Department of Mechanical and Aerospace Engineering

Project

Title

Pre-Combustion & Post Combustion of methane (Natural Gas) processes, Flue gas decarbonization.

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Abstract

Hydrogen fuel is the most prominent fuel in this era. Mostly, it may extract from fossil fuels specially Methane (CH4). This fuel has quite huge impact in the production of energy and also in the production of Ammonia (NH3). The specialty of this fuel is that it doesn't contain the carbon foot print in their flue gases (emission). In contemporary world, everyone is focusing on the minimal exhaust of carbon foot prints into the environment. For this intent the processing of this fuel is most dominating and variety of techniques are being utilizing in order to achieve the safe and environmentally friendly fuel. Because, now a days it is a heating debate in this industrialization world regarding their discharge should be not harmful for our ecosystem. Moreover, the main purpose is to make our environment safe to the deteriorating impact of Green House gases.

Scientist and Researchers are focusing on the renewable energy techniques and resources. But currently it is quite hard to meet the requirement by using only renewable energy aspects/resources. So, it is our responsibility to conserve the existed and conventional processes in the dramatic way to make our environment preserve. Therefore, we will see the present technique to the acquiring of Hydrogen and Carbon compounds. In a way that our necessity should be meet and our pollutants become inert/eliminate to the environment.

In this process combustion of Methane should perform by conventional method and the flue gases neutralize by using decarbonization technique and also vigilant about the scaling of carbon accumulation on the surface. Generally, the aim is the separation/ trapping of Carbon Dioxide (CO2) before releasing our exhaust into the environment. Furthermore, we keenly see another step that it works in such a way that, pre-combustion of our Methane gas, where Hydrogen and Carbon will produce. But here we burn the hydrogen as fuel in combustion chamber in order to mitigate the carbon foot prints in our flue gases, control ratio of air and fuel would be mandatory.

Moreover, here we discussed the variety of technique for methane combustion with merits and demerits and limitations. Air-fuel ratio is also important factor to understanding of the percent of individuals elements. It accommodated in the capturing of Carbon Dioxide with statistic approach.

Acknowledgements

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Nomenclature

Symbol	Description	Units
CH_4	Methane/NG	
CO_2	Carbon Dioxide	
CO	Carbon Monoxide	
NG	Natural Gas	
NH_3	Ammonia	
SMR	Steam Methane Reforming	
CO_x	(CO_2/CO)	
ΔH SR	Enthalpy of Steam Reforming	KJ/Mol
ΔH WGSR	Enthalpy of Water-Gas Shift Reaction	KJ/Mol
ΔH DSR	Enthalpy of Direct Steam Reforming	KJ/Mol
HTS	High Temperature Shift	°C
MEA	Mono-Ethanol Amine	
CCP	Combined Cyclic Plant	
CSMR	Conventional Steam Methane Reforming	
GHR	Gas Heated Reformer	
POX	Non-Catalytic Partial Oxidation	
CPO	Catalytic Partial Oxidation	
ATR	Auto Thermal Reforming	
N_2	Nitrogen	
Ar	Argon	
AFR	Air-fuel ratio	
$\boldsymbol{M_a}$	Mass of air	Gram
$\boldsymbol{M_o}$	Mass of Oxygen	Gram
$\boldsymbol{M_f}$	Mass of Fuel	Gram

1.0 Introduction

Contemporary two energies Electricity and Hydrogen fuel are classified as non-Carbon sources. Hydrogen fuel is dominating among rest of other, because of its carbon free nature. But as we know that the Hydrogen is not available as a single compound but with other elements. The Hydrogen, is mostly collected from Fossils fuel especially Natural Gas that's name is Methane and chemical formula is CH4. While the extracting of Hydrogen a byproduct CO2 Carbon Dioxide is also produced ultimately.

Reducing net Green House Gases emission by 80 to 100% by 2050 is most essential factor to diminish the severe impact of climate change. For this the given name is decarbonization. Recently, 2016 at White House it was heating debate on climate change and reducing of emission up to 80% was considered most prominent milestone. Also, should be obligatory to safe our beloved globe.

Carbon Dioxide is need to capture or trap through the flue gas before leaving it to the environment. Decarbonization process is broadly used in energy sector and currently pursued techniques are: capturing or sequestration of Carbon Dioxide before and after combustion, capturing of Carbon Dioxide in solid particles form, capturing of atmospheric Carbon Dioxide and so on so forth.

Here we analyzed the pre-combustion and post-combustion of methane. Look at the it's dissociation into Hydrogen and Carbon Dioxide. Hydrogen considered the decarbonize or low carbonaceous fuel for power and heat industry and Carbon Dioxide removal or capturing technique and its limitations to trap. Close look upon their reactions and process how it may produce. One thing is clear Carbon Dioxide has severe impacts on our ecosystem, so and its obligatory to capture through the flue gases before releasing into the open air.

The rapid change in climate is alarming situation for mankind to cut off or minimize the use of fossil fuels, which may the greenhouse effect and release profound amount of CO_2 into climate. This is an important aspect in our context also. Developments in energy and heat sectors widely deployment of renewable energy resources have been proposed to overcome on the currently running fossils fuel and to this toxic exhaust production. However, all the currents scenarios and states show that no other option is compatible or sufficient excepts fossil fuel and it has dominating role still in our current energy resources whether these renewable or so on.

2.0 Literature Review

I appreciate the diverse and multi-disciplinary research. It provided the broad and so-called comprehensive knowledge about the steam methane reforming, pre & post-combustion of methane gas. It significantly enhanced my personal and research perspective about this written article.

Meanwhile this research I realized that few things are indispensable, certainly the methane fuel usage into the production of our basics desired energy and heat and electricity. Similarly, the consequences of its are quite dreadful for our climate and it's depleting the cleanliness of the entire globe.

Consequently, we must need to pace up the process in order to revive or safe our earth to the exhaust of these fossil fuels. Even though, majority of industries trying to capture the toxic remnants of which may produce during the production of methane gas. But these methods are quite hectic and monotonous.

So, we have to shift on renewable energy as soon as possible. Because, it's quite environmentally friendly and seems pretty safe for the world. It's our responsibility to make the environment safe and it is knitted with our survival either.

3.0 Post-combustion & Pre-combustion of Methane.

Two main system can be envisaged to the capturing of Carbon Dioxide and these listed below and both of these are also elaborated precisely in our article.

post-combustion capture: This method to collect/trapping CO_2 is happened when the Natural Gas/ Methane is burned in the presence of air. Ultimately, it may cause the reason to the production of toxic emission certainly, Carbon dioxide which has the most debating factor and reason of Greenhouse effect. Therefore, its mandatory to separate to the flue gases before releasing into the open environment.

pre-combustion capture: In this process, CO_2 is capture/separate when the syngas converted CO into CO_2 after partial oxidation reaction. In this process Hydrogen has been separated before using as a fuel. It means it has decarbonized property into it and its eco-friendly fuel respectively. [1]

These two methods are extensively applying in the power and heat industry. These methods are applicable according to the perspective and demand of the scenario. Because, each of it has its own merits and demerits. Also, the main purpose is to mitigating and controlling Carbon Dioxide from flue gases or pre-treatment separation as well.

