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Article

Hydrogen enriched 'Maroon Gas' and 'Pink Hydrogen'

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Abstract: This paper describes a novel concept of producing energy efficient ”Maroon enriched natural gas “ and then Pink hydrogen” from any hydrocarbon base. The key idea is the extraction of hydrogen from water in addition to that from the hydrocarbon in an optimal fashion. This has the benefit of higher water vapor to CO2 exhaust ratio than conventional carbonaceous fuels when generating energy via combustion, a prudent step in achieving Netzero goals in a shorter time, and creating energy independence in most places.. The process of production makes concentrated CO_2 available for use and or sequestration. The process also maximizes use of renewable electricity in hydrogen generation, and maximizes use of existing infrastructure, with a minimum capital cost by energy recycle in the process. The process design applies sound thermodynamic principles which evolved during the nineteenth century, and mimics the geochemical processes going on in some of the natural 'colorless hydrogen'.

Keywords: Maroon gas; synthetic natural gas; Pink Hydrogen; hydrogen source-water, hydrogen source-hydrocarbon; energy efficient hydrogen; Thermodynamic simulations; FACTSAGE; DWSIM

Significance Statement:

A new process concept not needed for the liquid fuel industry is introduced. This will revise the liquid fuel industry to a gaseous fuel, by using water as well as hydrocarbon for extracting hydrogen, the proposed process is more energy efficient than steam reforming for hydrogen production. Maroon gas or natural gas enriched with hydrogen will provide a higher water vapor to CO2 ratio when combusted and also is a source for pink hydrogen. This scheme fits well into the existing infrastructure of the petroleum industry. The focus from producing more carbon based liquid fuel from hydrocarbon sources is now shifted to utilizing the hydrogen from water and is applicable to any hydrocarbon base including different biomass types, complementing the Netzero 2050 program of the G7 countries.

Introduction:

The authors recently published The Thermoeconomic Dynamics of Energy Efficient Orange Hydrogen Production - an energy matter.[1, 2] In this we noted that hydrocarbon pyrolysis leading to carbon and hydrogen along with intermediate useful petrochemicals is more energy efficient than water electrolysis. The Russian Ukrainian battle since Feb.24, 2022, brought forth a possible quick need of alternate source of natural gas for Europa [EU Countries]. Our group created Project Ayroppa in achieving this objective. We also noted that Europa countries have also committed to reducing CO_2 emissions for COP26 and projected Netzero. This resulted in our discovering the need to put water to maximum use as possible in existing infrastructure to produce hydrogen enriched gas and 'Pink' hydrogen. We developed this study using Factsage thermochemical software, and DWSIM chemical simulations using Gibbs free energy minimization, and applying nineteenth century Le Chatelier principles in arriving at variety of options.

The past 150 years of petroleum industry saw the growth of liquid fuels surpassing coal - the solid fuel which has over 300 years of history. The use of coal continued with different uses coming to the fore. The 21st century seems to give way to fuels which are normally under gaseous state by supplying it as compressed gas through pipelines or as liquefied natural gas and hydrogen gas.

Climate change induced by use of carbonaceous fuels and increasing human population have increased the need for non-combustion based renewable energy sources. It is to be noted that the atmospheric air mass is a constrained quantity, and its heat content can be changed from combustion based energy conversions, and other waste heat releases into it. Renewable based electricity conversions from solar and wind power in addition to hydropower conversions do not have exhaust vapor and gas, compared to fuel based energy conversions. Conventional carbonaceous fuel based energy conversions can be quantified in terms of exhaust water vapor to CO2 ratios when combusted. Water vapors released in atmosphere do not accumulate as have CO2 releases, since they can cool and condense as saturation allows, by giving its heat to outer space during condensation. The return of CO2 back to earth also happens to a considerable amount by endothermic chemical reactions such as photosynthesis which require membrane forming nitrogen compounds as reactants along with water vapor and CO2.

