Gasification of Dry Biomass with Carbon dioxide Sequestration

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in

Thermal Engineering

Submitted By

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THAPAR UNIVERSITY, PATIALA

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CERTIFICATE

I hereby declare that the thesis entitled **"Gasification of Dry Biomass with Carbon dioxide Sequestration"** is an authentic record of my work carried out as requirements for the award of the degree of **Master of Engineering** in **Thermal Engineering** at **Thapar University, Patiala** under the supervision of **Dr. Sandeep Kumar**, Assistant Professor, Mechanical Engineering, Thapar University, Patiala during July, 2015 to July, 2017. No part of the matter embodied in this report has been submitted to any other university or institute for the award of any degree.

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It is certified that the above statement made by the student is correct to the best of my/our knowledge and belief.

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Dedicated to

All my respected teachers, caring parents and siblings

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Abstract

Gasification, a thermo-chemical process, is explored as a promising technology towards carbon capture. The present work focuses on using CO_2, from the product of combustion of fuels in an engine or a combustion device, as a co-reactant along with other reacting media. Experiments were conducted with CO_2 volume fraction varied from 0 to 15% in a mixture of O_2 and N_2. Increase in CO_2 fraction resulted in decrease in bed temperature, primarily due to reduction in O_2 fraction, in the gasifying medium, and the endothermic reaction of char and CO_2. Low bed temperature was addressed by maintaining the O_2 volume fraction in the input at 21% by introducing additional oxygen. At 15% CO_2 injection, the CO fraction increased from 13.1% to 16.3% and over 55% of the input CO_2 conversion was noted. Recorded an increase in cold gas efficiency by 30% owing to higher conversion rate of char. Working with the engine exhaust also eliminates the cost incurred in separation of CO_2 and makes the system less complicated.

Further, thermodynamic equilibrium studies has been performed addressing the issue of lower bed temperature during experiments. with CO_2 as reactant. NASA SP 273 software has been employed to study the temperature variation under adiabatic and isothermal condition. Equilibrium analysis has provided an oppurtunity to identify the optimum O_2 fraction required to maintain the bed temperature with CO_2 as reactant similar to those of air gasification. The higher O_2 fraction with increased CO_2 in input has been identified and analysed. The system is found to shift from gasification to combustion regime with the increase in Euivalence Ratio (ER) as O_2 fraction increases with CO_2 fraction. The operation at higher ER is leading to slightly lower efiiciencies.

Present work recommends to operate at O_2 fraction of 21% when CO_2 fraction in reacting media is low but to operate at higher O_2 at higher CO_2 fractions. The experiments at higher O_2 fractions is suggested as future work.

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Nomenclature

CO_2	Carbon dioxide
CO	Carbon monoxide
CH_4	Methane
H_2	Hydrogen
H_2O	Water
O_2	Oxygen
H/C	Hydrogen carbon ratio
CCS	Carbon capture and storage
NOx	Nitrogen oxide
SO_2	Sulphur dioxide
NO_2	Nitrogen dioxide
H_2S	Hydrogen sulphide
HCl	Hydrochloric acid
CNG	Compressed natural gas
SOx	Sulphur oxide

Chapter 1

Introduction

1.1 Biomass Gasification: Concept and Significance

With growing demand for clean energy and decaying reserves of fossils fuels, search for another energy sources has been originated which can substitute fossil fuel based economy (Kucuk and Demirbas, 1997). Carbon dioxide and other greenhouse gases emissions due to the immoderate use of fossils fuels lead to global warming resulting in climate change. Different renewable energy technologies based on solar, hydro, the wind, biomass resources are expressed as a clean, sustainable and most importantly less harmful towards nature (Mahapatra, 2016). The biomass share in current world energy consumption is 13.9% with 4.2% in North America, 37.8% on average in developing countries, and 86% in the least developed ones (Li, 2002) According to Renewable 2014 Global Status Report, overall energy utilization of biomass came to around 57 EJ in 2013, out of which just about 60% was conventional biomass, and the rest was current bio-energy (REN 21, 2014). It has also been recognized as an ideal energy resource that can be used for the decentralized energy systems. Renewable sources contributed approximately 22.1% of total electricity production, out of which 1.8% share is from biomass energy in the world (REN 21, 2014). Presently, thermochemical conversion and biological conversion are generally encomiastic technologies, which are generally accepted for economic usage of biomass as an origin of modern energy (Mahapatra, 2016).

Biomass energy is the energy accommodated in plants and non-fossil organic matter. It has a considerable range in form. Biomass fuels include wood, agriculture residue, garbage waste, sugarcane bagasse, field crop residue, sawdust, algae and organic wastes. Wood and wood waste account for more than 62% of the total. A typical empirical molecular formula derived from the ultimate analysis of the species for woody biomass can be expressed by $C_{3.3\text{-}4.9}H_{5.1\text{-}7.2}O_{2.0\text{-}3.1}$, considering a molecular weight of 100, when only three primary elements are assumed (Li, 2002).

Biomass is neutral in greenhouse emission circulation within the earth region as a result of the quantity of greenhouse it consumes through chemical change is that the same as that offers off by combustion. That's why; biomass is taken into account a “carbon-neutral” fuel. As

a renewable energy source, as a renewable energy supply, biomass is especially appropriate for countries with few fossil energy sources.

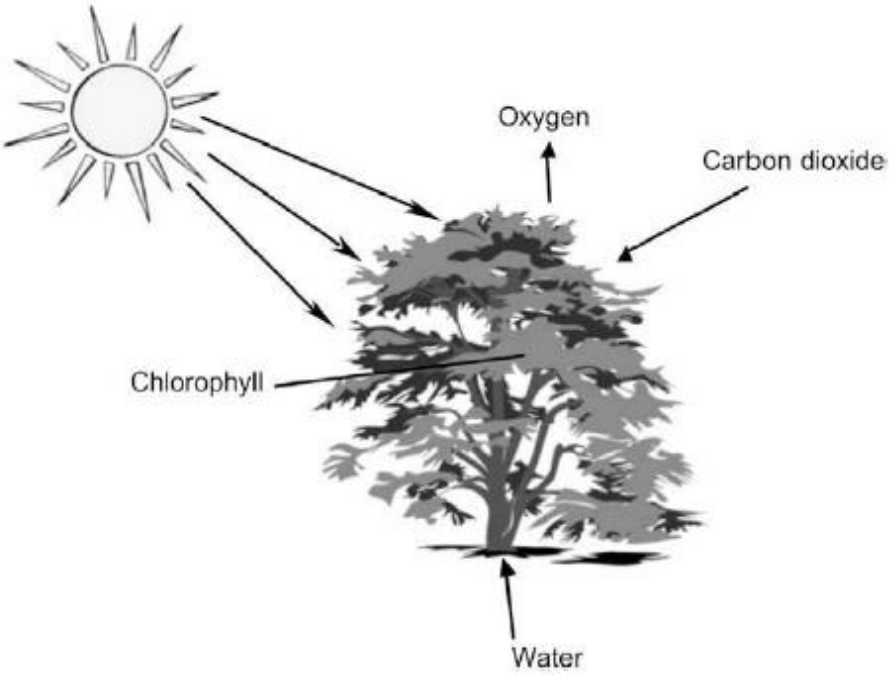

Figure 1.1 Biomass grows by absorbing solar energy, carbon dioxide, and water through photosynthesis (Basu, 2010)

1.1.1 Classification of Biomass Products

Classification of primary energy source is formed from biomass:

- Liquid (CH_3OH, C_2H_5OH, etc.)
- Gaseous (biogas, producer gas, syngas)
- Solid (charcoal, torrefied biomass).

1.1.2 Biomass Conversion

Due to inconvenient form and heavy mass of biomass, it is difficult to convert fossil to biomass fuels. Gases or liquids can be stored, transported or handled easily, but biomass cannot. This results in a big encouragement for the transformation of agriculture waste into fuel forms, which can be attained by given significant paths (Figure 1.2).

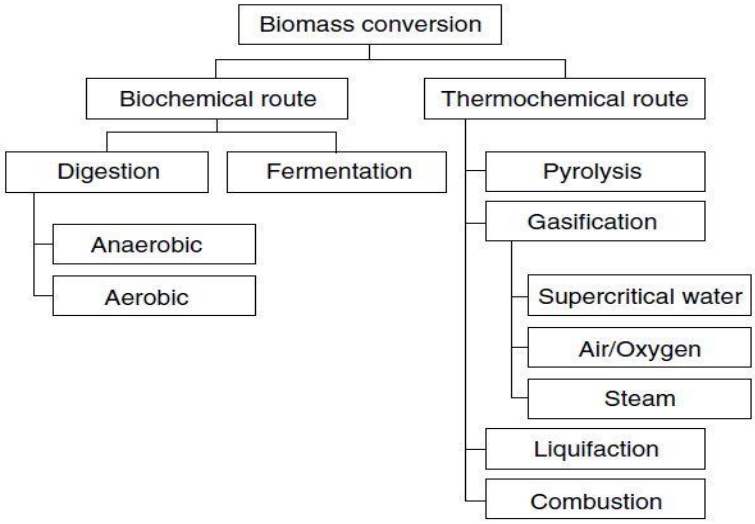

Figure 1.2 Two approaches, chemical and biological, for transformation of biomass into fuel, gases (Basu, 2010)

Biochemical Conversion

In biochemical change, biomass particles are dampened into smaller parts by micro organism or chemicals. This method is very slow than thermochemical transformation, however, doesn't need a lot of external energy. The principle routes for biochemical conversion are:

- Digestion (anaerobic and aerobic)
- Fermentation
- Enzymatic or acid hydrolysis

The principle results of anaerobic digestion are methane and carbon dioxide in addition to a solid residue. Microorganisms access oxygen from the biomass rather than from the ambient air. Aerobic digestion, or composting, is additionally a biochemical breakdown of biomass, except that it takes place in the presence of oxygen. It uses different kinds of bacteria that access O_2 from the air, producing CO_2, heat, and a solid digested.

In fermentation, a part of the biomass is transformed into sugars using enzymes. The sugar is then converted into ethanol or different chemicals with the usage of yeasts. The lignin is not reformed and is left either for combustion or for thermochemical change into chemicals (Basu, 2010).

Lignocellulosic feedstock, like wood, needs hydrolysis pre-treatment (acid, enzymatic, or hydrothermal) to interrupt down the cellulose and hemicellulose into simple sugars required by the yeast and microorganisms for the fermentation process. Acid hydrolysis technology is a lot of mature than catalytic hydrolysis technology.

Thermochemical Conversion

In this conversion process, the biomass is changed into the gaseous product, and then these are integrated into the desirables chemicals. The Fischer-Tropsch reaction gives synthetic gas which is further converts into liquid transport fuels (Basu, 2010). Major routes for thermochemical conversion are:

- Combustion
- Pyrolysis
- Gasification
- Liquefaction

Combustion

In this process, heat energy is liberated when reaction takes place between oxygen and carbon content in biomass. Here, the biomass is transformed into main steady constituents: water and Carbon dioxide. Heat energy emitted during the reaction is the major source of energy utilized by human beings.

Pyrolysis

Not at all like combustion, pyrolysis occurs in the non-existence of oxygen, other than the types wherever incomplete combustion is permitted to supply the energy required for this method. In this process, the breakdown of biomass into gaseous, liquid and solid products caused by application of heat. In pyrolysis, bigger molecules of hydrocarbon are split into smaller ones. Liquid fuel is the main product of fast pyrolysis and whereas slow pyrolysis process provides charcoal and gas which is being utilized for heating and extraction of metal.

Gasification

Gasification is the process in which fossil or non-fossil fuels are transformed into effective chemical and gaseous products. The medium required for the feasibility of this process can be supercritical water or gases like O_2, air, subcritical steam. For example, a usual biomass has around 40 to 60% oxygen by weight, but an effective gas carries a smaller proportion of O_2. Gasification of biomass additionally includes expulsion of O_2 from fuel to enhance its energy density. The removal of O_2 from biomass can be achieved by using dehydration or chemical change. The latter method, which emits the O_2 through Carbon dioxide, enhances the Hydrogen/Carbon ratio of the fuel to lower the emission of greenhouse gas.

