as the fluid package (Method). After converging the natural gas feed, hydrogen enhanced natural (HENG) gas fuel was modelled by varying the % composition of the natural gas. The (HENG) fuel was modelled using a mixer block. The natural gas was modelled as an independent feed which is mixed with hydrogen mixer (Figure 2). The amount of hydrogen was varied from 0.01,0.02,0.03, to 0.1 mole fraction of hydrogen in the natural gas.

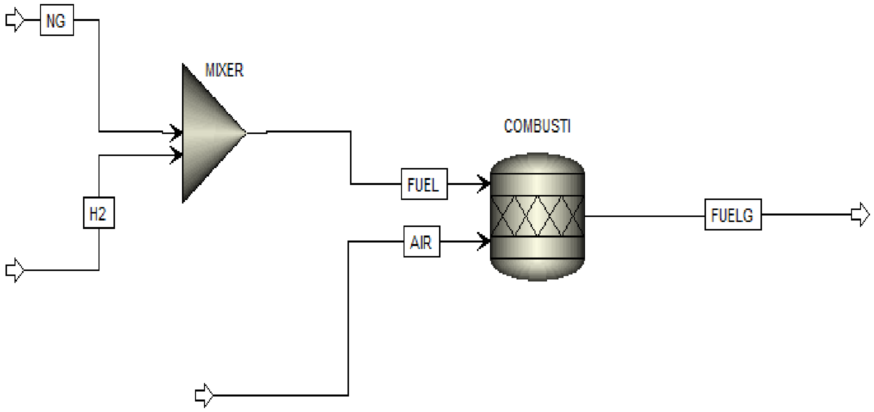


Figure 4. Flowsheet of the HENG combustion

The HENG from the mixer was fed to the reactor. The conversion type of reactor (RStoic) model was used. CO_2 generated and the amount of energy corresponding to each composition were recorded. The cost associated with the introduction of hydrogen was also simulated. The cost of hydrogen and natural gas were report from various literature. The average of those cost was used to carry out this work. A sensitivity analysis was performed by varying the mole fraction of hydrogen in natural gas while noting the corresponding change in the carbon dioxide, heat duty and operating cost.

Results and Discussion

As the mole fraction of the hydrogen was increasing, the CO_2 generated start to decrease. A plot of the relationship between hydrogen molar flow and the CO_2 is shown in Figure 3 From this figure, it can observe that the addition of hydrogen enhanced the performance of the natural gas in terms the reduction CO_2 emission. An increase in about 5% of hydrogen led to a decrease of 15% CO2 emission.

Table 4. Composition of Natural Gas after running simulation with zero molar flow of H_2.

H2= 0	SIU	AIR	FUEL	FUELG
Mass flow	kg/hr	30000	1000	31000
CO2	kg/hr	0	20.4421333	2608.69497
N2	kg/hr	23700	52.7872974	23752.7873
H2O	kg/hr	0	0.19018014	1968.07917
CH4	kg/hr	0	729.674767	0
C2H6	kg/hr	0	87.6115684	0
C3H8	kg/hr	0	47.0164501	0
O2	kg/hr	6300	0	2670.43857
C4H10	kg/hr	0	36.8151357	0
C5H12	kg/hr	0	15.2332357	0
C6H14	kg/hr	0	8.64251073	0
C7H16	kg/hr	0	1.58672124	0

AL2O3	kg/hr	0	0	0
CARBO-01	kg/hr	0	0	0
H2	kg/hr	0	0	0

Table 5. Composition of Natural Gas after running simulation with 0.1 molar flow of H_2

H2=0.1	SIU	AIR	FUEL	FUELG
Mass flow	kg/hr	30000	1000	31000
CO2	kg/hr	0	22.0766461	2566.410109
N2	kg/hr	23700	57.00806597	23757.00807
H2O	kg/hr	0	0.205386569	2022.749628
CH4	kg/hr	0	696.5688844	0
C2H6	kg/hr	0	94.61681725	0
C3H8	kg/hr	0	50.77579306	0
O2	kg/hr	6300	0	2653.832197
C4H10	kg/hr	0	39.75880161	0
C5H12	kg/hr	0	16.45125525	0
C6H14	kg/hr	0	9.333548902	0
C7H16	kg/hr	0	1.713592351	0
AL2O3	kg/hr	0	0	0
CARBO-01	kg/hr	0	0	0
H2	kg/hr	0	11.4912085	0