3.1 Steam Methane Reforming Hydrogen and Carbon capturing

The current using techniques into the energy and power sectors, in order to get Hydrogen, the most prominent reaction is (SMR), its stands for is that steam methane reforming and it's the most frequent and dominant method to the production syngas. Syngas is the mixture of Hydrogen and Carbon Monoxide, it's a primary reaction. This reaction proceeds in the presence of educts most probably Methane and water. Most important natural gas plays the role of feedstock. The key role of this reaction to accomplish the reaction to extract Hydrogen as a fuel. So, given balanced reactions indicates the chemical phenomenon of it:

$$CH4 + H2O \leftrightharpoons CO + 3H2 \qquad \Delta H_{SR} = 206 \text{ kJ/mol} \qquad (1)$$

This reaction is one of the strongest endothermic reactions & enthalpy of the reaction should be (ΔH_{SR} = 206 kJ/mol).

In this process Hydrogen and Carbonated gases (COx) are produced. Hydrogen used for the variety of purposes but the main are Industrial Ammonia (NH_3) production and as a Hydrogen fuel as well.

3.1.1 Steam Methane Reforming Reactions

Steam methane reaction main reaction is given below:

$$CH4 + H2O \leftrightharpoons CO + 3H2 \qquad \Delta H\ SR = \frac{206kJ}{mol} \qquad (2)$$

This shift reaction is performed between CO and Water. Resultantly, the educts are converted into the Carbon dioxide and Hydrogen. In given equation is illustrated (3)

$$CO + H2O \leftrightharpoons H2 + CO2 \qquad \Delta H\ WGSR = -\frac{41kJ}{mol} \qquad (3)$$

Few additional reactions are also occurring during steam reforming reactions. Commonly the direct steam reforming (DSR) reaction is also included:

$$CH4 + 2H2O \leftrightharpoons 4H2 + CO2 \qquad \Delta H\ DSR = \frac{165kJ}{mol} \qquad (4)$$

The noticeable thing in all reactions is that except Shift-reaction rest of others are endothermic. Means, it is so important that continuous and high amount of energy supply is indispensable to throughout this operation. More precisely, the range of temperature do need to maintain is 800 to 900°C and pressure into the operation should be 20-30 bar. This should be performed with high excess of steam that is represented by the molar ratio between steam-to-carbon. Typically, the steam-to-carbon ratio should be 2.5:1 – 3:1. [2]

3.2 Steam Methane Reforming & It's Execution Steps

Natural Gas (Methane), steam reforming is extensively used in industry contemporarily. In large industrial centralized plants are producing Hydrogen by using SMR technique and this Hydrogen fuel is utilizing in numerous way the major are Energy and Heat domains.

This process takes place in main steps in order to get Hydrogen and COx. These steps are briefly described below

3.2.1 Reforming of Natural Gas

In this step of Steam Methane Reforming, the endothermic reaction takes place between Natural gas (Methane) and Steam following reaction is discussed above. Resultantly, the it will dissociate into Hydrogen (H_2) and Carbon Monoxide (CO), it is also known as "Syngas". Means mixture of Hydrogen and Carbon Monoxide. The conditions of the reaction should be Temperature 750°C to 800°C and pressure will maintain between 3 bar to 25 bar. The Hydrogen gas is now considered vital and adequate non- carbonated fuel. However, Carbon is still a problem.

3.2.2 Shift Reaction

This step is known as (WGS), means water-gas shift reaction. Here, the Carbon Monoxide, which me produce while the Reforming of natural gas reaction will react with the steam in the existence Catalyst (Nickle-Cobalt) or the famous catalyst Hydrotalcite. This reaction will occur in two stages, first one is known as (HTS) high temperature shift at 350ºC and second one will occur at 190 ºC to 210ºC. Ultimately, under these conditions Carbon Monoxide will convert into Carbon Dioxide and Hydrogen will also produce. Reaction of this step is listed above. [3]

The Diagram of this Process is given Below:

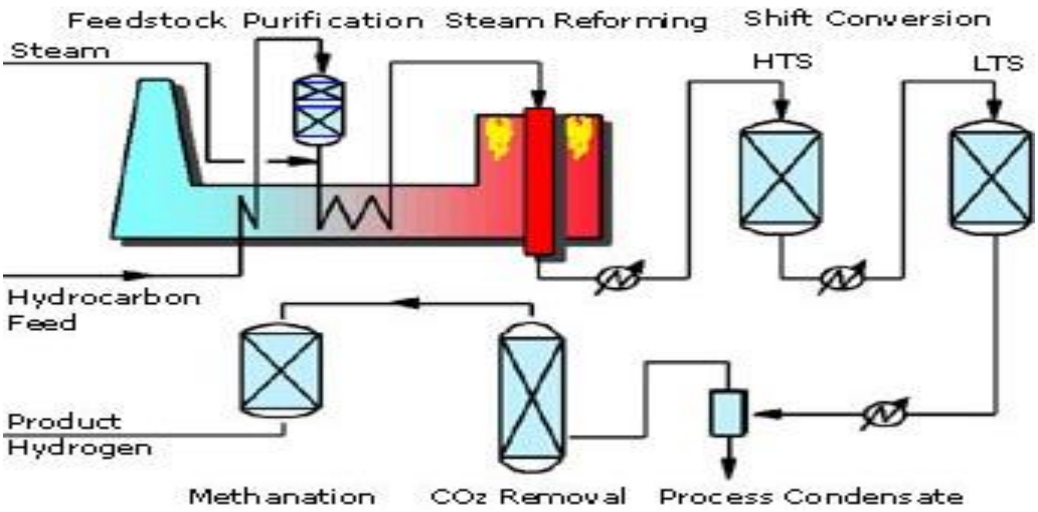

Figure 1. Steam Methane Reforming (SMR)

3.3 Capturing or Sequestration of Carbon Dioxide from Flue Gas

In modern time Hydrogen fuel has a broad role to fulfill the requirements of energy. Unfortunately, extracting of Hydrogen from other fuels some other impurities are also emerging. One of them is CO_2, which is also known as Green House Gas. This, gas has adverse effect in our climate change and considered most affecting compounds which is damaging our global environment. Many, approaches are using to get rid from this pollutant, like renewable energy, sequestration of CO_2, extracting CO_2 as a solid substance etc.

Carbon Dioxide in our climate is existed at harmful level and it has lethal impacts on living things and the basic reason to climate catastrophic failures. The concentration of Carbon Dioxide since 2007 to till, it has dramatic hike Figure 2. Here we can analyze its concentration on yearly basis and how it is remarkable ascending in the trending of Carbon Dioxide emission in given statistical figure of Carbon Dioxide data.