Liquefaction

Pyrolysis, Gasification and hydrothermal process may be used for transformation of solid biomass into liquid fuel. In this approach, biomass is processed into a liquid (oil form) by blending the biomass with H_2O at high temperature (305–355°C) and pressure (13–21 MPa) for certain time period.

1.1.3 Basic Components of Gasification process

Gasification is one of the most promising clean energy options to utilize biomass. Biomass gasification is a method that transforms carbon containing materials like biomass into gaseous fuels. This process gives clean and combustible gases by the pyrolytic reaction as compared to other processes. For thermochemical conversion of biomass for complete combustion the theoretically 5.9 to 6.4 kg of air is needed for one kg of biomass which is called stoichiometric and the end products are Carbon dioxide and water and for gasification, biomass is partially oxidised under sub-stoichiometric condition with the air quantity being restricted to 1.3 to 1.7 kg of air for each kg of biomass. The mixture of formed during gasification process is called producer gas, which contains carbon-monoxide (CO, about 20-22%)), Hydrogen (H_2, about 20 to 22%), Carbon-dioxide (CO_2, about 12-14%) Methane (CH_4, about 1-2%) and the rest is Nitrogen(N_2) and water vapour (H_2O). The product gas additionally carries tar and particulate, which must be expelled relying on the application. Although, this product can be burned at a moderately high efficiency and a good level of control without radiating unburnt fuel. Normally transformation efficiencies for the process of gasification are 62% to 81%. Producer gas is an imperative method reasonable for complete burning, relevant in prime movers, for example, motors and turbines, or for the yield of synthetic natural gas (SNG) and transportation fuels. In gasification, moisture is removed from biomass in drying zone after which its breakdown takes place in the pyrolysis zone with the application of heat. Char, tar, and gases are the end product that is obtained after pyrolysis which repeatedly reacts with each other and also gasifying medium to produce a final product of gasification with bio products such as tar, char and ash. In gasifiers that are used on an industrial scale, the energy required for drying, pyrolysis process and endothermic reactions attains exothermic combustion reactions permitted in the gasifier. A large amount of tar is contained in gas produced from this process which can create hindrance in the downstream process by obstructing gas coolers, filter parts.

Gasification process consists of a two-stage reaction which is oxidation and reduction processes. In the oxidation part, removal of volatiles from biomass and it is exothermic

reactions (1400 to 1500 K) and products such as CO, H_2. In the later part, CO_2 and H_2O which is converted into CO and H_2 by the hot bed of charcoal (C) produced during gasification process. The reduction is a reaction in which energy is utilized to produce flammable products such as carbon monoxide, hydrogen, and methane. Since char is produced during the gasification process due to which it is spontaneous. The reaction which takes places is as follows.

$C + CO_2 \rightarrow 2CO$ (Boudouard reaction)

$C + H_2O \rightarrow CO + H_2$ (Water gas reaction)

$C + 2H_2 \rightarrow CH_4$ (Methanation reaction)

$CO + H_2O \rightarrow CO_2 + H_2$ (Water gas shift reaction)

Gasification is better than the production of biogas because a variety of materials are available that can be subjected to gasification as compared to specific materials which can be used for biogas production. It is mandatory to evaluate the suitable working condition for gasifier operation in aspects of temperature, equivalence ratio, gasifying medium and coal to biomass ratio, taking into consideration the possible output gas composition from biomass-coal co-gasification. It should be kept in mind that quality of producer gas required for different applications are different viz., power generation and synthetic liquid fuel. In the former case, need to optimize the condition under which the producer gas has highest lower heating value, while in later situation, the hydrogen to carbon monoxide ratio is important. In this study, it has been tried to optimize the condition for maximum LHV and H_2 concentration, by Chemical Equilibrium with Application Program (CEA), developed by NASA based on Gibbs free energy minimization technique. This simulation is based on non-stoichiometric equilibrium modeling. The parametric evaluation over a wide range of operating conditions is studied for estimation of gas composition, LHV of the product gas. The variable parameters for the optimization process are viz., the percentage of coal to biomass ratio, equivalence ratio, gasification temperature, gasifying medium and carbon conversion. The main problem associated with the use of gasifier for power generation is the tar content of the producer gas. To use the output gas produced from the gasifier, in an engine for power generation, it must be clean, i.e., there should not be any particulate matter, dust or tar. The tar content in the producer gas besides only depending on operating conditions; it also strongly depends on the feedstock used in the gasifier.

1.1.4 Gasification Process Zones

Under the consideration of auto-thermal system, several stages of gasification process can be seen in sequence. Figure 1.3 reported the schematic description of the gasification process. The steps followed by the gasification process are:

(1) Drying (endothermic stage).

(2) Pyrolysis (endothermic stage).

(3) Combustion or oxidation (exothermic stage).

(4) Reduction (endothermic stage).

One additional step has been introduced for decomposition of large tar molecules in order to form of light hydrocarbons.

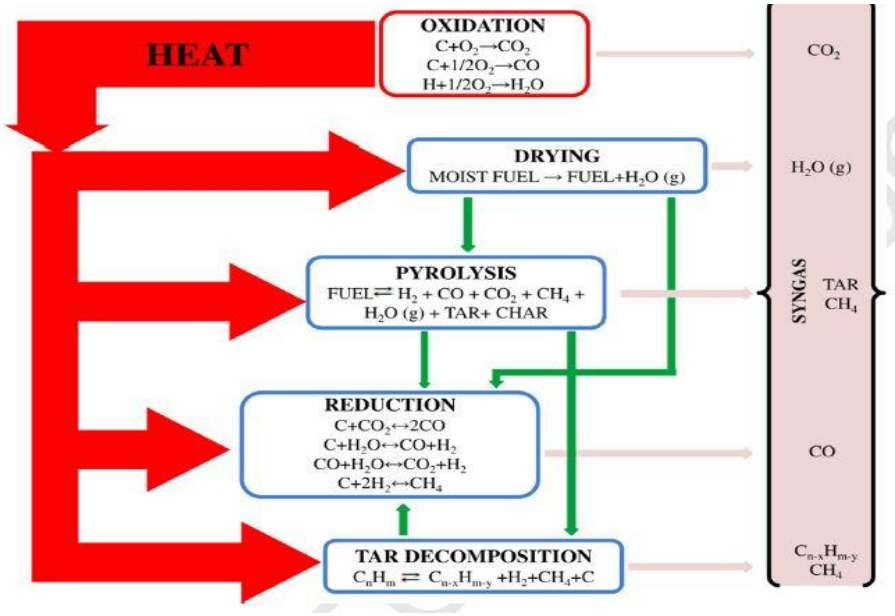

Figure 1.3 Biomass gasification processes (Molino et al. 2015)

a. Drying Zone

The main aim of this zone is drying of wood. Wood has a moisture content of 10-30% during the entering in the gasifier. A number of experiments has been done on different gasifiers in different conditions which showed an average condensate formed of gasified wood i.e. 6-10% of the weight. During the drying process, some organic acids were also come out which increased the chance of corrosion in the gasifiers.

b. Pyrolysis zone

Wood pyrolysis is very complicated process still that is not understood completely. The products obtained from pyrolysis depend upon different parameters i.e. temperature, pressure, residence time and heat losses. The moisture present in the biomass is removed at about 200^{o}C temperature. Between 200 to 280^{o}C CO_2, CH_3COOH and H_2O are released during the reaction. The pyrolysis process was carried out in between 280 to 500^{o}C temperature which produced a large amount of tar and gases containing carbon dioxide. On the other hand, light tar and some methyl alcohol are also formed. A small amount of production gas was observed between 500 to 700^{o}C temperature. Thus it was seen that updraft gasifier was produced much more tar than that of downdraft gasifier. In downdraft gasifier, the tar passed through combustion, reduction zone and is partially broken down. Downdraft gasifier is selected over others because of fuels alike wood and biomass residue have a large amount of tar.

The pyrolysis process can be schematized with the following overall reaction:

Biomass $\rightarrow H_2 + CO + CO_2 + CH_4 + H_2O$ *(g)* + Tar +Char *(*Endothermic*)*

c. Combustion zone

The solid fuel is usually formed of different elements such as carbon, hydrogen and oxygen. In complete combustion, carbon dioxide is attained from carbon present in fuel and water is formed from hydrogen (steam). This reaction is exothermic in nature and maximum theoretical temperature can be obtained by oxidation is 1450^{0}C. The main reactions are:

$$C + O_2 = CO_2 + 393 \text{ MJ/kg mole} \quad (1.1)$$

$$2H_2 + O_2 = 2H_2O - 242 \text{ MJ/kg mole} \quad (1.2)$$

d. Reduction zone

After combustion zone, the products such as water, un-combusted partially cracked pyrolysis products and carbon dioxide from partial combustion were passed through a red hot charcoal bed and then the subsequent reaction occurred.

$$C + CO_2 = 2CO - 164.9 \text{ MJ/kg mole} \quad (1.3)$$

$$C + H_2O = CO + H_2 - 122.6 \text{ MJ/kg mole} \quad (1.4)$$

$$CO + H_2O = CO + H_2 + 42 \text{ MJ/kg mole} \quad (1.5)$$

$$C + 2H_2 = CH_4 + 75 \text{ MJ/kg mole} \quad (1.6)$$

$$CO_2 + H_2 = CO + H_2O - 42.3 \text{ MJ/kg mole} \quad (1.7)$$

Reactions (1.3) and (1.4) are main reduction reactions and being endothermic have the ability of decreasing gas temperature. As a result, the temperatures in the reduction zone are generally 800-1000^{0}C. Reducing the reduction zone temperature (~ 700-800^{0}C), lesser is the calorific value of gas or higher is the tar content. Also, reactions (1.3) and (1.4) are known as Bouduard reaction and Water gas reaction respectively.

1.1.5 Biomass Gasification Technologies

Based on the model of gasifiers and variety of fuels used, there are distinct types of gasifiers. The figure demonstrates the distinctive technique of gasifiers: fixed bed type, fluidized bed type, and entrained flow. Every one of these procedures can be worked at atmosphere or higher pressure and perform the basis of chemical conversion of biomass. Classification of gasifiers is updraft, downdraft, cross-draft, fluidized bed, and circulating fluidized bed. Differentiation is relying upon the methods for supporting the biomass in the reactor, the path of flow of the solid biomass, oxidation medium, and source of heat is provided to the vessel. Fixed bed gasifiers are usually simpler, cheap, and generate lower heat content producer gas. Fluidized bed gasifiers are generally complex, costly, and generate a gas with an HHV.

Updraft or Counter Current Gasifier

In this type of gasifier, biomass descends downwards the gasifier and gasification air flows upwards while undergoing thermochemical reactions. The moisture and tar contents in PG are high. So, the bottom lit updraft gasifier can be described as “char burning and tar making” gasifier. Due to high tar content, the PG generated by this type of gasifier is not suitable for engine application. During gasification process, tars and volatiles will be carrying in the gas stream. The bottom ash that is produced, removed from the lower part of the gasifier.

There are several advantages of this type of gasifier over traditional gasifiers are they have simple design to built, high burning ratio of charcoal, very efficient in terms of efficiency and decreases the low gas exit temperature due to internal heat exchange, this gasifier has many possibilities to operate with several types of feedstock (sawdust, hulls, etc.). As this gasifier has also had few disadvantages over several advantages like several possibilities of channeling of this gasifier, cause dangerous explosive situation by break-through of the of the oxygen, it require to install some automatic moving grates, and this also require to get rid from the disposal of tar-containing condensates it requires a frequent cleaning operation.

