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THE HY-C PROCESS
(THERMAL DECOMPOSITION OF NATURAL GAS:) POTENTIALLY WITH THE LOWEST COST SOURCE OF HYDROGEN WITH THE LEAST CO_2 EMISSION

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Potentially the Lowest Cost Source of Hydrogen with the Least CO_2 Emission

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Abstract

The abundance of natural gas as a natural resource and its high hydrogen content make it a prime candidate for a low cost supply of hydrogen. The thermal decomposition of natural gas by methane pyrolysis produces carbon and hydrogen. The process energy required to produce one mol of hydrogen is only 5.3% of the higher heating value of methane. The thermal efficiency for hydrogen production as a fuel without the use of carbon as a fuel, can be as high as 60%. Conventional steam reforming of methane requires 8.9% process energy per mole of hydrogen even though 4 moles of hydrogen can be produced per mole of methane, compared to 2 moles by methane pyrolysis. When considering greenhouse global gas warming, methane pyrolysis produces the least amount of CO_2 emissions per unit of hydrogen and can be totally eliminated when the carbon produced is either sequestered or sold as a materials commodity, and hydrogen is used to fuel the process. Conventional steam reforming of natural gas and CO shifting produces large amounts of CO_2 emissions. The energy requirement for non-fossil, solar, nuclear, and hydropower production of hydrogen, mainly through electrolysis, is much greater than that from natural gas. From the resource availability, energy and environmental points of view, production of hydrogen by methane pyrolysis is most attractive. The by-product carbon black, when credited as a saleable material, makes hydrogen by thermal decomposition of natural gas (the Hy-C process) potentially the lowest cost source of large amounts of hydrogen.

Space

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INTRODUCTION

Hydrogen has been thought of as the fuel of the future, in terms of the most environmentally acceptable fuel. The problem has been that there is no natural resource of hydrogen and therefore it is not a primary fuel. Hydrogen must be generated from other abundant resources and water being the most abundant source. However, much energy is required to produce hydrogen from water. Conventionally, fossil fuel energy has been used for a long time to produce hydrogen by the well known water gas reactions.(1) The fossil fuels, coal, oil and natural gas are all carbonaceous and contain various other contaminants inluding sulfur, nitrogen and mineral matter and therefore large amounts of either oxidized or reduced compounds of carbon, sulfur, nitrogen and minerals are emitted to the environment. The two primary sources of energy that would be most acceptable for hydrogen production from an environmental point of view are nuclear and solar. Mainly from safety considerations, in addition to numerous other factors, nuclear energy has lost public acceptability. Much research effort is going into the use of solar energy to split water for hydrogen production. Indeed this method may turn out to be the major source of hydrogen in the very long term future.

Presently the most widely used and cleanest source of hydrogen is the reforming of natural gas with steam. This method is most widely used for supplying hydrogen for the production of such basic chemicals as methanol and ammonia. Natural gas reforming also provides hydrogen as a rocket fuel for the space program. The main problem is that natural gas reforming produces and emits relatively large quantities of CO_2 which is a greenhouse gas (GHG) that causes global warming leading to adverse global climate change effects. Another nearer term alternative that could eliminate this major concern for hydrogen production from natural gas appears possible. Natural gas can be thermally decomposed to carbon and hydrogen. The carbon can be sequestered or sold as a materials commodity. Thus hydrogen can be produced from natural gas cleanly without the productions of CO_2. We named this process Hy-C, acronym for hydrogen and carbon. The following is a first order mass and energy balance comparison analysis comparing the thermal decomposition of methane with various other processes for hydrogen production.