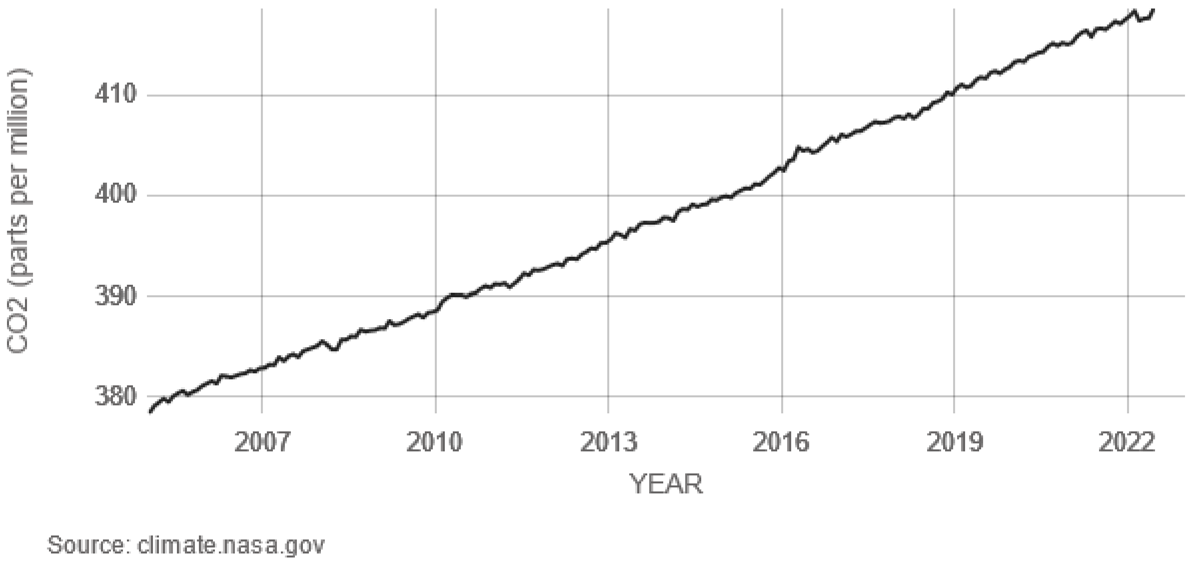

Figure 2. CO_2 emission yearly data, since 2007 to 2022 in parts per million (PPM)

Here we also discussing a technique to capture the CO_2 from the flue gases and this mechanism is discussed below:

3.3.1 Flue gas Characteristics

In the Characteristics of Flue gas i.e Carbon Dioxide Concentration, Flow rate of Gas and other impurities are the key notes those directly elaborate the performance of the capturing the process. These features are less or more figured out by the plants type. The Carbon Dioxide content for the Methane gas is between 3 to 4%. This concentration will fall in the category of standard atmospheric pressure.
If the presence of Carbon Dioxide in flue gas for this high amount driving forces will take for absorption. Also, the flue gas flowrate has impact which decide the capacity of the absorber vessel. Moreover, other impurities like Sulfur Oxide or Nitrous Oxide presence in flue gas will affect the overall cost of the Carbon capturing unit.

3.3.2 Fractional Removal of Carbon Dioxide

The fractional trapping or capturing of Carbon Dioxide is most important parameter which we can choose freely in principle. But in application must look at the economical limitations or technical limitations. If we gaze currently capturing efficiencies of Carbon Dioxide it falls between 80 to 95% overall. The exact value of it depends upon the optimal recovery of CO_2. If we consider the maximum value of recovery of need to recover as much possible it possible but the cost should be exaggerated and with this all-associated cost while the operation will increase. Moreover, the main vessel Absorption column which may use to trap the CO_2 will be required large and also directly may cause the enhancement of energy penalties as well. Hence, our system should be optimized according to our ecological and cost effective either and this it's rare to meet.

3.3.3 Solvent Type

This is an important factor which must be note down while the absorption of CO_2. Because, this factor represents and help to determine the performance of the process. Also, the flowrate it matters in it and may cause the evaluation of vessel capacity and energy demands. Mostly, flowrate will be determined the CO_2 production capacity. In this unit the vapor pressure should be low and our solvent should be stable. Because, under this typical operation condition it must need to be control. Thus, the thermal and oxidative stability should be in our first priorities. If, we neglect this step it causes the corrosion in our vessel. [4] For this intent, sometimes Oxygen scavengers and corrosion inhibitors are need to be add. In our case we are using Mono-ethanol Amine (MEA) solvent. Chemical absorption is based on reactions between CO2 and the amine. It has been reported that chemical absorption does not increase significantly with pressure. Here you can see how the amine and CO_2 reactions takes place in order to absorb CO_2 amines ($R\text{-}NH_2$) with CO_2. [5]

$$2R\text{-}NH_2 + CO_2 \leftrightharpoons R\text{-}NH_3^+ + R\text{-}NH\text{-}COO^- \qquad (5)$$

$$R\text{-}NH_2 + CO_2 + H_2O \leftrightharpoons R\text{-}NH_3^+ + HCO_3^- \qquad (6)$$

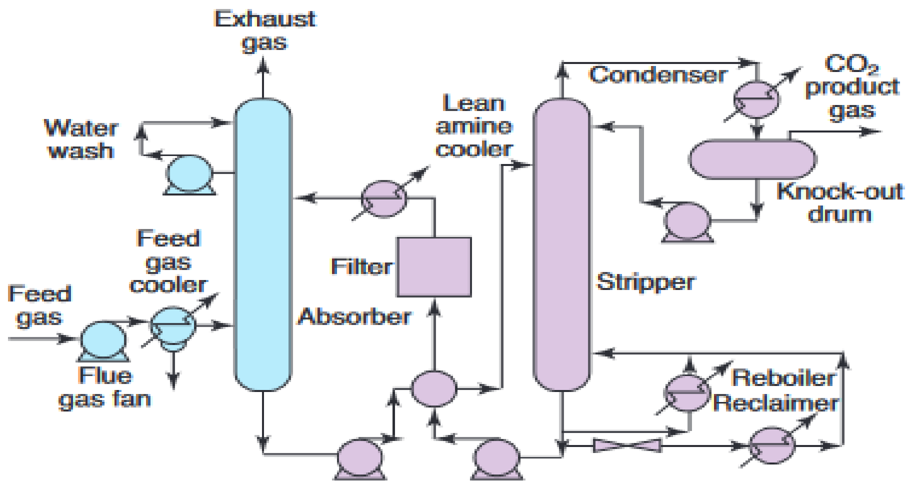

Figure 3. Carbon Dioxide Recovery from Flue Gas by Using Chemical Solvent (MEA)

After capturing from flue gas. Here, we look after the different fuels and their compositions of containing toxic components. This information is given in Table 1. For understanding the containing variety of other components in multiple fuels. [6]

Table 1: Composition of Different in Their Emission/Flue Gases

	Heavy oil	*Coal*	*Natural gas*	*Municipal solid waste*	*Black liquor*
O_2	3	4.2	3.3	9.0	1.2
CO_2	14.5	13.6	9.1	10.9	14.2
H_2O	10.5	5.5	16.7	19.5	16.8
SO_2	0.1	0.12	–	19 ppm	–
HCl	–	0.02	–	0.11	4 ppm

3.4 Capture & Storage of Carbon Dioxide CCS, Management

Carbon Dioxide sources are indispensable to quit yet, power plant, industrial emission, petroleum processes, public transport and many other sources are reason of CO_2 in our climate and have detrimental affect either. So, for this reason its mandatory to deal with it.

