

How to make hydrogen for less than Rs. 100 per kg?

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We have been reading a lot about green hydrogen, clean fuels, fuel cells, conversion of solar electricity to hydrogen, automobiles operating on hydrogen, trains mounted with solar cells on the rooftop and running on hydrogen, and so forth. I do not want to sound negative but from a business perspective all these are distant possibilities. Most depend heavily on subsidies. Simple electrolysis of water requires 55 kWh of electricity with the latest zero gap membranes. Even if one generated solar electricity to produce hydrogen only 5-6 hours a day, the capital & depreciation costs, rent for the land, operation & maintenance of solar cells, cost of purified water, and the opportunity cost of selling electricity at about Rs. 10 per kWh do not bring down the cost of hydrogen below Rs. 100 per kg.

The question remains: "If electricity can be sold for Rs. 10 per kWh, why waste it in generating hydrogen and get only Rs. 1.81 per kWh if hydrogen is to be sold for Rs. 100 per kg?"

Hydrogen as a co product

One way to reduce the cost of hydrogen is make it as a coproduct. There are two industries that do so: caustic soda & chlorine and sodium perchlorate.

Caustic soda production

For each tonne of caustic soda produced, 880 kg chlorine and 50 kg hydrogen are co-produced. Caustic soda has good demand in India and fetches a reasonable price, though chlorine does not have adequate use and often is in surplus with a price, which, at times, may be even negative. [There have been instances when chlorine consumers

were even given up to Rs. 6,000 per tonne to cart it away]. For many years now the Indian caustic soda industry has been using most of the hydrogen to convert excess chlorine, a hazardous gas, to hydrochloric acid (HCl), which was, at times, disposed by neutralizing with limestone. Earlier, the hydrogen also contained mercury vapour and could not be used for hydrogenation of fats or for pharmaceutical applications. But with the use of membrane cells for caustic soda manufacture, the mercury contamination problem no longer exists, and the hydrogen produced now can be readily used for hydrogenation of fats, and for pharmaceutical and food applications.

The overall reaction in a caustic soda production unit is:



The electricity required to produce one tonne of NaOH used to be 2,700 kWh. Over time, with developments in membranes, this has come down to 2,400-2,500 kWh. With improvements in the demand for chlorine, such as for making secondary plasticizers for polyvinyl chloride (PVC) processing (chlorinated paraffins) and aluminium chloride (for water treatment), hydrogen can be spared the pain of conversion to HCl.

In the current market, about Rs. 20,000 is realised for the hydrogen (per tonne of caustic soda), benefitting the industry.

Sodium chlorate/perchlorate manufacture

Hydrogen is also produced as a co-product in the chlorate industry.



Chlorates are useful chemicals used in paper, effluent treatment, disinfection, fireworks, and matchstick industries, amongst others.

It is produced by electrolysis of salt solution as below:



There is a good demand for NaClO₃ in pulp & paper industry; for water treatment; as well as removal of iron, manganese and arsenic from water supplies. NaClO₄ is used by the matchstick industry.

Several small plants can be set up for manufacturing sodium chlorate and sodium perchlorate for local consumption. Associated hydrogen can be sold to industry or for automobile use or for enrichment of town gas. A 30,000-tpa sodium chlorate plant will have the capacity to produce 1,700-tpa of hydrogen. Power required per tonne of sodium chlorate and sodium perchlorate is about 4,600-6,000 kWh. Realization of commercial value for hydrogen can



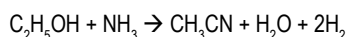
considerably increase the profitability of the unit.

Manufacture of acetaldehyde

Dehydrogenation of alcohol to manufacture acetaldehyde is another case in point. Here one has to account for the higher energy needed for the conversion of alcohol (350-kcal/kg alcohol), compared to oxidative dehydrogenation which is -900-kcal/kg alcohol. Thus, the net difference is about 1,250-kcal/kg alcohol. The hydrogen so generated would be 43 kg per tonne of alcohol. In the past, this process was used for the manufacture of n-butanol from alcohol, using the hydrogen so produced to hydrogenate crotonaldehyde to n-butanol. This was done by spending 30,000-kcal/kg of hydrogen, which is the calorific value of hydrogen.