1. Methane Pyrolysis (Thermal Decomposition of Methane)(3)

The thermodynamics of the thermal decomposition of methane can be determined from the decomposition reaction.

$$CH_4 = C + 2H_2$$

Equilibrium calculations(2) can be made to indicate under what conditions a high degree of decomposition can be achieved. Figure 1 is an equilibrium diagram of the mole fraction of methane left in the gas phase as a function of temperature and pressure. Hydrogen and methane in the gas phase are in equilibrium with carbon in the solid phase. The figure indicates that at one atmosphere total pressure very little methane remains and the gas phase hydrogen content is over 95% above temperatures of 800°C. At higher pressure the equilibrium shifts to higher methane concentrations and thus higher temperatures are required to decompose most of the methane. It has also been shown that the rate of decomposition can be increased by the presence of catalysts, the most practical of which is carbon itself.(5)

For a process it may require separating the hydrogen from the methane and recycling the methane to obtain a high purity hydrogen stream at higher pressures. Figure 2 shows a process flow sheet. The broken lines indicate alternate process fuel conditions for providing the endothermic heat to the methane decomposition reactor. Hydrogen, methane or methane and hydrogen and even carbon from the decomposer can be used as fuel for indirectly heating the reactor. It is also possible to use electrical energy either in resistive or inductive heating. If gas separation is needed to produce high purity hydrogen, pressure swing adsorption using activated carbon or membrane separation can be used to separate the hydrogen from the methane.

To evaluate the energetics of the process, the basic enthalpy of reaction is the minimum amount of energy needed to produce a mole of hydrogen. To account for some inefficiency in providing the thermal energy for decomposition it is assumed that the overall thermal efficiency of the process is 80% efficient.

The process energy needed per mole of hydrogen is then as follows:

$$Process\ Energy = \frac{\Delta H_{Reaction}}{0.80 \times 2} = \frac{18\ Kcal/mol\ CH_4}{1.6} = 11.3\ \frac{Kcal}{mol\ H_2}$$

Thus the process energy amounts to only 5.3% of the higher heating value of the combustion of methane 212 Kcal/mol CH_4. There are several ways of providing the thermal energy for the decomposition:

A) Hydrogen as process fuel:

The hydrogen produced by the above methane decomposition reaction can provide the endothermic process energy for decomoposition. In this manner there is no CO_2 emission since all the process energy is provided by combustion of hydrogen. The higher heating value for combustion of hydrogen amounts to 68 Kcal/mol H_2. The net moles of H_2 produced from a mole of methane is then:

$$Net\ H_2\ produced = 2.0 - \frac{2 \times 11.3}{68.0} = 1.67\ mol\ H_2\ per\ mol\ of\ CH_4\ .$$

The total energy required per unit of hydrogen which is based on the heating value of the total amount of natural gas consumed per unit hydrogen. The higher heat value of combustion of methane is 212 Kal/mol CH_4 so that:

$$Total\ Energy = \frac{1 \times 212}{1.67} = 126.9\ Kcal/mol\ H_2$$

This amounts to a thermal efficiency for hydrogen formation of

$$Thermal\ Efficiency = \frac{68.0}{126.9} \times 100 = 53.3\%$$

In this case the CO_2 emission per unit of hydrogen is zero. The reason for this relatively low thermal efficiency is the fact that the carbon is not being used as fuel. If the carbon can be sold as a material commodity then the thermal efficiency really has no meaning because it is the carbon conversion efficiency, which is the fraction of carbon in the methane converted to carbon black and carbon in the methanol produced which counts and this can be as high as 100%. In this case, the economics of producing the carbon, which includes the cost of raw material feedstock and the capital investment becomes the important factors, not the thermal efficiency. Some current uses for carbon include a vulcanization agent for rubber, a pigment in inks and paints, a solid absorbent for air and water purification, and an electrode material. Possible new uses might include carbon as an animal food additive, a material of construction and as a soil conditioner. Indeed there is an incentive to find more uses for bulk pure carbon in order to credit the cost of hydrogen to reduce its cost as much as possible. If ever a regulation imposing a tax on CO_2 emission comes about, then just storing or sequestering the carbon may become economical.

B) Methane as process fuel.