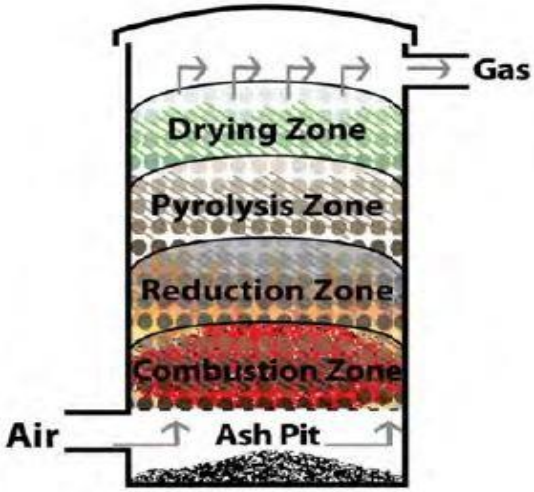

Figure 1.4 Updraft or counter-current gasifier (Gasification, 2015)

Downdraft or Co-current Gasifiers

The co-current or downdraft gasifier has been introduced to solve the problem of tar entrainment in the gas flow. It could be possible by designing the primary gasification air supplied at or above the oxidation zone in the gasifier. Hence, producer gas is obtained at the bottom of the gasification and also fuel and producer gas move along the same direction in gasifier as shown in figure 1.5. The tar and acid distillation products from the fuel along the bottom of gasifier must go through a charcoal which is a glowing bed. In this way, products are changed into permanent gases carbon monoxide, hydrogen, carbon dioxide and methane. Also, the more or less fully breakdown of the tars depends on the temperature of the hot zone and maximum residence time the tar vapors.

The main advantage of downdraft gasifiers lies in the possibility of producing a tar-free gas suitable for engine applications. In practice, however, a tar-free gas is seldom if ever achieved over the whole operating range of the equipment. Because of the lower level of organic components in the condensate, downdraft gasifiers suffer less from environmental objections than updraft gasifiers. A major drawback of downdraft equipment lies in its inability to operate on a number of unprocessed fuels. In particular, fluffy, low-density materials give rise to flow problems and excessive pressure drop, and the solid fuel must be pelletized or briquette before use.

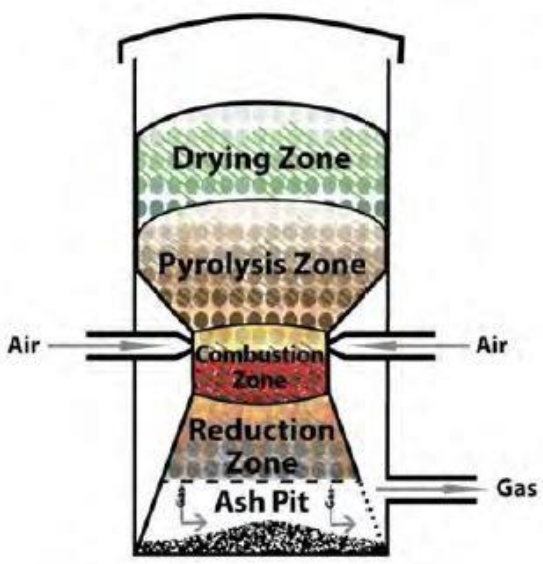

Figure 1.5 Downdraft or co-current gasifier (Gasification, 2015)

1.2 Gasification for Energy use of Biomass

Gasification is a thermochemical process where less than the stoichiometric amount of oxygen is supplied to convert carbonaceous materials into gaseous fuels using media such as air, oxygen, and steam. Biomass can be pyrolyzed or gasified for many energy uses, such as producing synthesis gas, hydrogen, methanol, bio-oil, fuel-cell applications, as well as for making raw fuel gas for combustion in process applications or for combined cycle power generation. Because of the relatively small size of biomass gasifiers compared to coal units, it is rarely economically justified to build an oxygen plant to supply pure oxygen for gasification. Instead, air-blown biomass gasifiers can be used to produce low-calorific value gases with higher heating values of typically 3-7 MJ/m^3. Such low-quality gases cannot maintain high enough temperature to maintain combustion in a furnace cooled with membrane walls when fired independently. Instead, the gas can be co-fired in a PC boiler to partially displace coal (Babu, 1995). Another reason for co-combustion is that the process requires virtually no gas cleaning since the gas is directly fired. In addition, little integration is needed. In co-combustion, the gasifier is integrated into the steam cycle instead of a gas turbine cycle, greatly reducing the maintenance and service cost. If the gasifier is shut down, the rest of the plant can continue to operate without being much affected.

Alternatively, biomass fuel gas can be used in a combined cycle power plant with a gas turbine, as in the biomass integrated gasifier/gas turbine (BIG/GT) system. A recent study(Williams and Larson, 1996) shows that a biomass integrated gasifier/ steam injected gas

turbine(BIG/SIGT) and its modified version, the biomass integrated gasifier/intercooler steam-injected gas turbine (BIG/ISIGT) both enjoy major cost reductions compared with the double extraction/condensing steam turbine (CEST) system. The viability of this highly integrated configuration depends on a number of factors, the most important being the removal of tars and alkali metals from the gasifier product. The tolerable tar and alkali loading for toady's gas turbine usually do not exceed 100 ppb and 250 ppb respectively (Williams and Larson, 1996; Babu, 1995).

Over the past century, many processes have been developed for gasifying different feedstocks from biomass, coal and municipal wastes. Because of the common fundamental principles, processes for biomass gasification are closely related to coal-based processes, but with some distinct characteristics. These processes can be classified in a number of ways.

There are high-temperature processes operating at 850-1200^{0}C discharging ash as smelt, and low-temperature processes at 600-850^{0}C discharging solid ash, depending on the fuel and process employed. Since the ash content is very low (<3% for most woody biomass), ash discharge is hardly needed. However, biomass gasification generally involves particulates materials like sand and dolomite, either as the bed material or as catalyst or sorbent. Depending on the working pressure, gasification processes can be classified as atmospheric, as most biomass gasifiers are, and pressurized (Kurkela and Stahlberg, 1992; Knight, 2000).
Depending on the hydrodynamic properties of reactors, gasifiers can be fixed or moving beds, bubbling or circulating fluidized beds, spouted beds, rotary kilns or some combination of these types. Gasifiers may be directly heated (most gasifiers), or indirectly heated, usually employing molten salt designs (Pletka et al., 2001).

A number of gasifying agents can be used. While air, oxygen, and steam are most common, some gasifiers employ hydrogen, carbon dioxide or mixtures of these gases (Hebden and Stroud, 1981). Other possible gasifying agents include molten salt ballast and supercritical water. Air-blown processes produce low-quality gases with a higher heating value (HHV in the range of typically 3-7 MJ/Nm^3, while oxygen- and steam-blown processes provide gases with HHV of 10-18 MJ/Nm^3.

1.3 Carbon Sequestration

Carbon sequestration is storing atmospheric CO_2 that is removed from the atmosphere or before it enters the atmosphere. Carbon sequestration also defined the long-term stock of CO_2 or other forms of carbon (C) to either mitigate or defer global warming and avoiding dangerous

levels of environmental change. It has been suggested as a method to slow the atmospheric and marine accumulation of greenhouse gases, which are emitted by burning fuels. Carbon dioxide is naturally trapped from the ambient through biological, chemical or physical processes. Some artificial sequestration forensic techniques exploit this natural scientific procedure, while some use entirely artificial processes.

CO_2 is a secondary product that outcomes when the energy of a carbon containing fuel is outcomes during the burning of these fuels. It comprises the deployment of technologies for selectively:

(1) Capturing CO_2 from power stations and industrial sites

(2) Compressing and transporting

(3) Storing it in geological formations by injecting it into suitable, permanent sites underground.

The foremost application of CCS is to control the CO_2 formation from carbon contained fuel. However, CCS may also be utilized to CO_2 demanding industries, for example, petrochemicals, oil and gas processing, cement, iron, and steel.

CCS technology could minimize the CO_2 exhaust from large industrial and power stations by around 85% depending on the kind of non-capture plant displaced. CCS has the capacity to minimize significantly greenhouse gas radiations and permit the continual utilization of carbon content fuels for energy safety.

1.3.1 Carbon Sequestration Strategies

There are three generic process routes for capturing CO_2 from fossil fuel combustion plants:

- Post-combustion capture
- Pre-combustion capture.
- Oxyfuel combustion.

Each of these processes involves the separation of CO_2 from a gas stream. There are five main technologies available for doing this, with the choice depending on the state (i.e. concentration, pressure, volume) of the CO_2 to be captured:

- Chemical solvent scrubbing.
- Physical solvent scrubbing.
- Adsorption/desorption.
- Membrane separation.
- Cryogenic separation.

Pre Combustion Capture:

Pre-combustion capture produces hydrogen by eliminating of carbon dioxide before combustion. Hence, the water vapor being the only secondary product remains left after hydrogen combustion (carbon dioxide emission free). However, free carbon dioxide (CO_2) emission fuel could be provided by this technology that is used with carbon storage.

The capture process is comprised three stages are as follows: Firstly, Hydrogen and carbon monoxide (CO) produce by converting the hydrocarbon fuel to form a synthetic gas. Further, the carbon monoxide (CO) convert into carbon dioxide (CO_2) by reacting it with water that is known as shift conversion, in the second step. At last, carbon dioxide and hydrogen are separated because the hydrogen can be combusted without carbon dioxide emission. After that, the carbon dioxide can be compressed to convert it into liquid for easily transporting to a storage site.

Pros:

- Demonstrated modern scale innovation in oil refineries, however, requires three times scale-up for power plants.
- Around 90% emissions of carbon dioxide can be trapped.
- Suitable for coal fired Integrated Gasification Combined Cycle power plants.
- Hydrogen can be obtained from coal but with poor efficiency.

Cons:

- The chemical plant is installed near to gas turbine which is dangerous from a safety point of view.
- High initial capital cost.
- Costly scrubbers are needed to minimize emissions of oxides of nitrogen.
- The efficiency of turbines with hydrogen as a fuel is lesser than traditional turbines.
- Not suitable in a situation of load fluctuation.

Post Combustion Process:

Post-combustion capture process includes after hydrocarbon combustion to remove the lean carbon dioxide (CO_2) from flue gases. It can be easily integrated to existing power stations and industrial plants (known as retrofitting) with minimal modifications to the original plant. This is the technology that was preferred by the UK Government.

There are a lot of methods are available for capturing the carbon dioxide (CO_2). The very common method is flowing the carbon dioxide through solvent (amine solvent are usually used) and absorbing it. Further, the carbon dioxide will drive off by changing temperature and/or pressure. Secondly, the carbon dioxide can be removed by developing calcium cycle capture. In this method quicklime produces limestone by capturing carbon dioxide and further, it can be heated for releasing carbon dioxide and hence, quicklime can again use. In both of this method, there is a requirement of extra energy input for releasing carbon dioxide from the solved. Hence, this increases the additional energy costs approximate 20 to 30 % as compared to no capture. However, the new solvents are in developing stage and estimated to reduce this penalty to 10%.

Pros:

- It is possible to modify to industrial and electricity generation plant
- Applicable to trap carbon dioxide for which can be used in beverage industries.

Cons:

- More operational costs
- Constrained extensive scale working experience.

Oxy-Fuel Combustion Capture:

The pure oxygen is used for burning fossil fuels instead of air in an oxyfuel combustion capture process and its result provides a complete combustion. Hence, exhaust stream comprises only water vapor and pure carbon dioxide (usually 90%). While carbon dioxide and water vapor can be easily separated by condensation.

The challenging problem of this method is extracting oxygen from the air. However, this is usually done cryogenically that requires a huge amount of energy (generally for 500MW coal-fired power station providing pure oxygen requires an energy at least 15% of the electricity the plant produces annually). While a new technology named as chemical looping is in developing stage. By this technique, the oxygen in the air is extracted by oxidation of a metallic compound that can be reduced during combustion allowing the oxygen to be driven off.

1.3.2 Transportation

In the present time, transport is slightly complex part in the carbon dioxide trapping and storage as technique is already in use and cost can be calculated. The main troublesome with

transportation of carbon dioxide is that it acts separately under changing pressure and temperature due to which its transportation should be handled with care to avoid any blockage
There are two approaches used for transporting large volumes of carbon dioxide by industry:

- Pipeline Transport
- Ship Transport

Pipeline Transport

Carbon dioxide is transported in supercritical/dense phase, so all the pipeline is designed for these conditions. This prevents solidification of the carbon dioxide and permits it to be pumped as a liquid phase. Usually, the pressure is maintained above 10 MPa by pressurizing along the pipelines.
Methane, nitrogen, hydrogen sulfide and water are the impurities which the properties of carbon dioxide. While water is the most dangerous of these because an acidic solution generates when carbon dioxide dissolved in the water that attacks metal pipelines. Furthermore, solid ice like carbon dioxide hydrate crystals can generate when water and carbon dioxide mix resulting pipeline blockages and these indicate that the carbon dioxide must be dried during transportation.