Bergius in the early 1910s updated chemistry by a method of production of liquid hydrocarbons for use as synthetic fuel by hydrogenation of high-volatile bituminous coal at high temperature and pressure. The Fischer-Tropsch process was the competing technology. This involved steam reforming of coal to produce Syn-gas (a mixture of hydrogen and carbon monoxide) that was subsequently converted to synthetic oil. Initial coal industry knew how to make gases containing 50 to 65% hydrogen along with Carbon Monoxide. The steam reforming technology, as well as hydrogenation of less saturated hydrocarbons into making saturated aliphatic liquid hydrocarbons were adapted by the petroleum industry. Natural gas coming from the ground has been known - and the recent four decades saw a tremendous growth in developing more gas fields by technologies such as fracking, and distributing across land by pipelines, and in the liquefied natural gas across continents. Steam reforming has been done using petroleum fraction as well as methane which were part of the crude oil distillation process in petroleum refineries.

In this communication we discuss a new process concept that has not been needed for the growth of the current liquid fuel industry. By using water as well as hydrocarbon for extracting hydrogen, the proposed process is an energy efficient method than current steam reforming methods of hydrogen production. Maroon gas or natural gas enriched with hydrogen will provide a higher water vapor to CO2 ratio when combusted and also is a source for pink hydrogen.

Present Processes:

Electrolysis of water by reaction [1] is a near zero CO2 emissions system.
H_2O + electricity[+membrane] = $H_2 + 0.5\ O_2$ - [1] $DH_1 = 285.8$ kJ/mol

Conventional Steam reforming [SR] was geared towards making liquid fuels - this has been the method of making grey hydrogen in a two-step process. First step is methane and steam reacting to make CO and H_2, the proportions in this step can be adjusted to making proper ratios of H_2 to CO -for a syngas step if the process requires it. This first step is usually performed using methane and steam around 1000 ^{o}C and 28 to 35 atm. pressure.[3] The second step is water gas shift [WGS or HTS] reactor where partly cooled SR gases, or reheated syngas is reacted with water around 350 to 400 ^{o}C making CO_2 and H_2. The overall reaction [3] consumes energy as shown by the heats of reactions
The equations for SR are:
$CH_4 + H_2O = CO + 3H_2$ -[2] 1000 ^{o}C 28 -35 atm DH_2=+206.1 kJ/mol
The shift reaction equation is
$CO + H_2O = CO_2 + H_2$ -[3] 350 ^{o}C 1-3 atm DH_3= - 41.0 kj/mol
combining reactions 1 and 2 gives
$CH_4 + 2H_2O = CO_2 + 4\ H_2$ -[4] DH_4= +165.1 kj/mol

This hydrogen is called 'grey hydrogen' consuming a lower energy than water electrolysis which produces 'green hydrogen' by reaction 1. DH_4 of 165.1 kj/mol converts to 20.47 kwh/kg H_2 in product. The process produces less than 4 moles of H_2, energy is correspondingly lower. The cost conscious petroleum industry reduces the net energy required for reaction 2 by utilizing heat content in the product CO and H_2 while cooling it down to lower temperatures needed for further use. This is called co-generation - which makes the overall DH_4-cogen much lower. IRENA, in Table ES1 on Key performance indicators for four electrolyser technologies today and in 2050.reports that water electrolysis consumes energy in the range 50 to 78 kwh/kg with an average of about 55 kwh/kg H_2, and is expected to come down to <45 kwh/kg by 2050 for the current commercial electrolysis. .[4]