When natural gas is used as the fuel to provide the heat of thermal decomposition of methane at 80% efficiency, the net hydrogen production per unit of methane becomes:

$$Net\ H_2 = \frac{2.0}{1 + \frac{2\times 11.3}{212}} = 1.81\ mol\ H_2/mols\ CH_4$$

The total process energy is then:

$$\frac{1 \times 212}{1.81} = 117.1\ Kcal/mol\ H_2$$

and the thermal efficiency is:

$$\frac{68.0}{117.1} \times 100 = 58.1\%$$

Because methane is used as fuel some CO_2 is emitted and therefore the moles CO_2 emitted per unit hydrogen then becomes:

$$\frac{11.3}{212} = 0.053\ mol\ CO_2/mol\ H_2$$

C) Carbon as process fuel.

When carbon is used as process fuel, none of the hydrogen produced by thermal decomposition of methane is lost, however more CO_2 is generated. The heat of combustion of carbon is 94 Kcal/mol C.

Net H_2 Generated = 2.00 mols H_2/cal CH_4

Total Process Energy = $\frac{212}{2.00}$ = 106.0 Kcal/mol

Thermal Efficiency = $\frac{68}{106.0}$ = 64.2%

Mole CO_2 Emitted = $\frac{11.3}{94.0}$ = 0.12 moles CO_2/mol H_2

It should be pointed out that the total energy required per unit of hydrogen produced and the respective thermal efficiency is of secondary importance if carbon is sold as a materials commodity. In this case the carbon efficiency becomes important. Therefore for case C where carbon is used as fuel, the carbon efficiency is 76% conversion of the carbon in methane to carbon as a product.

D) Electrical energy for process.

It is possible to use electrical energy either in the form of resistive heating elements or inductive heating to thermally decompose methane in the methane decomposition reactor (MDR). Assuming natural gas fired turbines with a combined steam cycle, a thermal to electrical energy generation efficiency of 55% is achievable. Resistance heating using proper materials could achieve 80% electrical to thermal efficiency. Induction heating might also approach this efficiency value. Thus the overall thermal efficiency of utilizing natural gas for supplying electrical energy to the methane decomposition reactor for hydrogen production is 55% × 80% = 44%. Based on this value, the following is determined:

Natural gas used in power plant to supply electrical energy to methane decomposer

$$\text{Natural gas} = \frac{18\ \text{Kcal}}{212 \times 0.44} = 0.193\ \frac{\text{mol natural gas}}{\text{mol CH}_4\ \text{decomposed}}$$

$$\text{Net H}_2\ \text{generated} = \frac{2.00}{1 + 0.193} = 1.68\ \text{molH}_2/\text{mol CH}_4$$

$$\text{Total Process Energy} = \frac{212}{1.68} = 126.2\ \text{Kcal/mol H}_2$$

$$\text{Thermal Efficiency} = \frac{68.0}{126.2} = 53.9\%$$

The methane fuel used in the combined cycle electrical power plant emits CO_2 so that

$$\text{mole CO}_2\ \text{emitted} = \frac{0.193}{2} = 0.10\ \text{mol CO}_2/\text{mol H}_2$$

2. Methane-steam reforming(4)

The conventional process for hydrogen production is the steam reforming of natural gas which takes place in two steps as follows:

Steam Reforming	$CH_4 + H_2O = CO + 3H_2$
Shift	$\underline{CO + H_2O = CO_2 + H_2}$
Overall Reactions	$CH_4 + 2H_2O = CO_2 + 4H_2$