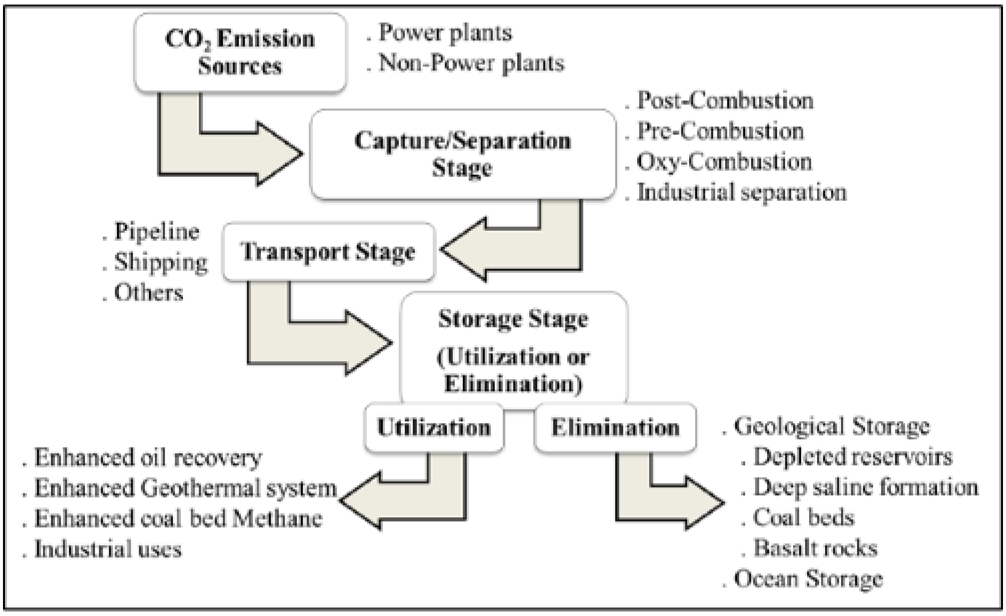

Figure 4 Hierarchy of CCS Mechanism

According to the state of, 2011, the emission of fossil fuel like coal, oil and natural gases have the tremendous impact on emitting the carbon Dioxide into environment. Figure was approximately 33.2 billion tons of greenhouse gas. In which coal is on top by releasing 43% of Carbonaceous exhaust, on second number oil is that imparting 36% emission: whereas, natural gas is on 3rd by releasing 20% of the global emission. These figures are published by IEA 2012.

3.4.1 CO_2 storage and transportation management

After capturing of CO_2 which we had done in previous steps, now the major challenge how to deal and what to do with this captured gas. Then, this captured gas transports for utility or mostly disposed in appropriate dumped/storage sites. So, what would be the option but the transportation should be economical. Pipelines, trucks, ships are the modes of transportation of Carbon Dioxide for most probably pilot plants operation.

3.4.2 Carbon dioxide Utility

Now a days, scientist, researchers and experts are trying to minimize the release of greenhouse gas for this intent they are trying comprehend the best way to deal with Carbon dioxide. So, they discovered few techniques where this gas utilizes as a raw material. For example, in oil & gas industry, or many industrial processes as a raw material. Moreover, this CO_2 take parts in industrial processes of chemical & biological. Here, it is use as a reactant. Like in the urea industry, in the production methyl or wood alcohol and many other applications Beverage industries for carbonated drinks, food packing as a cooling agent, for firefighting to build obstacle for air may cause the reason to stop the fire etc.

3.4.3 Elimination of Carbon Dioxide

Although, after having the limited option to deal with CO_2 but still we few great opportunities to hold this issue. Whereas, geological underground storage is good option to dump the gas. Rapidly descending of oil reservoir, deep saline hindered mine able coal voids are impressive options for the capturing carbon dioxide. And now a days another popular technique is the formation of salt in underground origin and basaltic rocks also is utilizing to trapping the huge amount of CO_2. [7]

3.5 Cost estimation and scalability of CO_2 capturing from flue gases power plant

The different configurations of the Natural Gas Combined Cycle with Carbon Dioxide capturing, contains possibilities to decrease in the efficiency of absorption by applying exhaust gas recirculation in assessment of thermodynamics performance NGCC. In fact, the characteristic parameter is utilizing for the cost of electricity comparisons. Moreover, by considering power plant those are equipped with technologies of CO_2 capture the fundamental for the scaling includes the carbon management costs by collecting the cost of CO_2 avoidance calculated with the help Equation (7). This parameter demonstrated the operational cost and increased capital incurred in the result of additional machinery and lower cycle efficiency in the relation with the trapped Carbon Dioxide through the flue gases. The electricity producing estimated cost according to the economic point of are given in Table 2.

$$CO_{2\ avoid\ cost} = LCOE_{with\ capture} - \frac{LCOE_{without\ capture}}{CO_{2,without\ capture}} - CO_{2,with\ capture} \qquad (7)$$

Table 2. Economic assumptions employed.

Parameter	**Value**	**Unit**
Natural gas price	4.74	€/GJ LHV
Capacity factor	90	%
Capital charge rate CO_2	15	% per year
Interest during construction	16	% of overnight capital
Operation and maintenance (O&M)	5	% of overnight capital/year
CO_2 transport and storage costs	6.97	€/ton (CO_2)

The Carbon Dioxide transportation and storage is consisted on dozens of km pipelines, a well with aquifer injection approximately in the depth of 2km and with the 2500ton/day injection rate as well. Also, the plant capacity in this process of Carbon Dioxide removal is 142 ton/hr for the EGR case, storage and transport cost here considered modest. Unfortunately, the prediction of a cost of power plant is every time hectic and almost impossible. Just, roughly estimate we can predict that is associated with the absorption and stripping system and also the absolute effect of these variations on the levelized cost of electricity. The main idea regarding the capital cost of the power plant units is acquired from the detailed capital cost data for NGCC power plants given in the study by (NETL 2007). The overnight cost "C" of a component with the size" S", of single train of a reference component of size S_0 is shown in given formula:

$$C = n^e C_0 \left[\frac{S}{nS_0} \right]^f$$

C= overnight cost of component
S= Size of component
S_0=single train of a reference component size
f = cost scaling factor
n= number of equally sized equipment trains operating at a capacity of 100%/n
e= the exponent of the cost scaling for multiple train equipment. [8]