On an average basis, SMR [steam methane reforming to grey hydrogen] with co-generation of using high temperature heat content has an energy consumption of about 17.8 kwh/kg H_2, per Oni, et al.[5] Reaction [4] shows that there are 5.5 kg of CO_2 per kg of H_2 product. Oni, et al.'s reports summarized table shows the energy required for the process as - natural gas as fuel in GJ/kg H_2 and electricity in kwh/kg H_2. The energy required as fuel can be converted to kwh/kg H_2 by multiplying by 277.78 conversion factor. The energy required for grey H_2 totals to 17.83 kwh/kg and for Blue H_2 it is 40.53 for 85% sequestration. The sequestration energy is based on carbon capture, compression, transportation to ground site where injected and for injection. This is the energy conversion required to carry out the process - as a sum of kwh in the natural gas used as a fuel for reformer and the electricity used for process equipment - pumps, and compressors. Compare this with 55 kwh/kg H_2 for green hydrogen. This shows that 3.1 kg hydrogen can be produced by 'grey' hydrogen - instead of just 1 kg 'green' H_2 for the same 55 kwh of the renewable electricity from solar-wind-hydro. Another report, prepared in 2017 for IEAGHG for merchant hydrogen production with feed preheating using the heat content in SMR reformer product, along with co-generation saleable electricity, indicates that the industrially practiced 17.8 kwh/kg for grey H2 can be further reduced. Most of this saleable electricity can be gainfully used for capturing 90% carbon dioxide generated in the process.

When the fuel hydrogen from reaction [1] or [4] is recombined with O_2 of air, during energy conversion, it can give a water vapor to CO_2 ratio of infinity. But when one looks at the life cycle emissions green hydrogen seems to have a theoretical edge over the grey hydrogen, only in terms of exhaust water vapor to CO2 ratio, but not in all other energy conversion basis, which is a considerable part of the cost of production. The water vapor to carbon dioxide exhaust ratios for conventional fuel burning are: 0.67 for coal, 1.13 for gasoline, and 2.0 for CH4 - based on following equations:
Bituminous coal $C_{10}H_{13.4}O_{3.2} + 11.73\ O_2 = 10\ CO_2 + 6.7\ H_2O$ - [5]
octane $C_8H_{18} + 17\ O_2 = 8\ CO_2 + 9\ H_2O$ - [6]
methane $CH_4 + 2\ O_2 = CO_2 + 2H_2O$ - [7]
If 85% CO_2 is sequestered from equation [7], the net water vapor to carbon dioxide exhaust ratio goes up from 2 to 13.33 [= 2/(1-0.85)].

Novel Maroon Gas and Pink Hydrogen Process:

As noted in the prior sections, essentially all of the reforming processes revolved around methane as the hydrocarbon, water as the most used reforming oxidant, with partial oxidation using oxygen, or dry reforming used as oxidant and the intended product being syngas CO and H2, and from that if necessary hydrogen gas can be separated and processed as merchant hydrogen. This evolved into 'Blue' hydrogen with carbon dioxide capture and sequestration. Large scale sequestrations have been considered. First being Enhanced Oil Recovery by using CO_2 injection into ground, while producing 'Blue Hydrogen' from methane sources from the well or in refineries. The second sequestration being injecting captured, compressed CO_2 into basalt underground soil and rocks with reduced iron oxide component, or ophiolites with wet calcium or magnesium silicates which can form carbonates.

We show that use of water as oxidant can be extended further by appreciating fundamentals of chemical reactions, and the hydrogen formed can also come from water by judicious application of equilibrium principles.
In any reaction, e.g. A + B = C + D the reaction has an equilibrium constant, K_e, defined by the ratio of $[\text{Product}]_{\text{activity}}$ / $[\text{Reactant}]_{\text{activity}}$, and that Le Chatelier principle notes that the reaction will go forward as products are continually removed.

The following reactions using hydrocarbon and water, each show an asymptotic formation of hydrogen production possibility including extracting hydrogen from water in addition to extracting hydrogen only from hydrocarbons. We define the maximum H2 mass per C atom in the hydrocarbon as one of the variables defining the asymptote. The asymptote is where the practical limiting value of the steam to Hydrocarbon ratio where the hydrogen concentration in the vapor levels off and the gas is mainly made up of CO2 and hydrogen with very little CO and methane

As known, SMR gives part of hydrogen occurring from water, but there is room to increasing the water vapor to CO_2 exhaust ratios beyond what methane combustion gives from hydrocarbon or the infinite ratio given by use of highly energy intensive hydrogen produced from water alone. We illustrate it with a few different hydrocarbons, that are known. We show water in the product in equilibrium reactions, which is usually the case in all steam reforming.