The heat of reaction for the overall steam reforming is +60 Kcal/mol CH_4 reformed. At 80% thermal efficiency, the amount of process energy needed per unit of hydrogen is:

$$\text{Process Energy/Unit } H_2 = \frac{60}{0.8 \times 4} = 18.8\ \mathit{Kcal/mol\ H_2}$$

$$\text{Mole } CH_4 \text{ for process heat per mole } CH_4 \text{ reformed} = \frac{60}{0.8 \times 212} = 0.354$$

$$\text{Moles } H_2 \text{ produced/mol } CH_4 = \frac{4.0}{1.0 + 0.354} = 2.95$$

$$\text{Total Process Energy} = \frac{212}{2.95} = 71.9\ \frac{\mathit{Kcal}}{\mathit{mol\ H_2}}$$

$$\text{Thermal Efficiency} = \frac{68}{71.9} = 94.6\%$$

$$CO_2 \text{ Emission} = \frac{1.354}{4.0} = 0.338\ \mathit{cal\,CO_2/mol\,H_2}$$

The value of 18.8 Kcal/mol H_2 for the process energy is 8.9% of the molar heating value for combustion of methane, 212 Kcal/mol CH_4. Thus the process energy for steam reforming is 68% higher than for methane pyrolysis. But, the overall thermal efficiency for steam reforming of methane is higher than that for methane pyrolysis by as much as 75%. However, the CO_2 emission is at least of 3 times greater than that for the methane pyrolysis. As mentioned above, another way of looking at this system is that in the case of methane pyrolysis there are two products, hydrogen and pure carbon (black). The carbon can be considered as a materials commodity and thus thermal efficiency has no meaning if the carbon is not used as fuel. The conversion of carbon in methane to carbon in the products is meaningul because carbon can be sold as a materials commodity. Thus in the case for methane pyrolysis when hydrogen is used for providing the energy of pyrolysis (zero CO_2), the carbon conversion efficiency is 100%, while when carbon is used to fuel the methane decomposer, the carbon conversion decreases to 76%.

The only other abundant natural resource for hydrogen is water. A number of methods can be used to split water, this includes electrolytic, thermochemical and photolytic.

The following discusses the energetics and CO_2 emissions for these alternative methods for hydrogen productions.

3. Electrolysis of water using natural gas fueled combined cycle power plant.

Because it takes a large amount of electrical power to electrolyze water, it is important to obtain the lowest cost power. Natural gas direct fired turbines with combined steam cycle can obtain a thermal to electrical efficiency of 55%. Coal gasification combined cycle power plants have somewhat lower efficiency in the order of 45% and therefore as far as fossil fuel derived power plants is considered, natural gas yields the highest thermal efficiency. The electrolysis of water is fairly efficient reaching as high as 80% electrical to hydrogen thermal efficiency. Thus the overall thermal efficiency based on the most efficient natural gas fired power plant is 55% × 80% = 44%. Both the process and total thermal energy are:

$$\textit{Process and Total Thermal Energy} = \frac{68}{0.44} = 154.5\ Kcal/mol H_2$$

and the ratio of H_2 to methane is

$$moles H_2/mol CH_4 = \frac{212}{154.5} = 1.37$$

and the CO_2 emission is $= \dfrac{1}{1.37} = 0.73$ moles CO_2/mol H_2.

4. The thermochemical splitting of water using coal heat.

Because the electrolysis of water requires electrical energy and the production of electrical energy from fossil fuels is not very efficiency with loss of thermal energy, there was a large effort expended about a decade ago searching for methods which can use thermal energy directly to split water. As a result, thermochemical cycles which require chemical oxidation-reduction steps were developed. One such cycle used an iodine and sulfuric acid cycle. It was determined that these cycles were Carnot limited and depending on operating temperatures there was some claim that efficiencies as high as 60% could be obtained. Therefore process and total thermal energy amounts to:

$$\textit{Process and Total Thermal Energy} = \frac{68}{0.60} = 113.3\ Kcal/mol H_2$$

$$\textit{and the ratio of } H_2 \textit{ to coal} = \frac{100}{113.3} = 0.88\ \textit{moles } H_2/\textit{mol coal}$$

the heating value of bituminous coal being 100 Kcal/mol $CH_{0.8}O_{0.1}$ and

$$the\ CO_2\ emission = \frac{100}{113.3} = 1.14\ .$$

5. Nuclear energy for electrolysis of water

Nuclear energy can generate electricity without formation of CO_2. The present light water cooled nuclear reactors are limited to generating electricity at 30% thermal efficiency based on fission energy.