3.5 Air & its components, certainly Nitrogen and Molecular structure of air

Table 3. Detailed Analysis of Dry Air Standard Composition

Gas	% By Volume	% By Weight	Parts per Million (by vol.)	Chemical Symbol	Molecular Weight
Nitrogen	78.08	75.47	780790	N_2	28.01
Oxygen	20.95	23.20	209445	O_2	32.00
Argon	0.93	1.28	9339	Ar	39.95
Carbon dioxide	0.040	0.062	404	CO_2	44.01
Neon	0.0018	0.0012	18.21	Ne	20.18
Helium	0.0005	0.00007	5.24	He	4.00
Krypton	0.0001	0.0003	1.14	Kr	83.80
Hydrogen	0.00005	Negligible	0.50	H_2	2.02
Xenon	8.7×10^{-6}	0.00004	0.087	Xe	131.30

The three major constituent of air are: Nitrogen (N_2), Oxygen (O_2) and Argon (Ar), respectively. These can be captured or recovered from. These three major constituents have specific and significant values. All these gases are utilizing industrially.

O_2: Oxygen is mainly valued for reactivity. This gas is widely applying in various industrial processes, combustion and biological purposes mainly. This gas also using in steel making, petroleum processing, environmental protection and so on.
Oxygen is promptly used with or without air to triggering the level of available oxygen in combustion process. Oxygen is vital for living things, most importantly its use in hospital to assist breathing. Moreover, Oxygen is use in industry to boost or stimulate the reaction rate.

N_2: The one of the prominent characteristics of Nitrogen is inertness. For this reason, it considered worthy for industrial purposes. It works like, it may displace the other effluent or gases in a vessel and plays a shield role to against any reactivity on the surface with Oxygen. This Gas also assist regarding quality perspective, and make sure the safety in many places. Liquid N_2 have values for coldness and inertness. If liquid nitrogen vaporized at ambient temperature, it causes the reason of sudden down of temperature of the surroundings. However, it has intense quality of being cold make this gas an ideal cooling agent. Because of this property its highly applicable in food industry, where instance freezing require with minimum cell destruction. This gas in liquid form is used as machining and also for fracturing of soft or most probably for those materials which have heat sensitive property. Like, specific metal, pharmaceuticals, plastics, shred tire manufacturing, etc.

Ar. Argon is the third highly existing gas in air the constituents of air. Argon is gas that very important because it considered absolute inert gas. This specialty of Argon gas is so helpful for industrial purposes that’s why it may use in critical processes. Examples of these application are: in steel industry specifically those which may produce prime quality of steel

& grow impurity free silicon crystals and this is precisely for the manufacturing of semi-conductor. The next property of Argon is shield gas and now a days argon welding is very popular. In light bulb as a filter gas, multi-pane windows etc. are also the application of Argon gas. [9]

3.5.1 Nitrogen & its properties

Nitrogen is the most abundantly present element in our air approximately 78%. Its chemical formula is N_2. This gas is color and odorless gas at standard conditions. Its cryogenic gas refrigerant that is use in refrigerated as well.

Moreover, Nitrogen is non-combustible and non-toxic gas. Although, it is not dangerous but it has asphyxiation effect when it displaced by air. Also, it may cause the frostbite because liquid nitrogen has tremendously low temperature. In fact, if the container of Nitrogen place in heat pr fire for a while it may cause the reason of drastic blast.

The phase diagram of Nitrogen illustrates the different behaviors of Nitrogen accordingly different temperature and pressure. The given picture is the phase diagram of Nitrogen and its behavior with respect varying temperature and pressure: [10]

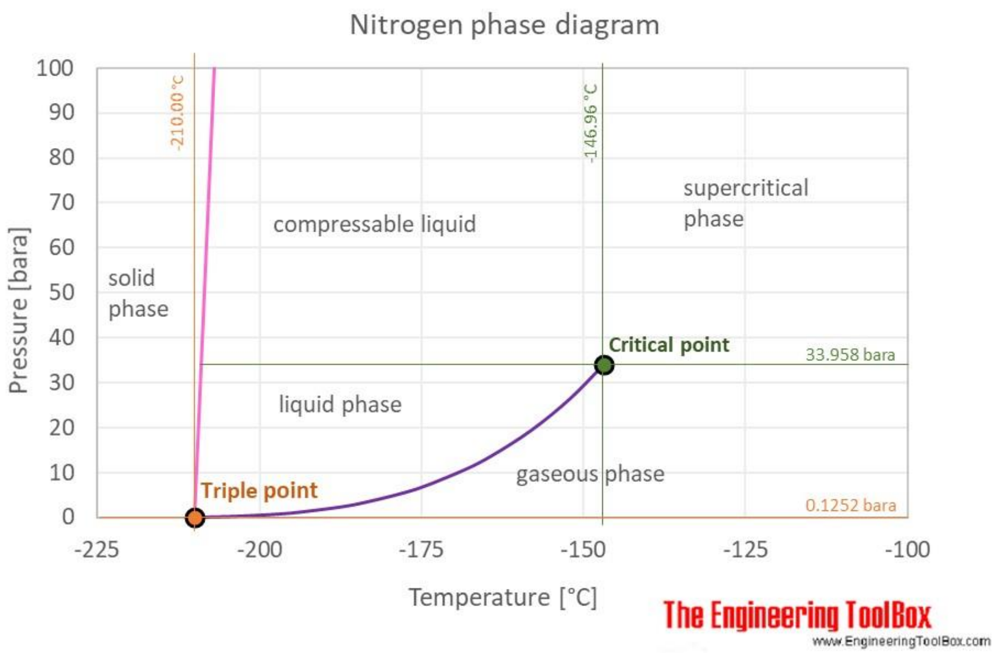

Figure 5. Phase Diagram of Nitrogen (N_2)

3.5.1 Molecular Structure of Air

As we know that Air is the mixture of bunch of gases, which is 78% Nitrogen, 21% Oxygen, 0.93 Argon, Carbon dioxide 0.04% and very minute percentage of Neon, Helium, Methane, Krypton and other substances. Similarly, it’s impossible to depict the single molecular/structural formal. But we can represent it by the individual of these substances. The main molecular structure of the air constituents air given in Figure 4.

Here we can see that molecule of Nitrogen, Oxygen, Carbon Dioxide, Methane all those have covalent bond structure in their molecular structure. [11]

Figure 6: Molecular/ Structural formulas of the air main constituents.