Ship transport

Large amount transportation of carbon dioxide has been fixed to the brewing and food industry to date. These industries transport nearly 1 lakh tons of carbon dioxide per year. Whereas the transportation of carbon dioxide by ship is in a discrete manner so, the storage tank facilities would be required in the interim.

1.3.3 Storage

CO_2 storage is simply the process of taking captured CO_2 and then placing in a location where it will not be in contact with the atmosphere for thousands of years. Storage of the CO_2 in underground sites beneath a layer of impermeable rock (cap rock) which acts as a seal to prevent the CO_2 from leaking out is the most popular option at present.
There are three main types of proposed underground storage sites:

Depleted Oil and Gas Reservoirs

CO_2 can be pumped into the reservoirs to fill the empty spaces left by removal of hydrocarbons. The geology of these reservoirs is well understood and they have stored oil and gas for a long time making them good sites for CO_2 storage.

Deep Saline Aquifers

CO_2 can also be stored in deep salt water-saturated rock formations. These exist worldwide and have the potential to store large amounts of CO_2. However, the geology and effect of the CO_2 on these aquifers are not yet well understood and more research is needed.

Deep Un-Mineable Coal Seams

CO_2 can be stored in deep coal seams where it will be held in the pores on the surface of the coal and in fractures. This has the additional benefit of forcing methane from the coal beds which can be used as fuel.

1.4 CO_2 Sequestration using Gasification

Amongst the technologies s receiving the most such attention to decrease CO_2 impacts is CO_2 capture and sequestration. This main function of this process to reduce and capture CO_2 from the burning fuel, either earlier, during, or after the combustion and to avoid its release to the environment. While other greenhouse gases (e.g., methane) are more effective in references to global warming effects per unit of mass,

The released gas especially carbon dioxide from the power plant and industries are so high as to dwarf the influences from other gases in terms of the inclusive effect on global warming. Hence, the main attention is on carbon dioxide sequestration technologies.

The comparative contributions of various fossil fuels to total energy-related carbon dioxide emission have changed over time. In 1920, CO_2 emission to the environment accompanying with liquid fuels made up an estimated 42% of the world total. In 2007, their percentage associate was 38 %. The pursuit of greenhouse gas emissions reductions has the potential by reducing global coal use significantly. The reduction of the carbon dioxide emissions will hike the price of coal comparative to the prices of other fuels (Kumar, 2016).

Amongst the emerging CO_2 capture technologies, absorption of CO_2 has received considerable attention. Absorption of CO_2 from the main flue gas stream is the most significant process. Alkanol amines (e.g., MEA - Mono-ethanol amine, and diethanolamine) are mostly utilized in the chemical absorption of CO_2 process. whereas methanol, dimethyl ether, polyethylene glycol, and sulfolane are generally used in the physical absorption of CO_2 (Halmann et al. 1998). The presence of SO_x and NO_x in flue gas stream also has a negative impact on the performance of the solvent based process. Comparatively, the ammonia

scrubbing technique has advantages for example lower cost of absorption material, higher absorption efficiency, a greater absorption capacity and less corrosion to the absorber, as well as capacity to save energy (Yeh et al. 1999).

The quantity of carbon dioxide that can be released from the exhaust is a function of the size of the absorption unit and the percentage of carbon dioxide in the exhaust. The recovery of flue gas from the typical plant is around 85% for 3% CO_2 in the exhaust and 90-92% for 8% (Bai et al. 1997). Adsorption processes are based on the selective adsorption of CO_2 on a solid adsorbent, such as zeolites, alumina molecular sieves, and activated carbon. Cao is one of the very promising high-temperature chemical sorbent, which can be utilized either directly or in modified form. It is freely obtained from limestone, which is abundantly available (Li et al. 2006). The sorption /desorption temperature is varied form 650-850 °C for modified Cao. The porous membranes, that are able to separate the different size of gas molecules, are existing in many forms, including polymers, metals and rubber composites. The separation membrane has some drawback in which the main drawback is its law gas throughput, and the need for a multistage operation or stream recycling (Hossain et al. 2008). The advancement of a membrane separator for the selective reduction of CO_2 in the existence of CO, H_2, H_2O, and H_2S (fuel gas) or N_2, O_2, H_2O, SO_2, NO_x, and HCl (flue gas) would be of incredible economic value. A membrane separation technique needs very less maintenance and power compared to the absorption system. Table I gives a glimpse of carbon capture and separation technologies with limitations and advantages.

This work involves an alternative strategy for dealing with CO_2. This propitious use of CO_2 involves its recycling into the fuel making process. Biomass gasification is explored as a promising technology to convert CO_2 to a fuel gas, identified as producer gas. CO_2, from the engine exhaust, is used as a co-reactant in the gasification medium, along with air. This work concentrates on capturing CO_2 from a typical combustion system like engine exhaust where CO_2 fraction varies from 12% (CNG) to 15% (diesel), on a dry basis. Scrubbing of SO_x/NO_x or particulate matter is not required. Condensing H_2O and mixing exhaust with a proportionate amount of O_2, eliminates the cost of separation and storage of CO_2 as well.

1.5 Challenges

There are a number of existing challenges that ultimately must be resolved before CCS can be demonstrated and widely deployed as a CO_2 emissions control option. As important as timely technology development is to establishing CCS, having definitive standards, practices, and

procedures; encouraging private-sector investment; and addressing liability and regulatory issues are also essential. Current barriers that could delay or if not resolved prevent the rapid deployment of CCS essentially fall into two categories: technical and non-technical. The key technical challenges to CCS include: (1) addressing the cost and energy penalty of capture; (2) proving CO_2 storage permanence; (3) verifying that sufficient storage capacity exists; and (4) developing best practices for the lifecycle of a CCS project, from site selection through to site closure and post-closure monitoring.

Non-technical challenges primarily consist of: (1) the global need for significant financial investments to bring numerous commercial-scale demonstration projects on-line in the near future; (2) establishing an adequate legal and regulatory framework to support broad CCS deployment, including dealing with long-term liability, and; (3) building public understanding, awareness and acceptance.

How Can These Challenges Be Effectively Addressed?

The climate change challenge has a global nature, both in terms of sustaining economic growth and in taking effective steps to reverse the increase in CO_2 and other GHG in the atmosphere. Consequently, an international effort of developed and developing countries, focused on technical, political, and scientific cooperation, is necessary to effectively address the challenges facing CCS. The Carbon Sequestration Leadership Forum (CSLF) is helping in this regard. It is a Ministerial-level organization, and an international climate change initiative focused on confronting issues and fostering the deployment of CCS technologies worldwide. Accumulating data suggest that nations will need to work collaboratively to curb CO_2 emissions within the short timeframe of 10 years or less to avoid IPCC predictions of dire consequences. While research and development need to be accelerated, simultaneous progress must be made internationally on a legal and regulatory framework for CCS that deals with the varied liability issues connected to long-term CO_2 storage, and other challenges. In the final analysis, all nations would be affected by the impacts of global climate change. But technology and energy choices like CCS may provide policymakers with the basis for balancing and meeting their national economic, energy and environmental needs in a sustainable manner.

Chapter 2

Literature Review

2.1 Review of previous research work:

Numerous researchers have carried out a lot of research to study the gasification of biomass with air & CO_2,H_2O, Ar and CO_2-H_2O. This section reviews the previously published literatures on gasification of biomass with carbon dioxide sequestration. It permits better understanding of the topic and also act as foundation for the present work. This chapter deals with literature reviews on the gasification of biomass with different medium such as steam, air, carbon dioxide etc.

Karatas et al. [2012] investigated the gasification of waste tire with air&CO_2, air&steam and steam in a bubbling fluidized bed gasifier. In this study various parameters such a s bed material particle size (average 450 μm), steam to air ratio (0.204 - 0.269), CO_2 to air ratio (0.095 - 0.229), steam temperature, steam to fuel ratio (0.273 - 0.520) and gasification a gents effect were investigated on the quality of product gas. The results showed that 9.59, 7.34 and 15.21 MJ/Nm^3 LHV was obtained for air&CO_2, air & steam and steam agents respectively.

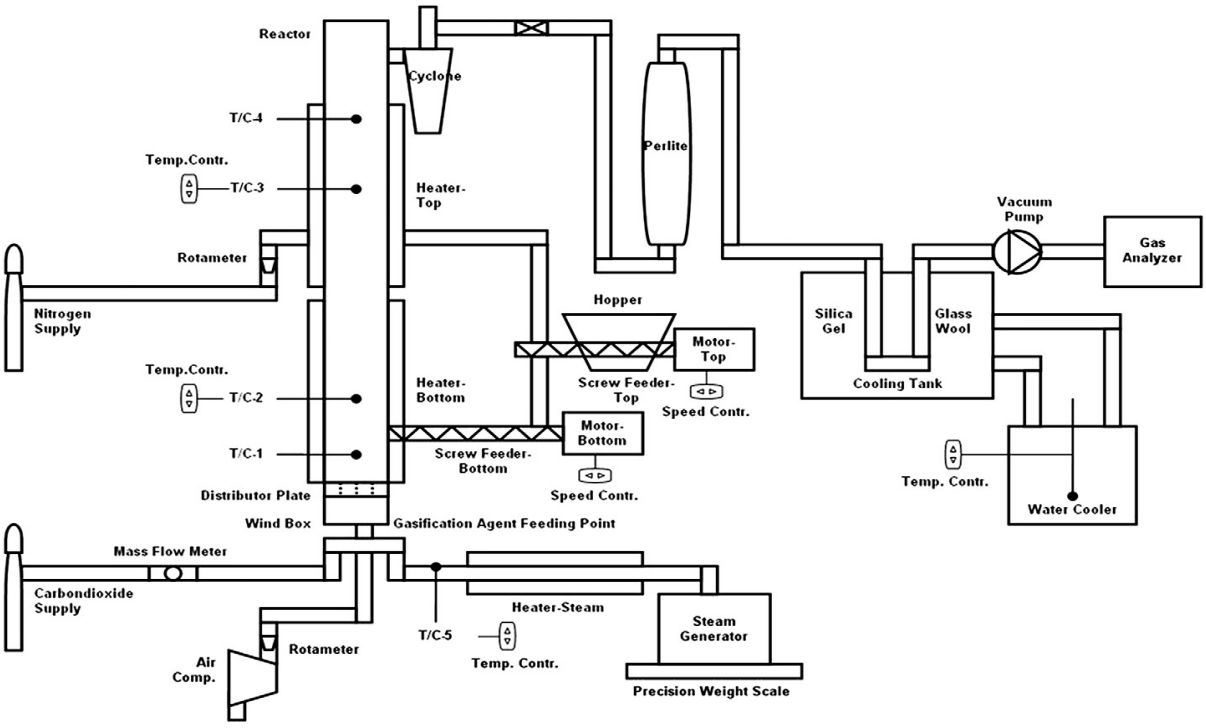

Figure 2.1 Schematic diagram of experimental facility

Butterman et al. [2009] studied the influence of CO_2 on steam gasification of walnut shells using thermo gravimetric analysis and gas chromatography. The co-reactant CO_2 was varied from 0 to 100% with steam and experimentally found that the concentration of CO increased by a factor of 10 whereas H_2 decreased by a factor of 3.3 at 900^0C when it was used 0-5%. It is reported that the yielded ratio of H_2/CO was decreased from 5.5 to 0.25 by introducing CO_2 fraction (0-50%). The net CO_2 was reduced and higher energy efficiency was observed.