Since the optimum electrolytic conversion efficiency of electrical energy to hydrogen thermal energy is 80%, the overall thermal energy efficiency is 30 × 80 = 24% and therefore the total energy per unit of hydrogen is:

$$Process\ and\ Total\ Thermal\ Energy = \frac{68}{0.24} = 283.3\ Kcal/mol H_2$$

The CO_2 per unit hydrogen is zero.

6. Solar photovoltaic energy for electrolysis of water

Solar energy can generate electricity directly using solar photovoltaic cells. The present cells can generate electricity up to 10% efficiency based on the incident solar energy. The electricity is then used to electrolytically decompose water to hydrogen at 80% electrical efficiency thus yielding and overall thermal efficiency of 10% × 80% = 8%.

The total solar energy per unit hydrogen is then

$$Process\ and\ Total\ Thermal\ Energy = \frac{68}{0.08} = 725.0\, Kcal/mol H_2$$

and the CO_2 emission is zero.

7. Hydropower, windpower and geothermal energy for electrolysis of water

Actually hydropower and windpower are solar energy derived because its the sun that evaporates water in the lower regions and condenses in the colder higher elevations so that it runs down stream to provide the kinetic energy for turning turbogenerators. By the same token wind currents are created by thermal gradients caused by the sun around the earth. Geothermal energy actually is derived from radioactive heat stored in deep underground earth strata. But since these are available as natural energy sources around the earth they can be treated as primary energy sources. The conversion of hydro and wind energy and geothermal heat are achieved through mechanical turbines motivated by water, wind and steam, which turn electrical generators. These machines are rather efficient in the order of as high as 80% conversion to electrical energy. Using this electricity in water electrolysis cells at 80% thermal efficiency, an overall efficiency of 80% × 80% or 64% is obtained.

$$\text{The total equivalent thermal energy} = \frac{0.8}{0.64} = 106.0 \text{ Kcal/mol } H_2$$

and the CO_2 emission is zero.

DISCUSSION

Table 1 summarizes all the data on energy and efficiency for H_2 production and the CO_2 emission data developed in the foregoing systems. The general conclusions that can be drawn from an analysis of the data in Table 1 are as follows.

1. Nuclear and solar energy requirements for hydrogen generation are much higher than the use of fossil fuel energy and hydro and wind power.

2. For the lower energy requirement cases (below 155 Kcal/mol H_2), the CO_2 emission when producing hydrogen can be reduced to very low values and even eliminated.

3. The least amount of process energy required for hydrogen production is the thermal decomposition of methane.

4. The least amount of total thermal energy based on total fuel value of feedstock required for hydrogen production is the steam reforming of natural gas, however, the CO_2 emission per unit of hydrogen is at least 3 times greater than that produced by methane pyrolysis.

5. If carbon is considered as a marketable material commodity, then the process energy is the only energy that counts in considering efficiency of the process and the carbon efficiency then becomes mainly important.

It is interesting to note that using electrical energy to thermally decompose methane, supplying electrical energy from an efficient electrical power generator, might compete with the use of fuels supplying energy thermally to the methane decomposer by combustion.

Besides the above considerations, selection of the optimum hydrogen production process must depend on economics and capacity. The capital investment in the non-fossil energy sources are relatively high compared to present fossil sources. Furthermore, hydro- and wind-power and geothermal heat are relatively limited in supply, capacity and location considerations. The availability of natural gas over the next 100 years appears to be sufficient for large scale production of hydrogen. The thermal decomposition of natural gas when considering both energy requirement and CO_2 emission as well as the use of carbon as a marketable materials commodity makes for a good combination for its selection as the optimum method for production of hydrogen.