3.6 Analysis of pre & post-combustion, of carbon that is it possible to process and manage it.

Let’s start with the pre-combustion it refers to eliminating the Carbon Dioxide from the fossils fuels and it may occur before combustion completion. Look at the example, like the process of gasification a feedstock which is most probably partially oxidized this process execute with steam and presence of oxygen, temperature maintains high and pressure as well. Ultimately, it may cause the reason of synthesis gas. The syngas (synthesis gas), contains carbon dioxide & carbon monoxide. After this, syngas gas deal with the WGSR. Here CO and water converts into Carbon dioxide and Hydrogen. Though the concentration in this stream has contain 15 to 50% Carbon dioxide. Then this Green House Gas captured and sequestrated.

If contrast with the post-combustion, where eliminates the 5 to 15% concentrated Carbon Dioxide to the flue gas and pressure keeps quite low comparatively Pre-combustion. In post-combustion process the shifted gas is contains the high amount of Carbon Dioxide into it. Therefore, high concentration of Carbon dioxide in the gas stream makes the less valuable and efficient comparatively, with the pre-combustion process. Even though, the efficiency of pre-combustion is far better than post-combustion but the capital cost of pre-combustion is so high because of gasification section into these plants.

So, researchers are working the cost issue which is associated with the pre-combustion methods. Also, they keenly advanced turbine and gasification unit. Their main purpose is to make the pre-combustion carbon capture technology to make cost competent. [12]

4.0 Pre-combustion of methane splitting into Hydrogen & CO_2 capturing

This process Pre-combustion of methane to trapping Carbon Dioxide is famous in power generation and that is applying on the industrial scale in order to produce Hydrogen and chemical commodities. Carbon dioxide is a by-product in this industry. In chemical industry it is a quite old technique to capture CO_2 by pre-combustion process and it's almost 90 years old method.

4.1 Pre-combustion CO_2 capturing & Hydrogen Combustion

Pre-combustion processes, these are associated with two reactions. Primary reaction is occurred between Natural gas and steam and its so-called steam methane reforming. Secondary, it is known as partial oxidation reaction and it may occur between oxygen and natural gas.

$$Steam\ Methane\ Reforming:\ \ CH4 + H2O \leftrightharpoons CO + 3H2 \qquad \Delta H\ SR = \frac{206kJ}{mol} \qquad (8)$$

$$Partial\ Oxidation\ Reaction:\ \ CH4 + \frac{1}{2}O2 \leftrightharpoons CO + 2H2 \quad \Delta H\ POR = \frac{-36kJ}{mol} \qquad (9)$$

The process of partial oxidation is occurred due to oxygen. This oxygen mostly separated from air. The exothermal partial oxidation reactions are balanced with the endothermic reaction that time this state is named as auto-thermal reforming. After this, syngas production is executed by the well-known reaction water-gas shift reaction (WGSR), here conversion Carbon Monoxide (CO) to Carbon Dioxide (CO_2) and Hydrogen (H_2) is also produce. This reaction will take place in the presence of steam (H_2O).

The Chemical equation is listed here as:

$$Water\ Gas\ Shift\ Rxn.:\qquad CO + H2O\ \leftrightharpoons H2 + CO2 \qquad \Delta H\ WGSR = -\frac{41kJ}{mol} \qquad (10)$$

At ambient temperature CO_2 is separated by using conventional washing steps. Now, we have the Hydrogen rich and low Carbonaceous fuel that is consider safest ecological friendly and highly demanding as well, which may use for the combustion purpose or in combined cyclic plant (CCP) for the generation of energy (Brayton + Rankine Cycle). [13]

Carbon dioxide can remove easily, because high pressure stream of water gas shift product accommodated to the removal of CO_2. The percentage of Carbon Dioxide at the inlet point of Carbon Dioxide/Hydrogen most probably founded 15% to 60% in dry basis. The plus point of pre-combustion of methane in this case is it performs under the pressure of 2 and 7Mpa, which is very low comparatively with post-combustion process. It also represents that CO_2 compression and separation consume less amount of energy. This Carbon Dioxide is now available for storage. And, Hydrogen is ready as a fuel also now we do not need to put much attention on flue gases. Because after this process Carbonaceous compounds has been separated. The flue gases maybe contain negligible percentage of Carbon contents into it.

The pre-combustion process is almost same for fossil fuel, coal and natural gas (Methane). But, in case of coal and oil combustion it may requires many steps in order to remove ash contents, Sulfur compounds and many other impurities these are not problem in case methane problem. The five steps are mainly use in the pre-combustion of methane or coal in power generation. These steps are listed and below and Figure 6, is depicting the flow and mechanism of the pre-combustion of methane.

- Syngas island
- Separation of CO_2
- Compression of CO_2
- Power island
- Oxygen island

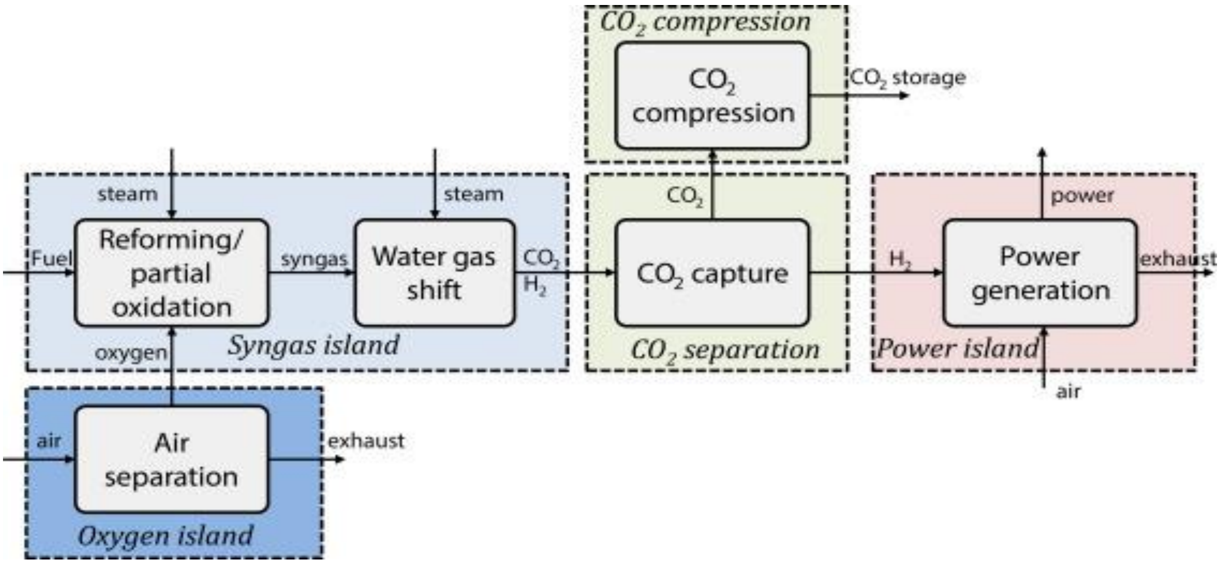

Figure 7. Pre-combustion process of methane, CO_2 capturing & Hydrogen power generation.