Hydrocarbon	reactants	products	reaction number	asymptote H2mass /C
carbon	$C + 2H_2O$	$= CO_2 + 2 H_2$	[8]	0.333
glycerol	$C_3H_8O_3 + 7H_2O$	$= 3CO_2 + 7 H_2 + 4H_2O$	[9]	0.392
methane	$CH_4 + 4 H_2O$	$= CO_2 + 4 H_2 + 2H_2O$	[10]	0.667
octane	$C_8H_{18} + 25 H_2O$	$= 8 CO_2 + 9 H_2O + 25 H_2$	[11]	0.525
eicosane [wax]	$C_{20}H_{42} + 61 H_2O$	$= 20 CO_2 + 21 H_2O + 61 H_2$	[12]	0.512
cyclohexane	$C_6H_{12} + 12 H_2O$	$= 6 CO_2 + 6 H_2O + 18 H_2$	[13]	0.504
butyl benzene	$C_{10}H_{14} + 27 H_2O$	$= 10 CO_2 + 7 H_2O + 27 H_2$	[14]	0.454
toluene	$C_7H_8 + 18 H_2O$	$= 7 CO_2 + 4 H_2O + 18 H_2$	[15]	0.436
chrysene	$C_{18}H_{12} + 42 H_2O$	$= 18 CO_2 + 6 H_2O + 42 H_2$	[16]	0.392
'b'-coal	$C_{10}H_{13.4}O_3 + 23.7H_2O$	$= 10 CO_2 + 6.7 H_2O + 23.7 H_2$	[17]	0.398
'a'-coal	$C_{239}H_{103}O_4 + 262.25H_2O$	$= 239CO_2 + 262.5H_2O + 525.5H_2$	[18]	0.369

Some of the known efficient SMR base cases give a 0.447 hydrogen mass per carbon mass in natural gas feed by the conventional 2 step reaction of high pressure, high temperature SMR followed by atmospheric pressure shift reaction with water, which is typically carried out using a steam to carbon mole ratio of 3.[4] Compare this with the possible asymptote of higher 0.667 ratio, which can be achieved by judicious application of chemical equilibria understanding. Water can act as both as a hydrogen provider and an oxidant in the reaction.

It is possible to achieve higher CO2 asymptote in the present SMR based grey hydrogen by introducing sorption based methods, as has been proposed in the recent years.[8,9] Sorption based methods are applicable to hydrogen enriched maroon gas processes as well. All naturally occurring oxygenated hydrocarbons, such as biomass, MSW, spent coffee grinds, etc., can also be processed to maroon gas and pink hydrogen, we have given only a few examples in the sample calculations with equations shown above. If char is required part of orange hydrogen will be followed if necessary, followed by maroon gas approach in optimizing final product heat and hydrogen values.

Above equations are simple stoichiometric equations which do not happen due to multiple intermediate formations major intermediates being CH_4, and CO and in some cases C_2H_6[ethane] may be formed but in much lower concentrations, due to chemical equilibria considerations.

The recent geopolitics had necessitated Europa [EU countries] to wean out of dependence of natural gas from Russia. Our studies show that it is possible to make hydrogen enriched methane - Maroon gas, by utilizing indigenous water along with higher hydrocarbons which have asymptote hydrogen to carbon mass ratios of 0.5 or above, as shown for eicosane, or butyl benzene which act as surrogates for cleaned crude oil.

Above set of equations also show - if the intent is to make hydrogen, the process should be geared to making little or no carbon monoxide, allowing a mixture of methane, carbon dioxide, hydrogen and water vapor in the product stream. From such a product stream , it is easy to separate water by condensation as a first step, and design a process to sequester portions of initial CO_2 formed, i.e. partial sequestration needed to market hydrogen enriched methane - Maroon gas. The need for condensation indicate that the process energy can be considerably reduced utilizing the heat of condensation for preheating the incoming hydrocarbon and or water to the reactor temperatures, in an 'energy recycle' mode and thus minimizing the process reaction need. Such practices are common in oil refineries and chemical industry. Similar 'energy recycle' mode is not feasible from most of the green hydrogen production using electrolysis of water at around 60^{o}C. Some of this is feasible in solid oxide membrane based steam electrolysis.