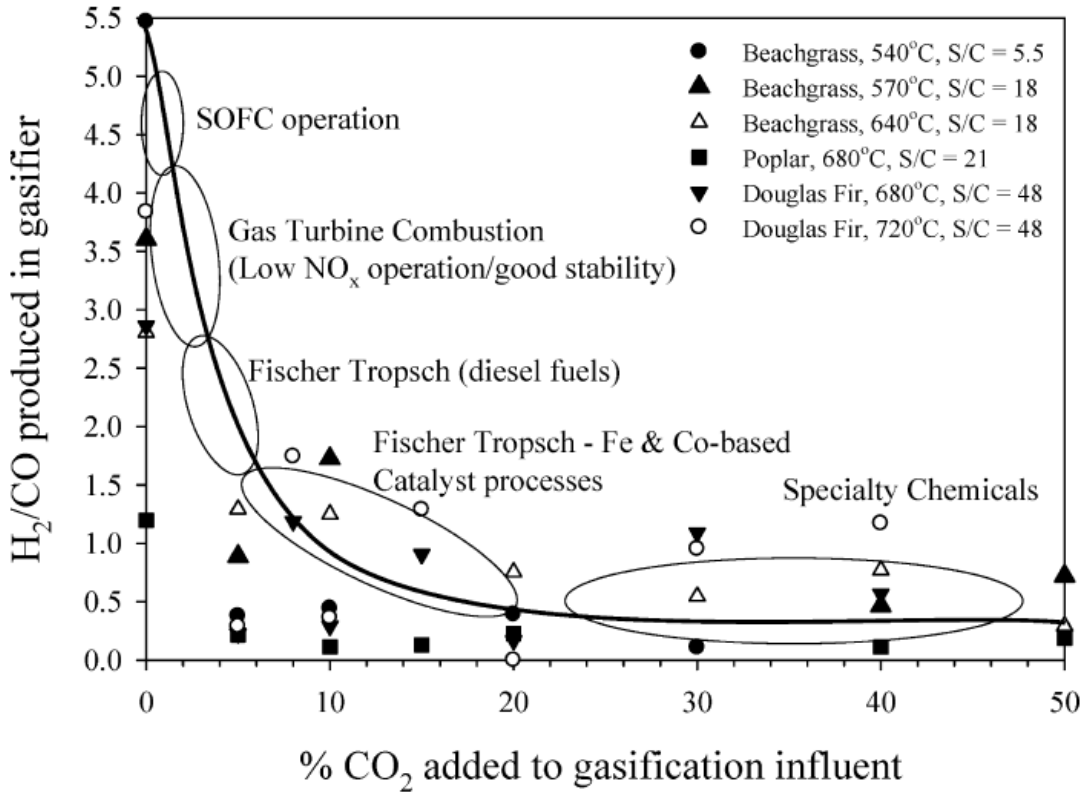

Figure 2.2 Syngas adjustment as a function of CO_2 reactant

Minkova et al. [2000] investigated the pyrolysis and gasification of biomass in H_2O, Ar and CO_2-H_2O. This experimental work was carried out a t atmospheric pressure and 750^0C reactor temperature. The character of oxygen functional group was observed acidic in nature during oxidation occurred at above 200^0C whereas oxidation functional group was attained basic in character at above 500^0C. It was seen that the yield of solid residue decreased in the presence of reactive agent such as steam and CO_2.

Butterman et al. [2007] investigated the influence of CO_2 injection on biomass gasification using thermo gravimetric analysis – gas chromatography. In this experimental work, atomic absorption spectroscopy (AAS) and scanning electron microscopy/energy dispersive X-ray

analysis (SEM –EDX) were used for analysis of biomass fuels and their ash residue. It was observed that at above 700^0C temperature, the enhancement of CO was become significant whereas evolution of H_2 was decreased for all wood and grasses.

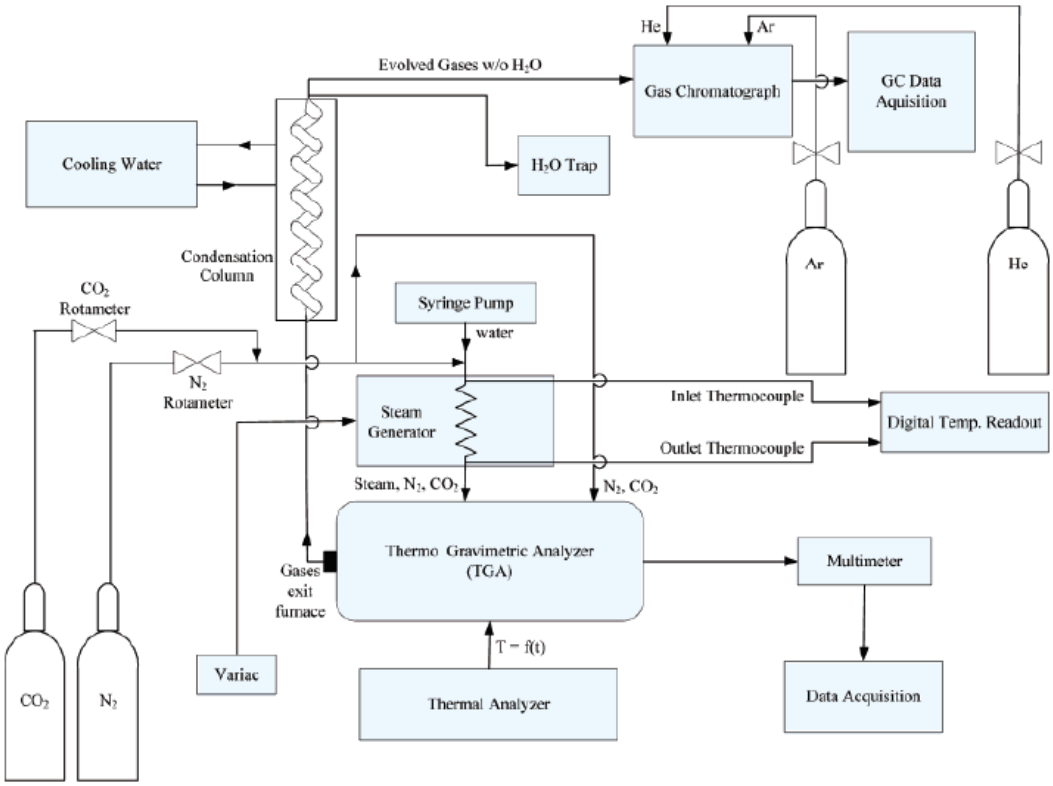

Figure 2.3 Schematic of experimental apparatus.

Kumar et al. [2011] investigated a carbon dioxide capture through biomass gasification. In this experimental work, CO_2 was used as a co-reactant a long with reacting media like oxygen. This study was carried out a t open top downdraft gasifier with varied CO_2 volume fraction from 0 to 15% in a mixture of O_2 and N_2. It is observed that the volume fraction of CO was increased from 13.1% to 16.2% and cold gas efficiency of system increased upto 30% because of higher conversion rate of char.

Chen et al. [2016] investigated the gasification of juniper wood biomass using CO_2–O_2, air and effect of various gasification parameters on the tar yield and product gas properties. In this study, fixed bed updraft gasifier has been used for juniper wood chips gasification with air and mixture of oxygen and carbon dioxide. It is reported that at maximum gasification temperatures, higher production of carbon monoxide was observed by oxy fuel gasification (the reaction of woody fuels with carbon dioxide). Apart from that lowest tar yield was found because of low gasification temperature followed by high moisture content 23.5% presence.

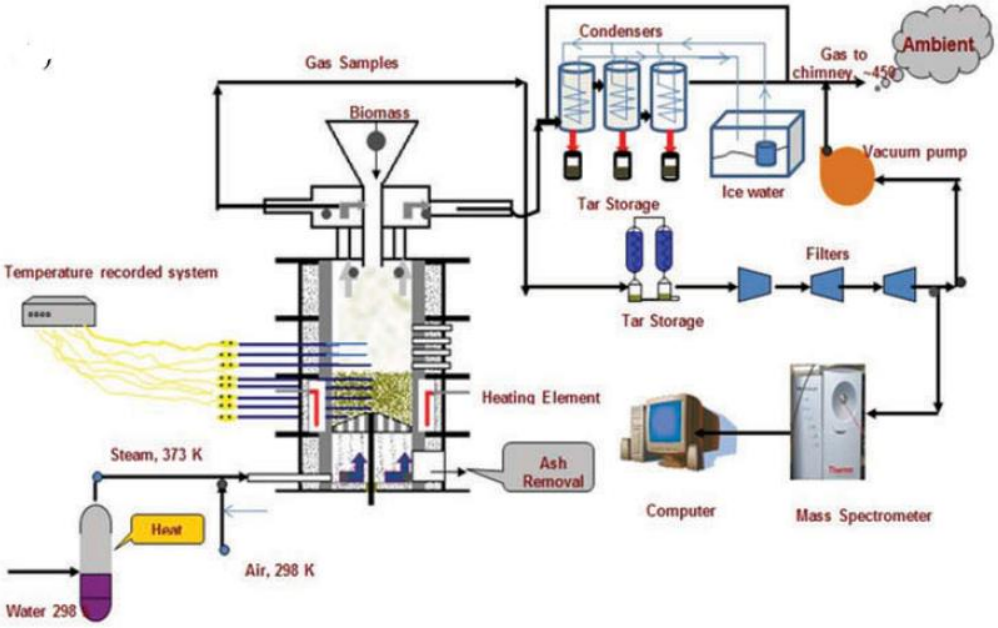

Figure 2.4 Gasification facility

Dogru et al. [2012]studied gasification of the olive pits in a fixed bed downdraft gasifier system. In this experimental work, olive pits were used as a biomass feedstock for producing the clean synthesis gas. The average production of syngas per kilogram of olive pits was observed 2.5 Nm^3 with calorific value ranging from 4.5 to 5.0 MJ/Nm^3. It is found that more than 97% conversion of carbon to product gas was attained by applying this process.

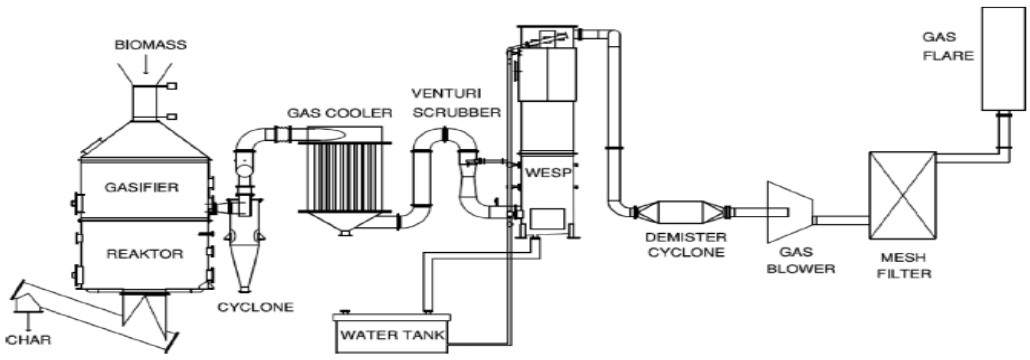

Figure 2.5 Gasification system with experimental setup

Qadi et al. [2016] investigated the Co-gasification kinetics of coal char and algae char under CO_2 atmosphere.This study was carried out at fixed bed reactor and two type of feedstock have been used in this experimental investigation such as Newland coal char and spirulina algae. The thermogravimetric analyser was used for evaluating the isothermal CO_2 co-gasification

experiment with temperature range of 800-1000C. In this study, the author was used four types of model namely volumetric model (VM), the shrinking core model (SCM), the random pore model (RPM) and the modified random pore model (MRPM) for find the gasification kinetic of the samples. It was found the 100-200 KJ/mol of activation energy by using the Arrhenius equation.