There is an advantage which may added the value in pre-combustion CO_2 capture route that is the co-production of power and hydrogen production. Means, there is availability to shift hydrogen production to power production but it depends how much electricity is required. Intermittency of power now a days is being quite catchy because of the wind mills and solar panels. Because of this we can see the fossils fuel plants especially CO2 capturing plant now they feel bit flexibility. It is simple and understandable that we are trying to fulfill our requirements via renewable resources that is Green House Effect free process. Beside this, pre-combustion process is still quite expensive in order to make syngas generation. That is the main reason, which makes pre-combustion process quite hectic and costly, main reason is chemical solvent which is use for capturing of Carbon Dioxide. Otherwise, as a safety point of view it pretty environmental-friendly.

4.2 Other Methods for Pre-Combustion of Methane

Now a days, we penalty of technologies and options for the natural gas reforming process and these all are applicable in pre-combustion Carbon Dioxide capture units. And their operating conditions and characteristics are concluded in given Table 4.

Table 4. Typical characteristics of commercially available natural gas reforming technologies

	SMR	**GHR**	**POX**	**CPO**	**ATR**
Operating temperature (°C)	750-900	Primary 450; Secondary 1000	1200–1600	850–1100	850–1100
Operating pressure (bar)	20–30	20–30	30–85	15–40	20–70
Outlet H_2/CO ratio (−)	3.0–6.0	3.4	1.6–2.0	1.6–2.0	1.6–2.5
CH_4 conversion (%)	65–95	95–100	95–100	95–100	95–100
Oxygen demand	None	Medium	High	High	High
Steam demand	High	Medium	Optional	Optional	Low

4.2.1 Steam Methane Reforming

Conventional Steam Methane Reforming (SMR): In this conventional way of production, it occurs in the presence of catalyst. For this endothermic reaction the heat source is provide separately and it may get from the additionally burning natural gas reserves.

4.2.2 Gas Heated Reformer

Gas Heated Reformer (GHR) or Heat Exchange Reformer (HER): In this technique steam reforming is the main purpose of reaction. In this system, hot gas stream use as a heating source and it will pass inside the tubes of the reformer and it cause the reason of the execution of the endothermic reaction. Here the special case reformer heat exchanger, pressurized combustion reforming. Hence, burning a fraction of Hydrogen as a fuel at high pressure to facilitate the acquiring of hot gas stream during the process.

4.2.3 Non-catalytic partial oxidation

Non-catalytic partial oxidation (POX): In this process partial oxidation exothermic reaction take place and may cause the generation of heat in the operating system. In a combustion chamber Methane or Natural Gas is added with an amount of sub-stoichiometric Oxygen or air. Consequently, partial oxidation reaction takes place at the condition of high pressure and high temperature.

4.2.4 Catalytic Partial Oxidation

Catalytic partial oxidation (CPO): In the presence of noble metal catalyst (rhodium or palladium), a mixture of fuel (NG) and air is ignited on the surface of illustrated catalyst. In this process vigorously high reaction rates allow so short stay times.

4.2.5 Auto Thermal Reforming

Auto thermal reforming (ATR): This type of reforming has involved dual reaction steps. First is Partial Oxidation and secondly, Reforming of steam. This process occurs when in a mixer Oxygen and steam are mixes. In the combustion chamber because of Methane Steam Reforming (MSR) and water-gas shift reaction equilibrium create the tendency to the execution of partial oxidation reaction. [14]

4.3 Method to calculation of air-fuel ratio by stoichiometry

Table 5. Different fossils fuels stoichiometric air-fuel ratio.

Fuel	Chemical formula	AFR
Methanol	CH_3OH	6.47:1
Ethanol	C_2H_5OH	9:1
Butanol	C_4H_9OH	11.2:1
Diesel	$C_{12}H_{23}$	14.5:1
Gasoline	C_8H_{18}	14.7:1
Propane	C_3H_8	15.67:1
Methane	CH_4	17.19:1
Hydrogen	H_2	34.3:1

Air-fuel ratio (AFR), is the representation of the ratio of air & fuel recipe which make ready for the combustion operation. Suppose, we have the mixture which and that is consist on the air and fuel, it has 17.5 ratio. 17.5 means that we have 17.5 kilo gram of air and & 1 kilogram methane of methane. Thus, it may cause the complete combustion during burning.

AFR formula

$$AFR = m_a/m_f$$

For understanding of AFR measuring technique look at the process of combustion of fuel. As we know that the combustion is the chemical reaction process which may occur because of the oxidation. Resultantly, it produced the flue gases and heat also.

$$Fuel + Oxygen \rightarrow Carbon\ Dioxide + Water + Energy$$

For the authentication let's look at the example where we measure the AFR value of the methane fuel.
This calculation will proceed step by step and these all steps are listed below. Here we will look at this calculation meticulously and more precisely:

- Write the balanced chemical equation of the combustion process:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

- Then write down the elements of balance chemical equation with their atomic weight.

Hydrogen=1.008 amu
Carbon=12.011 amu
Oxygen =15.999 amu

- Determine imparting mass of fuel, in our case its methane and its 1 mole impart also methane has 1 atom of carbon and 4 atoms of hydrogen as well.

M_f=12.011+4·1.008=16.043 gm. Here 1 Carbon= 12.011 & Hydrogen 4 atoms= 1.008*4

M_f= Mass of fuel

- Now determine the mass of Oxygen, it has 2 moles and each of this mole has 2 2 atoms.

M_o=2·15.999·2=63.996 g
M_o= *mass of oxygen*

- Here we calculate the necessary mass of air and specifically we have to encounter Oxygen mass. As we know that air consist of 21% Oxygen approximately.

M_a=100*M_o /21 =100 / 21·63.996=304.743 g

M_a = Mass of air

- Finally determine the AFR (air-fuel ratio) by using this formula

AFR=M_a/M_f=304.743/16.043=18.995 [15]

Air Fuel Ratio (ARF)			
Components	Hydrogen	Carbon	Oxygen
Atomic mass Unit	1.008 amu	12.011 amu	15.999 amu
Mass of Fuel (M_f)	12.011 + 1.008 = 16.043 gm		
Mass of Oxygen (M_o)	2 x 15.999 x 2 = 63.996 gm		
Mass of Oxygen in Air 21% (M_a)	$M_a = \frac{100 \text{ x } M_0}{21} = \frac{100 \text{ x } 63.996}{21}$ = 304.743 gm		
Air Fuel Ratio (ARF)	$ARF = \frac{M_a}{M_f} = \frac{304.743}{16.043}$ = 18.995		

4.5 Amount of Hydrogen & Oxygen which is used to get water

Let's suppose that we have 1 mole of water:

Water is compound of Hydrogen and Oxygen in which 2 atom of Hydrogen and 1 atoms of Oxygen existed. It means that, 1 mole of water contains 1 mole of oxygen and 2 moles of hydrogen atoms. Atomic weight of Hydrogen is 1.007gm and oxygen is 15.999 gm.