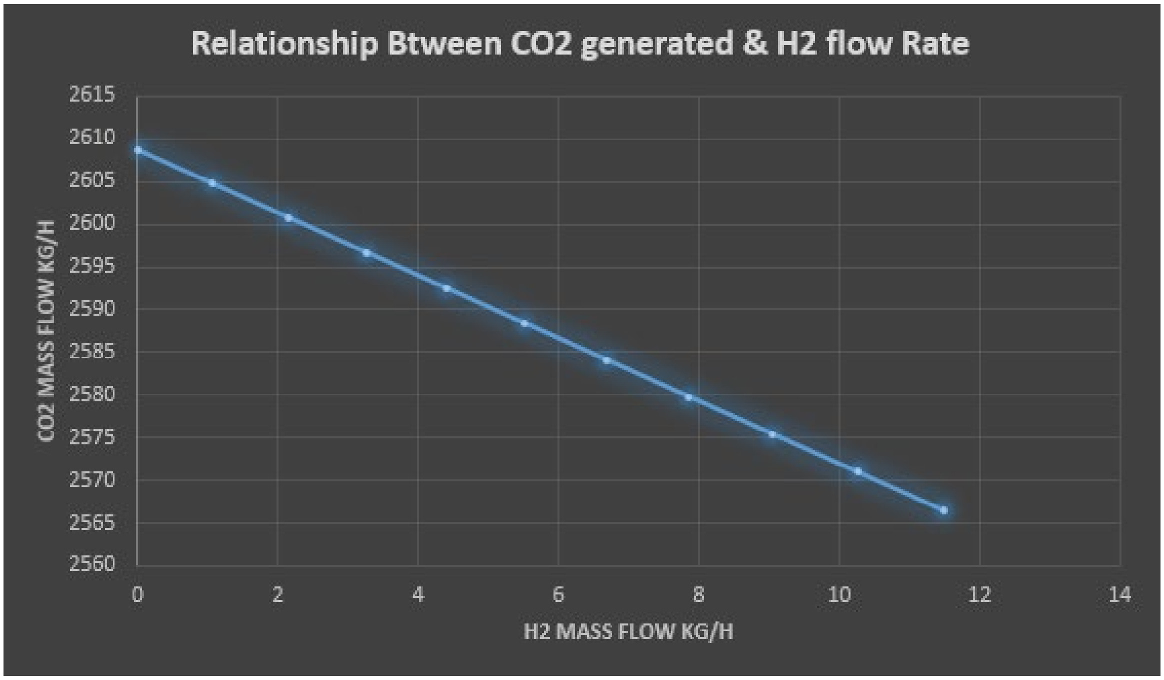


Figure 5. Change in CO2 emission with change in Molar flow of Hydrogen

The relation between the heat or the energy generated when we increase the molar flow rate of hydrogen:

Table 6. Relationship between heat duty and hydrogen molar flow

H2 (KG/H)	HEAT DUTY (KW)
0	7617.524001
1.07197886	7592.183394
2.160069755	7566.461872
3.264638686	7540.350768
4.386062823	7513.841164
5.524730937	7486.923934
6.681043847	7459.589531
7.855414891	7431.8282
9.048270418	7403.629851
10.26005031	7374.984142
11.4912085	7345.880272

Conclusion

Extraction of aluminum from its oxide, alumina, is known as aluminum smelting. Typically, the Hall-Héroult process is used. In a refinery for alumina, the Bayer process is used to extract alumina from the mineral bauxite. The results show a great change in the energy produced by the hydrogen when the molar flow increasing. The energy that hydrogen can supply or store is enormous, but it is not an energy source. Fuel cells may produce power, heat, and electricity from hydrogen. While transportation and utilities are emerging markets, the most common uses of hydrogen today are in fertilizer production and petroleum refining. The biggest obstacle to producing hydrogen, especially from renewable resources, is making it more affordable. Hydrogen must be cost-competitive with traditional fuels and technology for transportation fuel cells on a per-mile basis. Accordingly, the price of hydrogen must be less than $4 per gallon of gasoline equivalent, regardless of the production technology. Research is concentrated on increasing the lifetime and efficiency of hydrogen production technologies as well as lowering the cost of capital equipment, operations, and maintenance to lower the overall cost of hydrogen.

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