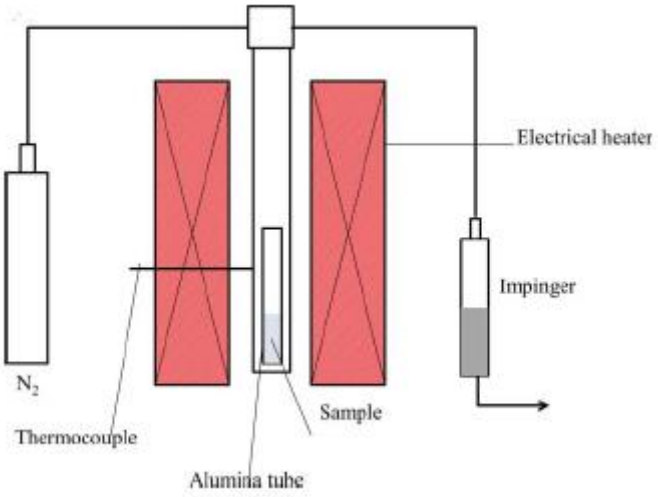

Figure 2.6 Schematic of experimental apparatus

Aresta et al. [2004] studied the contribution of the utilization option to reducing the CO_2 atmospheric. In this investigation the author was discussed the importance of CO_2 in biological, chemical, technological and its industrial applications. It is observed that 1Mt/y CO_2 was reduced followed by biological, chemical, technological option.

Chapter 3

Experimental setup and methodology adopted

This chapter deals with the methodology used for conducting the experiments and the analysis was done on an open top downdraft reactor for biomass gasification with carbon dioxide sequestration. The experimental setup was fabricated by itself and it was operated with oxygen and carbon dioxide volume fraction.

3.1 Experimental Setup and Design

The experimental work was conducted on a scaled down modified version of an open-top downdraft gasifier configuration (Figure 3.1)) at **Sardar Swaran Singh National Institute of Bioenergy, Kapurthala**.

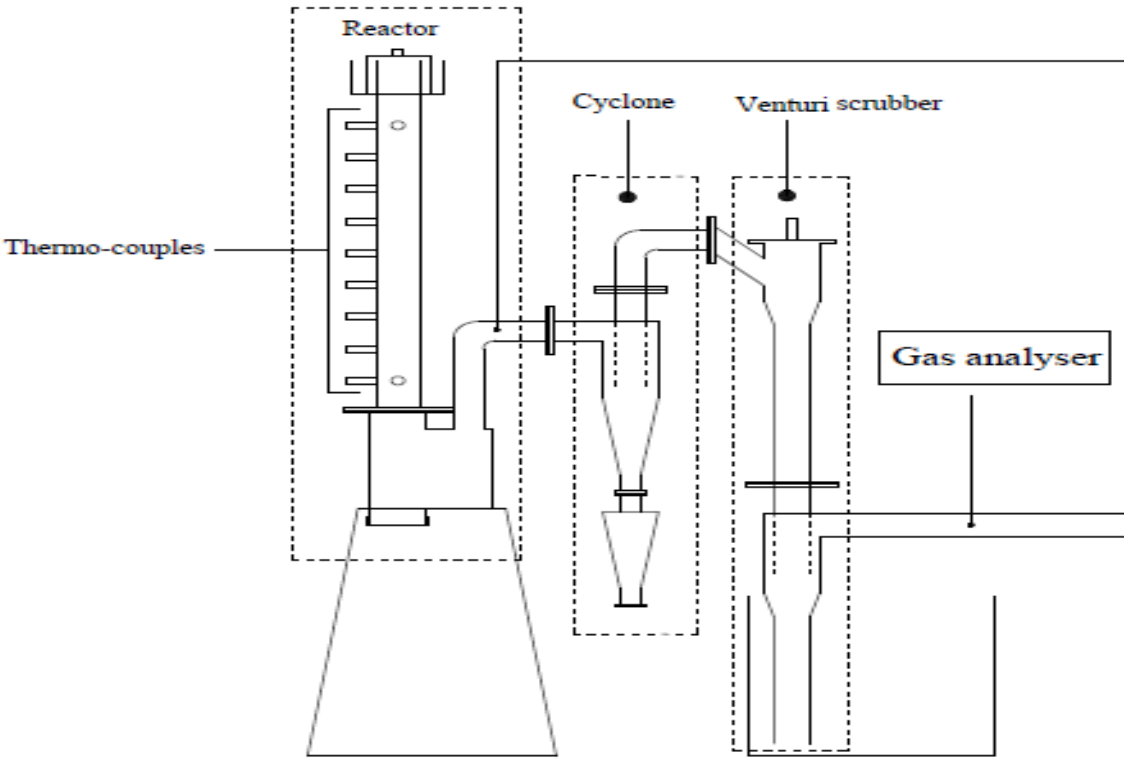

Figure 3.1 The standard open top downdraft gasification system

This system design has a long cylindrical reactor with air entry both from the top and through the air nozzle point. This gasification system has air flow shared between the top and the nozzle to stabilize the flame front. There are two advantages are (a) increasing the char consumption and (b) helping in re-burning the higher molecular weight compound released during pyrolysis. The principle used in the design of the reactor increases the residence time of gas inside the reactor, by maintaining a high temperature environment in the char bed, thus improving the char conversion efficiency and reducing the higher molecular weight compounds.

The experiments were performed in downdraft gasifier with a CO_2/air atmosphere. As shown in the figure, the gasification system consisted of a reactor, a gas cooling system, a temperature control system, a biomass feeder and other auxiliary devices. The height of the reactor is1200 mm and its inner diameter is 89 mm. Set of experiments were conducted in a 10kg/hr open top downdraft gasifier. Ash extraction provision was fixed at the bottom of the reactor. This ensured continuous operation for longer durations. Bed temperatures were measured using K-type thermocouples, placed at 100 mm distance in the reactor. The syngas composition (CO, CO_2, CH_4 and H_2 fractions) was measured using the gas analyzer. The gas analyzer data were taken at an interval of 30 s. Exit gas flow rate and air flow rate were measured using a pre-calibrated venturimeters.

In the open-top downdraft reactor configuration, air (gasifying media) is drawn from the top as well as side air nozzle whereas carbon dioxide (co-reactant) is drawn from the side CO_2 nozzle and product fuel gas is driven out from the bottom of the reactor.So, at any point of time any changes of air flow-rate into the gasifier were adjusted using a control valve, thus maintaining desired input mass flux rate of air or mixture of air, CO_2 and O_2. Char was loaded initially up to 300 mm height. Dry biomass (Eucalyptus wood chips) were fed above the char bed. Char bed was ignited from ignition ports and a blower was used to induce air flow inside the reactor. Reactor was kept under negative suction pressure throughout the experiments to maintain air flow at required rate. Once flame reached the wood particles; temperature, flow and gas composition data were recorded. After 45 minutes of air gasification, exact amount of CO_2 were injected through regulated flow meters from pressurized CO_2 cylinders, by mixing with air at the top. As, CO_2 participates in endothermic reactions 3 and 4; introduction of CO_2 induces endothermicity in the system, thus reducing bed temperatures with increased tar levels.

3.2 Biomass Fuel and Characterization

Eucalyptus wood chips were used as a fuel for gasification. The wood chips were dried in an electric oven at 378K to bring down the moisture content to less than 1%. The result of ultimate analysis of dried eucalyptus wood samples is presented in Table 3.1.

Figure 3.2 Eucalyptus wood chips used for the experiments

Table 3.1 Properties of biomass fuel used for experiments

Ultimate Analysis	**Mass fraction (%, dry basis)**
Carbon	46.25
Hydrogen	5.82
Nitrogen	4.54
Oxygen	43.39
Chemical Composition	$CH_{1.5}O_{0.7}$
Molecular weight	24.7kg/kmol
Proximate Analysis	**Mass fraction (%, dry basis)**
Fixed carbon	19.6% ± 0.2
Volatile matter	79% ± 1.5
Ash content	0.4% ± 0.05
Calorific value	**MJ/kg(Air Dried Basis)**
HCV	19.274
LCV	18.091

3.3 Measurement and Instrumentation

The instrumentation used for measuring temperature, gas flow rate, and gas composition while conducting the experiments is shown in the following section**.**

3.3.1 Flow Measurement

The instrumentation used for gas flow measurement is a combination of venturimeters and a manometer. The range of manometer is 0-100 mm of the water column with the least count of 1mm of the water column. The relation for calculating the gas flow rate is given below.

$$Q = K\sqrt{\Delta H}$$

Where Q is the gas flow rate (g/s), k is the venture constant and ΔH is the pressure head across the venture in mm of the water column.

3.3.2 Temperature Measurement

Nine K-type thermocouples were embedded in the reactor at intervals of 100 mm bed height to quantify the bed temperature in different zones. K-type thermocouple can measure temperature up to 1525K. The thermocouples are coupled to the personal data acquisition board employing a Teflon coated high temperature resistive cable. Data was noted at every 5 seconds.

Figure 3.3 Personal Data Acquisition System

3.3.3 Gas Composition Measurement

The syn gas composition was measured using the *Sick Maihak* S 517 continual flow gas analyser. This gas analyser can measure the composition of carbon monoxide (CO), carbon dioxide (CO_2), methane (CH_4) and hydrogen (H_2). The percentage composition of each of these

gases is directly displayed on the screen of the instrument. The measurement range for H_2, CH_4, CO and CO_2 is 0-100% and 0-25% for O_2. The measurement has a resolution of 0.01% with accuracy of ±0.5%. Analyser was calibrated before and after each run using a pre-calibrated gas mixture with all the species in the range of measurement.

Figure 3.4 Gas Analyser

3.4 Methodology

Experiments were designed to study the influence of reactant species concentration ($O_2/N_2/H_2O$) on the char conversion, gas composition, energy efficiency and gasifier performance towards sustained. Initial set of study was focused on understanding the gasification of biomass with air and introduction of gas CO_2 on the char conversion and gas quality.

Repeated experiments were conducted for a given set of process parameters to maintain repeatability during the experiments. Bed temperature, gas composition, reactant flow rate and syngas flow rate were noted and analysed.

3.4.1 Gasification of Dry Biomass with O_2- N_2 mixture

Preliminary investigations were focused on using air (O_2 – N_2 mixture) as the reactant. To address varying reactant mixture with desired O2/N2 fraction, air was pumped through blower with measured flow rate and then mixed with required O2 before injecting into the reactor. The mass flux of the O_2-N_2 mixture was kept constant for all the experiments and O_2 volume

fraction varied from 20 to 100% in steps if 10% O_2. Bed temperature, gas composition, reactant flow rate and syngas flow rate for each set of experiments were recored and analysed.

3.4.2 Gasification of Dry Biomass with O_2-CO_2 mixture

Experiment was conducted with air as the gasification medium, followed by injection of measured quantities of CO_2 along with air, as a co-reactant, to analyse CO_2 conversion levels. During the gasification process, once the hot char bed was established; input air mass flux rate was fixed to desired value. Producer gas flow rate, gas composition and bed temperature at different heights were measured. After 45 minutes of stable operation, CO_2 and O_2 were injected, along the air, maintaining the mass flux rate. With the injection CO_2, change in the gas composition and producer gas flow rate was recorded.

3.5 Elemental Mass Balance

Towards arriving at the overall mass balance, elemental mass balance technique has been adopted. Biomass and air or oxygen-carbon dioxide is considered as input; flow rate of which are measured during the experiment. Gas composition was measured on a dry basis. To account for the determination of gas composition, collect the gas sample at fixed gas flow rate in the balloon.