Now the maroon gas thus formed will give a higher water vapor to CO_2 exhaust ratio at the end use. The maroon gas is then amenable for transportation in regular gas pipelines. Several studies have been done in this field, including methods to separate pure hydrogen at the receiver end as needed. This can also be carried out at the processing end by PSA [Pressure swing adsorption] or membrane separation, this pure hydrogen is color coded as 'Pink' hydrogen following the earlier paper on making orange hydrogen or red hydrogen using pyrolysis of crude oils.

Thermodynamic Gibbs free energy of formation define the possibilities of equilibrium products which vary at different temperatures and pressures. Our team has computed them using Factsage software as well as DWSIM chemical engineering flowsheets. Besides the asymptotic max Hydrogen formation, we also have some minimum threshold steam to carbon [mole] ratios before hydrogen formation will occur from water - until them the hydrocarbon will be providing the free hydrogen molecules in the product. Under certain simulation conditions, In the case of methane water reaction, this threshold steam to carbon ratio, is about 6.5. Higher steam to carbon ratios are needed to give equal amounts of hydrogen from hydrocarbon and water, if methane is starting material which has the maximum hydrogen per carbon in the molecule. Higher steam to carbon molar ratios at a moderate water to hydrocarbon mass ratios are possible with crude oil whose molecular weight is very high.

Our process simulations are Gibbs free energy minimization equilibrium reactions, which demonstrate the flexibility of carrying out reactions at low temperatures and low pressures using flash reactors. The conventional SMR reactor requires higher pressures and temperatures in the current industrial practices. The simulations indicate that these low temperature process is amenable to converting liquid fuel producing refineries to partially or fully to gaseous fuels which give higher water to CO_2 exhaust ratios than current natural gas fuels. These processes can also be carried out at the well head if the producer choses, or make pink hydrogen at the user end.

One point to note that recent increase in studies in search of natural or native hydrogen, most of them have been found around gas and oil resources.[6, 7] Historically, wherever, there were visible flames near marsh or bog gases, one should note that these gases were enriched with hydrogen - as hydrogen in a gas can catch fire easily in ambient air unlike hydrocarbons which need to be ignited by a spark or other sources. Here we intend to mimic these low temperature processes.

Appendix 1:

Current Variations of SMR:There are variations of SMR discussed as options for producing syngas, and practiced on a small scale over the past 100 years . Autothermal reforming - which is a variation of steam methane reforming - instead of burning natural gas with air externally to bring the reactants to 1000 to 1200 ^{o} C reaction temperature, O_2 is added as a reactant along with methane and water - Autothermal reforming (ATR) is a combination of SR and Partial Oxidation Reaction (both reactions carried out in one compact reactor.

Autothermal reactor if it uses carbon dioxide as co-oxidant, the H_2:CO ratio produced is 1:1; if the autothermal reformer uses steam, the H_2:CO ratio produced is 2.5:1. The reactions are shown below. CO_2 and O2:

$2CH_4+O_2+CO_2 \rightarrow 3H_2+3CO+H_2O$+heat

steam and O_2: $4CH_4+O_2+2H_2O \rightarrow 10H_2+4CO$

Dry reforming of hydrogen production utilizes CO_2 as an oxidant - which is similar to pyrolysis of methane which also produces carbon and hydrogen as products

$CH_4 + CO_2 = 2H_2 + 2CO$	DHo 247 kJ/ mol
$2CO = C + CO_2$	DHo -173 kJ /mol
$CH_4 = C + 2H_2$	DHo 75 kJ/ mol

In the biofuel field 'hydrothermal' reforming is a term often used in producing synthetic liquid fuels.

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Competing interest:

On behalf of all authors, the corresponding author states that there is no competing interest in this self funded study of IND LLC and Sai Systems.

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