Research work is recommended to develop an optimum reactor design for the pyrolysis of methane for hydrogen and coproduct carbon production. Development effort is recommended to produce an optimized methane pyrolysis process for hydrogen production, taking into account equilibrium and kinetic considerations, conversion, gas separation, recycle and mass and energy balance.

REFERENCES

1. Faith, Keyes, Clarke "Industrial Chemicals" 4th Edition, John Wiley and Sons, New York (1975).

2. Thermodynamic values taken from JANAF Thermodynamic Tables, 2nd Edition NSRD-NBS 37, National Bureau of Standards, Washington, DC (1977).

3. "Process Cleaves Hydrogen from Hydrocarbon", Chem. Eng. 69, 90-9 (1962).

4. Steinberg, M. and Chen, H.C., "Modern and Prospective Technologies for Hydrogen Production from Fossil Fuels," Int. J. of Hydrogen Energy. 14 797-820 (1989).

5. Kobayashi, A. and Steinberg, M., "The Thermal Decomposition of Methane in a Tubular Reactor," BNL 47159, Brookhaven National Laboratory, Upton, N.Y. (January 1992).

TABLE 1

HYDROGEN PRODUCTION
Comparison of Basic Energy Requirements and CO_2 Emission

PROCESS	ENERGY EFFICIENCY		PROCESS FUEL	FEEDSTOCK	RATIO $\frac{mol H_2}{mol CH_4}$	ENERGY-Kcal/mol H_2		CO_2 EMISSION $\frac{mol CO_2}{mol H_2}$
	Process Energy	Overall Fuel				Process	Total	
1. Methane Thermal Decomposition $CH_4 = C + 2H_2$	(A) 80% (t) (B) 80% (t) (C) 80% (t)	53.3% (t) 58.1% (t) 64.2% (t)	H_2 CH_4 C	CH_4 CH_4 CH_4	1.67 1.81 2.00	11.3 11.3 11.3	126.9 117.1 106.0	0.00 0.05 0.12
Combined Cycle Power for Electrical Heating $CH_4 = C + 2H_2$	(D) 55% (ϵ) 80%(ϵ) 44%(t)	53.9% (t)	CH_4	CH_4	1.68	11.3	126.2	0.10
2. Methane Steam Reforming $CH_4 + 2H_2O = CO_2 + 4H_2$	80% (t)	94.6% (t)	CH_4	$CH_4 + H_2O$	2.95	18.8	71.9	0.34
3. Natural Gas Combined Cycle Power for Water Electrolysis $H_2O = H_2 + 1/2O_2$	55% (ϵ) 80% (ϵ) 44% (t)	44.0% (t)	CH_4	H_2O	1.37	154.5	154.5	0.73
4. Thermochemical Cycle - Coal Fired Heat for Water Splitting	60% (t)	60.0% (t)	Coal	H_2O	0.88 H_2/coal	113.3	113.3	1.14
5. Nuclear Energy for Electrolysis of Water $H_2O = H_2 + 1/2O_2$	30% (ϵ) 80% (ϵ) 24% (t)	24.0% (t)	U-235	H_2O	-	283.3	283.3	0.0
6. Solar Photovoltaics for Electrolysis of Water $H_2O = H_2 + 1/2O_2$	10% (ϵ) 80% (ϵ) 8% (t)	8.0% (t)	Solar	H_2O	-	725.0	725.0	0.0
7. Hydropower, Windpower and Geothermal power for Electrolysis of Water $H_2O = H_2 + 1/2\ O_2$	80% (ϵ) 80% (ϵ) 64% (t) (Thermal Equiv.)	64.% (t) (Thermal Equiv.)	Waterfall, Wind & Geothermal Heat	H_2O	-	106.0	106.0	0.0