With the introduction of CO_2, change in gas composition and producer gas flow rate were noted. Net CO_2 conversion was obtained from following equations.

$$\dot{m}_{PG(1)} = \dot{m}_{air} + \dot{m}_{bio(1)} \tag{3.1}$$

$$\dot{m}_{PG(2)} = \dot{m}_{air} + \dot{m}_{Bio(1)} \tag{3.2}$$

$$\dot{m}_{CO2(out1)} = \dot{m}_{PG(1)} \times \chi_{CO2(1)} \tag{3.3}$$

$$\dot{m}_{CO2(out2)} = \dot{m}_{pg(2)} \times \chi_{CO2(2)} \tag{3.4}$$

$$CO_2 seq = \dot{m}_{CO2(in)} - (\dot{m}_{CO2(out2)} - \dot{m}_{CO2(out1)}) \tag{3.5}$$

$$CO_2 \text{ conversion } (\%) = \frac{CO_2 \text{ conversion}}{\dot{m}_{CO2(in)}} \tag{3.6}$$

$$\text{Efficiency } (\eta) = \frac{LHV(PG)}{LHV(Biomass)} \tag{3.7}$$

$$\Delta\eta = \frac{(\eta(2) - \eta(1))}{\eta(1)} \tag{3.8}$$

Where $\dot{m}_{air}$ = mass flow rate of air during operation, in kg/hr. $\dot{m}_{PG(1)}, \dot{m}_{CO2(out1)}$, and, $\dot{m}_{Bio(1)}$, are mass flow rate of producer gas, CO_2 in output producer gas and biomass consumption rate respectively in case 1 (without passing CO_2), in kg/hr. $\chi_{CO2(1)}$ is mass fraction of CO_2 in the producer gas in case 1. $\dot{m}_{PG(2)}$, $\dot{m}_{CO_2(out\ 2)}$ and $\dot{m}_{Bio(2)}$, are mass flow rates of producer gas, CO_2 in output producer gas and biomass consumption rate respectively in case 2 (while passing CO_2), in kg/hr. $\chi_{CO_2(2)}$ is mass fraction of CO_2 in the producer gas in case 2. Hence, an attempt has been made to convert CO_2 to CO, which is an active component of producer gas.

Chapter 4

Results and discussion from experimental studies and thermodynamic equilibrium analysis

This chapter compares the results from the equilibrium analysis, experimental study and also from the literature. Aspects related to the bed temperature, change in gas composition, producer gas flow rate, which depict the overall performance reactor, are used for comparison. The input parameters are air mass flux and CO_2 volume fraction. The equilibrium provides theoretical limits for oxygen and carbon dioxide gasification of dry biomass before proceeding with experiments.

Chemical equilibrium analysis has been done under adiabatic conditions for reaction of biomass employing Gibbs free energy minimization. NASA SP-273 code was used for chemical equilibrium analysis. Results were obtained using air as an oxidizer ($\Phi = 0.25$) and subsequently adding CO_2 as a reactant. Over 45% CO_2 conversions were obtained from equilibrium studies. Reduction in adiabatic temperature was also noted with increase in CO_2 fraction. Addition of CO_2 along with air reduces the O_2 fraction, leading to reduction in bed temperatures and thus the reaction rates. Boudouard reaction is endothermic in nature and conversion of CO_2 to CO requires high bed temperature to be maintained in reduction zone. Mixing CO_2 with air reduces the volume fraction of O_2 which leads to reduced reaction rates and subsequently lower conversion rates of biomass/char.

4.1 Equilibrium Analysis

Equilibrium calculation estimates the result of gasification if the reactants are permitted to respond in a completely mixing condition for a limitless time. There are two kinds of equilibrium model. The first depends on equilibrium constants (stoichiometric model).The particular substance responses utilized for the estimations must be characterized, so this model is not reasonable for complex responses where the chemical formulae of the chemical compound, the response way, or the reaction conditions are not given. This requires the second model kind, which includes minimization of the Gibbs free vitality (nonstoichiometric demonstrate). This procedure is more complicated however it is profitable because reactions are not required.

Thermodynamic equilibrium computation does not depend on gasifier model and as is suitable for study the effects of fuel properties and its parameters. However, this equilibrium model does not give detail for the reaction within the gasifier, the results of this model well predicted of the feasible output of a given product. But, the prediction of the influence of geometric or hydrodynamic parameter such as fluidizing velocity, gasifier height is a difficult for it.
Chemical equilibrium is determined by either of the following:

- The equilibrium constant (stoichiometric model)
- Minimization of the Gibbs free energy (nonstoichiometric model)

4.1.1 Stoichiometric Model

This model needs a range of acceptable chemical reactions and data regarding the estimations of the constant values.

4.1.2 Nonstoichiometric Model

This model is predicted on the assumption that at ideal stage, the Gibbs free energy should be decreased.

4.2 Requirement of higher Oxygen ($O_{2)}$ %

Equilibrium analysis, maintaining O2 fraction as 21% in inlet gas mixture, results in stable adiabatic flame temperature at varying CO_2 fractions.

Addition of carbon dioxide (CO_2) along with air reduces the oxygen (O_2) fraction, leading to reduction in bed temperatures, primarily due to endothermic reaction of char and CO_2 (Boudouard reaction).Mixing CO_2 with air reduces the volume fraction of O_2 which leads to reduced reaction rates and subsequently lower conversion rates of biomass/char. On mixing 10% CO_2, O_2 fraction reduces to 19%. Hence, O_2 was mixed along with CO_2 to maintain O_2 fraction as that in air (21%).

4.3 Adiabatic Analysis

To find out the suitable ER or extra oxygen required in order to reach same adiabatic temperature in the system with increasing CO_2 fraction, as acquired in air gasification of biomass.

4.3.1 Effect of CO_2% fraction on H_2 yield and CO yield

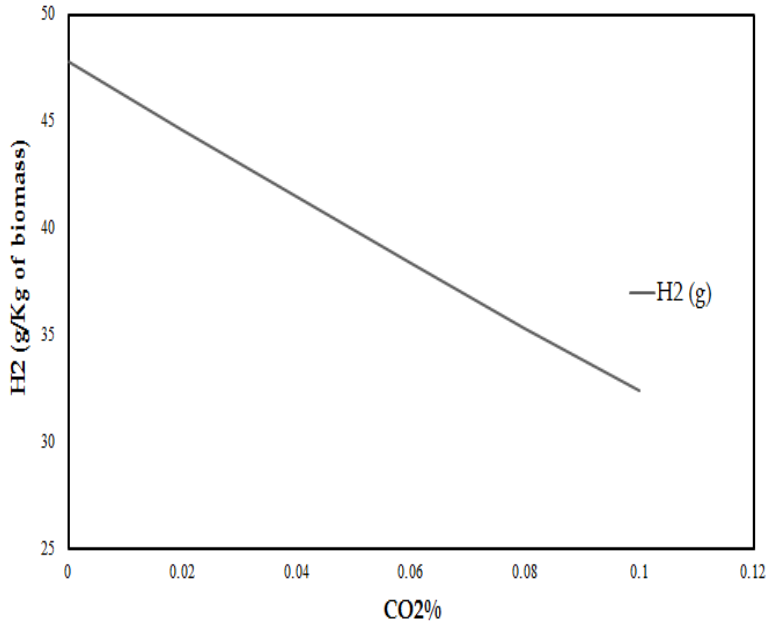

Figure 4.1 Variation of H_2 (yield) with CO_2 %

CO_2% fraction is varied from 0-10% as presented in fig. It is evident from the figure that the H2 yield and CO yield decreases with increase in CO_2% fraction. In order to reach same adiabatic temperature as acquired in dry biomass, with the increase in CO_2% fraction, extra oxygen is supplied. By increasing ER, the H2 yield and CO yield decreases.

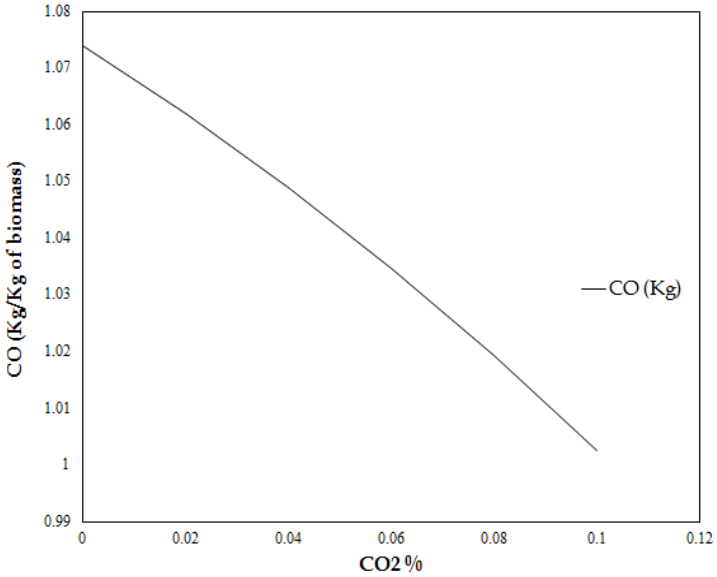

Figure 4.2 Variation of CO (yield) with CO_2 %

4.4Isothermal Analysis

Isothermal analysis is done to access the effect of bed temperature at a given CO_2 fraction and ER on the gas composition.

4.4.1Effect of CO_2 fraction on H_2 yield at varying temperature

Isothermal analysis is done to access the effect of bed temperature at a given CO_2 fraction and ER on the gas composition. The effect of CO_2 fraction on H_2 yield by varying temperature is shown in figure 5.3. It is observed that with the increase in temperature, H_2 (yield) decreases.

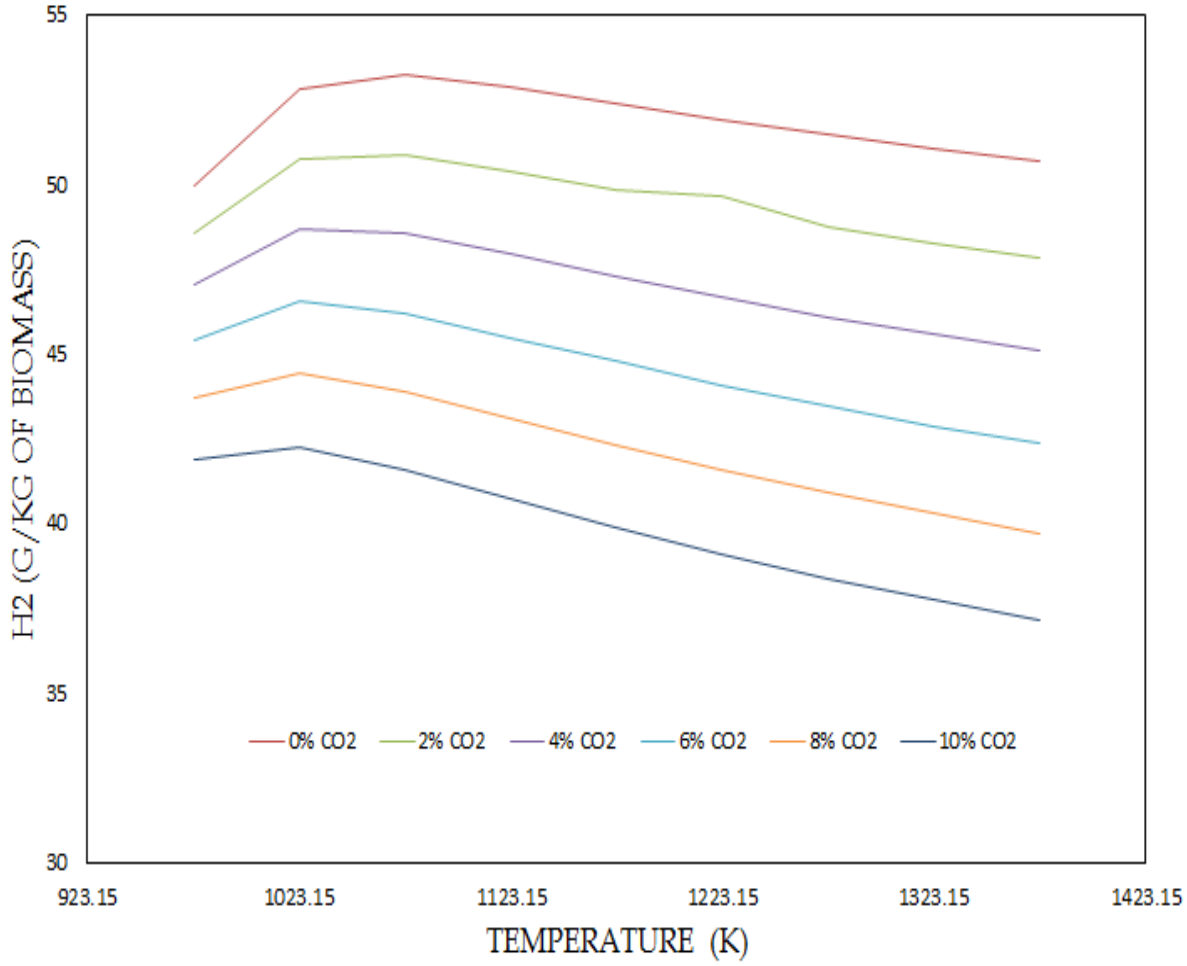

Figure 4.3 Variation of H_2 yield at all CO_2%

4.4.2 Effect of CO_2 fraction on CO yield at varying temperature

The effect of CO_2 % on CO yield by varying temperature is shown in fig.3.4. It is observed that with the increase in temperature, CO (yield) increases and with the increase in the CO_2%, CO yield decreases.