Reforming with intermediates

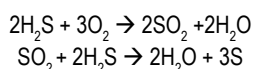
Acetonitrile is produced by dehydration of acetic acid and ammonia over a catalyst. Alternate possibility is dehydrogenation of ammonia and alcohol over a suitable catalyst. Every mole of acetonitrile generates two moles of hydrogen.



This amounts to about 9.5% of the weight of acetonitrile. It can change the economics of acetonitrile production. There is need to extend this reaction to other possible products, particularly, those produced by oxidation of hydrocarbons. Some ideas for catalytic research include conversions of propylene to acrylonitrile; vegetable turpentine to cymene + hydrogen; dehydrogenation of cyclohexane to adiponitrile – all in the presence of ammonia. Carboxylic acids can also be obtained by hydrolysis of the nitriles, with recovery of ammonia.

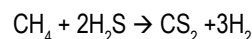
Replace oxygen with sulphur

The government implemented low sulphur fuel policy several years ago. Today, all hydrocarbon fuels are hydrodesulphurised to reduce its sulphur content. Diesel today has below 50 ppm of sulphur. The sulphur from the fuel emerges as hydrogen sulphide (H_2S), which is converted to elemental sulphur by the Claus Process. This process first converts a part of H_2S to sulphur dioxide (SO_2), which is then reacted with H_2S , as below:



Thus, all the hydrogen used for hydrodesulphurization is wasted as water.

All refineries have hydrocarbon waste that is finally flared, in addition to associated gas. All these hydrocarbons can be used for conversion of H_2S to carbon disulphide (CS_2) as per the following equation:



CS_2 is useful as a solvent, as an intermediate for fungicides, and for the manufacture of rayon (which use, however, is declining).

Sceptics might argue as to what the industry would do with so much CS_2 ? I have a suggestion. CS_2 is a liquid heavier than water. It can be safely transported in tankers and delivered to sulphuric acid plants. CS_2 also burns to CO_2 and SO_2 albeit with more energy generation (258 kcal/g mole or 3,400 kcal/kg, compared to 2,227-kcal/kg for sulphur). Sulphur being a low value material is transported in open trucks, which causes spillage, and gets contaminated by atmospheric dust. This dust cannot be removed from the SO_2 emitted from the furnaces and becomes a part of the gases emitted. In addition, burning sulphur involves melting it and feeding a molten liquid to the furnace. Against this, CS_2 is a liquid and can be fed to the furnace easily.

While working with a catalyst manufacturer I was exposed to sulphuric acid plants and have seen almost 1-m deep layer of catalyst being fouled by dust, requiring catalyst replacement every two years. If a clean liquid is used as a feed, both the catalyst life and activity will improve. At present a sulphuric acid plant generates about 140 kWh energy per tonne of sulphuric acid. This may go up due to higher exothermicity of CS_2 oxidation. I am no expert on sulphuric acid plants, so I leave it to young researchers to evaluate this idea.

Use oxygen for commercial purposes

Electrolysis of water produces 8 kg oxygen per kg of hydrogen. Value must

be realised from this oxygen. Besides conventional uses, there are several things that can be done with this oxygen. Here are some possibilities.

Use oxygen enriched air

Use oxygen enriched air in all power stations, refineries, and cement plants. When using normal air, these units lose a lot of energy in neutral off-gases, which are not cooled below the dew point to avoid problems of chimney corrosion. High sulphur coals have higher dew point of off-gases due to formation of sulphuric acid. Enriching the combustion air with oxygen would reduce the volume of nitrogen in off-gases and would save thermal energy. This saving can be attributed to the value of oxygen.