Fig. 1

Equilibrium Diagram For Methane Decomposition

$CH_4 = C + 2H_2$

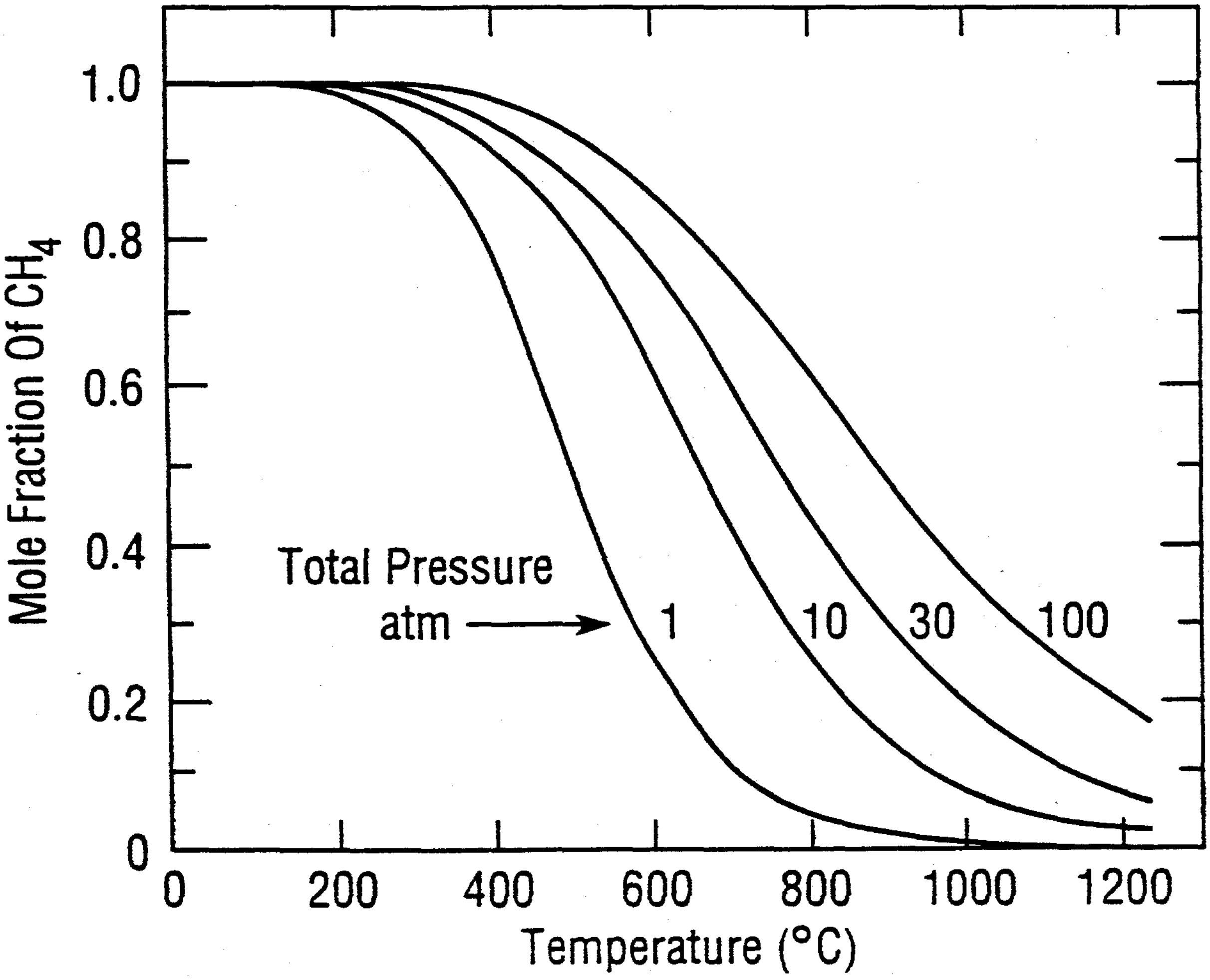

Fig. 2

Hy-C Process For Converting Natural Gas To Hydrogen and Coproduct Carbon