Thus, water would be:

- weight of water = 2(1.0079) g + 15.9994 g
- weight of water = 2.0158 g + 15.9994 g
- weight of water = 18.0152 g

Hence prove that, 1 mole of water keeps **18.0152 grams weight.** [16]

4.6 Comparison b/w Pre & Post Combustion Technology, in order to capturing of Carbon Dioxide & other parameters.

Here we gauge the features, merits and demerits of both pre-combustion & post combustion process. However, it will help to comprehend the desired of the current circumstances. So, look at the comparison between these processes.

Pre- combustion

Merits	***Demerits***
• This process executed for the production of carbon free fuel and it's occurred at very high pressure. • In this this technique variety of different hydrocarbon fuel can use. For example, natural gas, coal,	• The main disadvantage of the pre-combustion method is that its cost is very and great risk either exist in this method. • The process seems complicated due to the mandatory requirement of the Fuel conversion before the combustion into syngas. This process

biomass and many petroleum. • The most valuable product of pre-combustion method is syngas and it's used in combined cycle in order to produce power and sometimes as feedstock for the wide range of other chemical purposes.	is complex because of conversion of fuel before treating with the syngas and this step is essential for the execution.

Post-combustion

Merits	***Demerits***
• This method is swiftly applicable according to the current technology for the capturing of emission. Moreover, this may consider the quite economical and pretty important green technology as well. • Thus, after some retrofitting on power plants its efficiency of decreasing the concentration of emission can be minimized. • While maintenance or having trouble shootings we can proceed the operation with any delay or break and also can control easily. • By using an absorbent specifically "Activated Carbon" it has dramatic impact in order to establish environment clean and its eco-friendly. • For the deduction of Carbon dioxide by using these technologies have tremendous impact and its compatible for short term.	• In drawbacks first one is, need development for the absorbents efficiency and concentrated in order to make the process economical. • Also in this process is the problem is lack of availability of the compatible sorbent for the capturing of Green House Gas. • Extra energy needs for the compression of CO_2. Moreover, in flue gas Carbon dioxide concentration is low this makes the trouble to extract in low amount. • This process operates at low temperature in contrast with pre-combustion at high temperature, sometimes it's hard for the sloid sorbent to enhance their efficiency. • At low pressure appr. at 1 bar carbon dioxide is separated. Then, the low concentration stream (3 to20%) has high temperature like 120 to 180 Degree C. So, this stream also contains the nitrous and sulfur product into it. [**17**]

4.7 Exhaust gases in combustion of variety of fuels their Mass, and many other important factors.

In this era of technology dozens of fuels are consuming in order to the energy demands, like gases, liquified gas, liquid, thick liquid fuel, solid fuel and bio-fuel. For these reasons, it necessary to know the nature of these fuel according different state. In given table 6. Highly using fuels are discussed. [18]

Table 6: Mass of exhaust gases which may release due to burning of variety of fuel

Fuel	Liquid density	Specific carbon content	Specific Energy content		Specific CO_2 emission (amount of fuel basis)			Specific CO_2 emission (amount of energy basis)		
	kg/l	kg_C/kg_{fuel}	kWh/kg_{fuel}	Btu/lb_{fuel}	Kg_{co2}/kg_{fuel}	Kg_{co2}/gal_{fuel}	lb_{co2}/gal_{fuel}	kg_{co2}/kWh	kg_{co2}/GJ	lb_{co2}/mill Btu
Methane (natural gas)		0.75	15.4	23900	2.75			0.18	50	115
Propane	0.510	0.82	13.8	21300	2.99	5.78	12.7	0.22	60	140
Butane	0.564	0.83	13.6	21100	3.03	6.47	14.3	0.22	62	144
LPG (wt of C3=C4)	0.537	0.82	13.7	21200	3.01	6.12	13.5	0.22	61	142
Gasoline	0.737	0.90	12.9	19900	3.30	9.20	20.3	0.26	71	165.3
Kerosene (Jet)	0.821	0.82	12.0	18500	3.00	9.33	20.6	0.25	70	162.5
Diesel	0.846	0.86	12.7	19605	3.15	10.1	22.3	0.25	69	160.8
Heavy fuel oil (No.6/Bunker C)	0.980	0.85	11.6	18000	3.11	11.6	25.5	0.27	75	173.3
Petroleum coke		0.89	9.4	14500	3.26	14.7	32.4	0.35	97	225.1
Coal:										227.3
Anthracite		0.92	9.0	14000	3.37			0.37	104	229.5
Bituminous		0.65	8.4	13000	2.38			0.28	79	231.7
Subbituminous		0.4	6.8	10500	1.47			0.22	60	233.9
Lignite		0.3	3.9	6000	1.10			0.28	79	236.1
Coke		0.77	7.2	11200	2.82			0.39	108	251.5
Peat (dry) 1)		0.52	4.7	7300	1.91			0.40	112	260.7
Ethanol fuel (E100) 2)	0.789	0.52	8.3	12800	1.91	5.71	12.6	0.23	64	149.6
Methanol fuel (M100) 2)	0.791	0.37	5.5	8500	1.37	4.11	9.1	0.25	70	162.2
Biodiesel (B100) 2)	0.880	0.78	11.3	17400	2.85	9.48	20.9	0.25	70	162.8
Wood 1) 2)		0.50	4.5	7000	1.83			0.41	113	263.1
Bio energy 2)								0 2)		

5.0 Conclusions

This work is investigated the steam methane reforming in order to produce Hydrogen as a non-carbonaceous fuel/low-emission carbon fuel and consequently Carbon Dioxide a Green House Gas also produce as a by-product. The main aspect is that to separate carbon dioxide which may produce while SMR process, and it's separated from flue gas by using MEA solvent and this all phenomenon occur in post-combustion of methane. When the flue gases produce it is necessary to capture CO_2 and also its scalability is critical and quite serious issue. Because, it consumes high amount of capital of the investor.

However, another technique which is pre-combustion of methane gas, where methane combustion early and from the flue gas CO_2 separated and Hydrogen provide as carbon free fuel. It's pretty good approach but its not cost effective either. Moreover, this approach is going to be obsolete.

Currently, we have to pace up our R &D domain to find the alternate for our energy requirements by applying the renewable energy. The thing is clear fossil fuel is convenient and easily available option comparatively renewable energy but at the same time it has severe impact on our climate and if we do condition of its exhaust/flue gases it has dramatic capital cost impact. This reason create problem for power sector and also put stringent regularities.

Here is also precise explanation of air fuel ratio of methane fuel and many other fuels. By using this, we can determine the different fuel stoichiometric values and air-fuel ratio.

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