Use oxygen for effluent treatment

Currently, aeration is the process that transfers oxygen from air to effluents. BOC developed a process, known as *Vitox*, to accelerate biological oxidation by use of pure oxygen. Solubility of oxygen in water is about 35 ppm. Its concentration in air is 20%. Therefore, most effluent treatment plants do not reach a level of dissolved oxygen (DO) level beyond 7-8 ppm. This seriously increases the time for biodegradation. The *Vitox* process is capable of increasing DO levels to 30+ ppm. This increases the speed of biological oxidation. Even the Mithi river in Mumbai can be effectively cleaned up by use of gaseous oxygen. The typical energy requirement for transporting 1-kg oxygen to effluents by surface aerators is about 2-3 kWh, or about Rs. 22-30. This means, if one could get this price (Rs. 16-20) for the oxygen co-product, about Rs. 200 per kg hydrogen could be recovered by sale of oxygen. The target of Rs. 100 per kg hydrogen will very much be in sight.

Enrich all air used in industrial oxidation reactions

Examples are production of purified terephthalic acid (PTA), which

is produced in the scale of several million tonnes. Currently, air is used as an oxidizing agent. With it, four times nitrogen is also pumped into the reactor. The off-gases, primarily nitrogen, carbon dioxide and residual oxygen, exiting the reactor are saturated with acetic acid and represents a significant loss of energy and acetic acid, adversely affecting the economics. Use of pure oxygen to produce PTA can save huge energy in compressing all nitrogen and minimising the loss of acetic acid in the exhaust gas.

Ethylene oxidation to ethylene oxide

Ethylene oxidation to ethylene oxide already uses pure oxygen.

Vinyl chloride monomer (VCM) from acetylene and ethylene

There are two world-scale plants being set up in India to produce PVC. One is starting with ethylene and another with acetylene.

The first one is converting ethylene to ethylene dichloride (EDC) and then chlorine is regenerated by oxidation of HCl to chlorine. The hydrogen value is lost.

The other one is reducing chlorine by chlorination of methane and oxidizing the mixture to generate HCl. Again, hydrogen value is lost as HCl.

Instead, the two plants could collaborate and react acetylene with EDC on a catalyst to simultaneously dehydrochlorinate EDC and hydrochlorinate acetylene to generate two moles of VCM. This process is known as hybrid process.

Jointly, the two plants could save huge amount of hydrogen.

Alternately, all new PVC plants could be based on the hybrid technology to save hydrogen required for conversion of chlorine to HCl. Our country

needs close to 4-mt of PVC every year. Even with the two new plants coming up, the combined capacity would be about 1-mt short. Add further growth of about 10% per annum, and we would need almost 1-mt additional capacity every two years. So, there is a lot of scope to develop this hybrid technology.

PVC with 43.2% hydrocarbon and 56.8% chlorine (from sea water) is a real green plastic, especially if the ethylene is made from bioethanol. The electricity required to generate chlorine could be derived from solar power to make it totally derived from renewable resources. Every kg hydrogen saved is hydrogen earned.

Judicious subsidies

There are limited green sources of energy: solar, wind, hydel, geothermal and biomass. One could also add nuclear energy once all risks from its use are taken care of.

Subsidy is not the answer to cost reduction. A product development can be financially supported in the developmental phase provided there is a possibility of cost reduction with conventional commercial raw materials. It may be partially subsidised like through reduction of tax rates, low interest working capital, soft loans, etc. But paying outright 75% subsidy to make a product viable is not desirable.

It must be realized that the cost of money collected by the government as taxes is quite high. In the past when IT systems did not exist, it was as high as 85% of the collection. Now with GST, reduced rate of taxes, better compliance and automation, this cost must have come down. Still, it cannot be below 20% of the collected amount due to high labour costs. Subsidies, therefore, need to be paid out more judiciously.