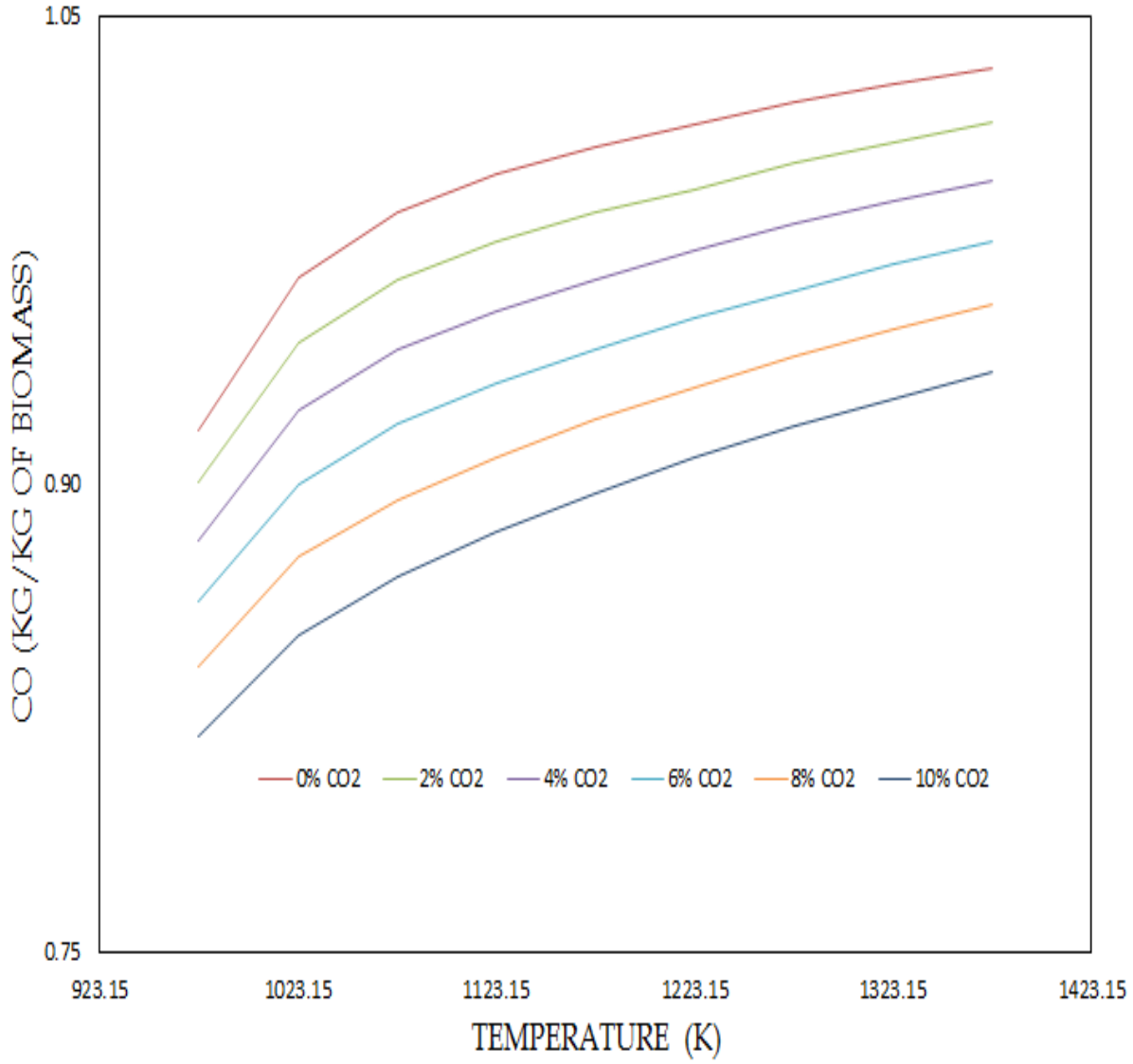

Figure 4.4 Variation of CO yield at all CO_2

4.4.3 Effect of CO_2 fraction on Efficiency and Calorific Value of Producer gas

The effect of CO_2 on efficiency and calorific value by varying temperature is shown in fig. and figure 5.5. It is observed that with the increase in temperature, there is slightly increase in efficiency and calorific value and with the increase inCO_2 %.

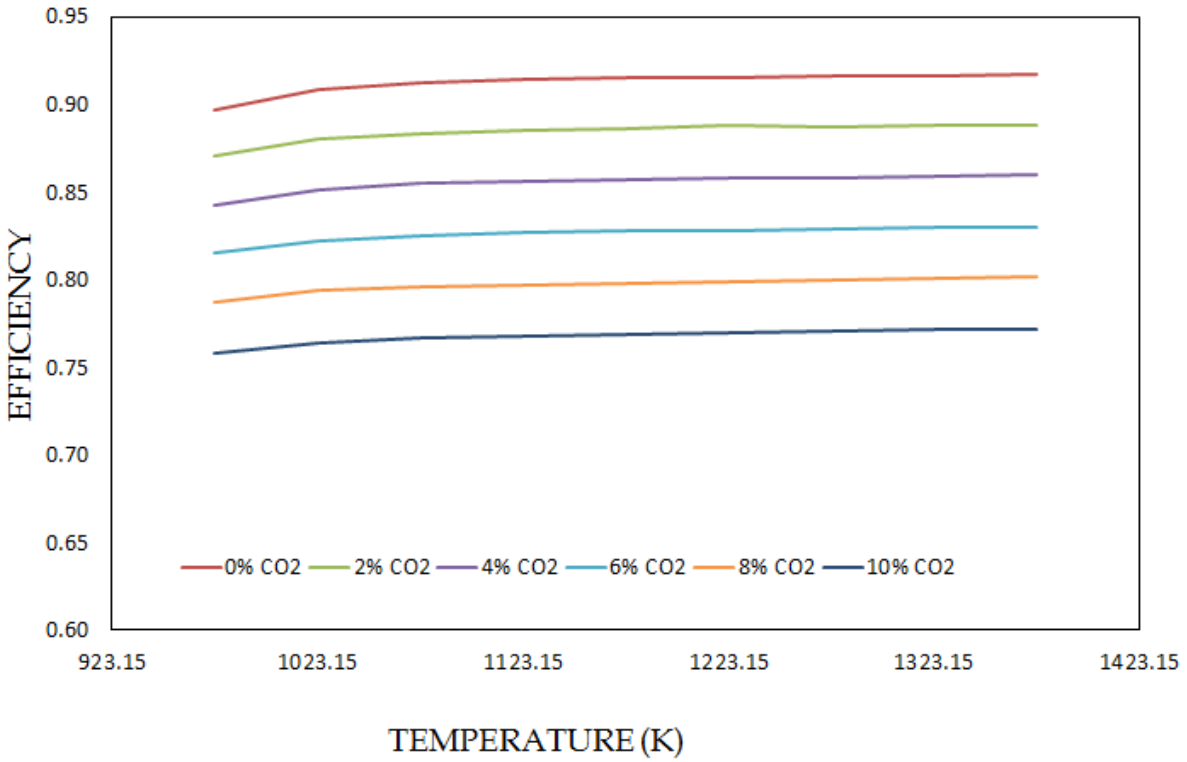

Figure 4.5 Variation of efficiency at all CO_2 %

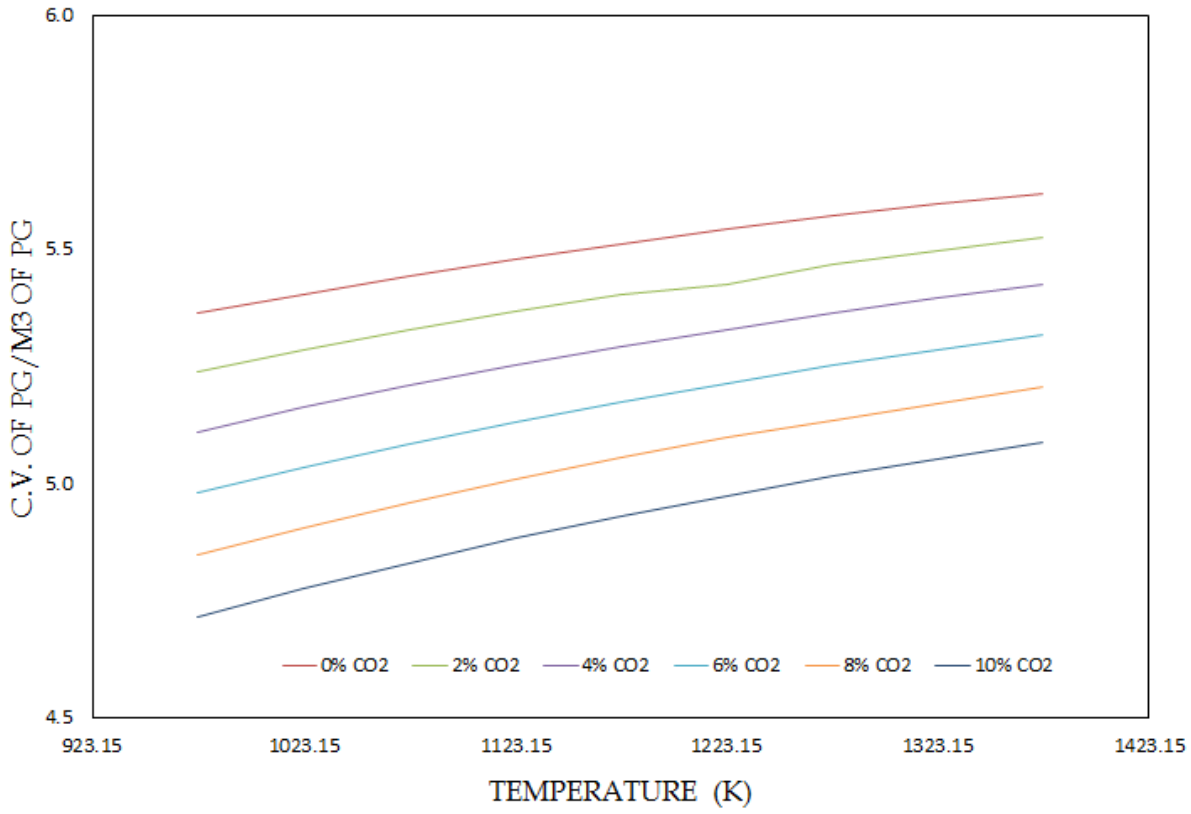

Figure 4.6 Variation of CV of PG/m3 at all CO_2 %

4.5 Experiments with O_2- CO_2 Gasification of Dry Biomass

Experiments were conducted using oxygen and carbon dioxide as the gasifying medium. Provisions were made in the reactor, to introduce O_2 and CO_2 from the side nozzles at different heights. Using a control valve, maintaining desired input mass flux rate of air or mixture of air, CO_2 and O_2.Char was loaded initially up to 300 mm height. Dry biomass was fed above the char bed. Char bed was ignited from ignition ports and a blower was used to induce air flow inside the reactor. Reactor was kept under negative suction pressure throughout the experiments to maintain air flow at required rate. Once flame reached the wood particles; temperature, flow and gas composition data were recorded.

Chemical equilibrium analysis has been done under adiabatic conditions for reaction of biomass employing Gibbs free energy minimization. NASA SP-273 code was used for chemical equilibrium analysis. Results were obtained using air as an oxidizer ($\Phi = 0.25$) and subsequently adding CO_2 as a reactant. Over 45% CO_2 conversions were obtained from equilibrium studies. Reduction in adiabatic temperature was also noted with increase in CO_2 fraction. Addition of CO_2 along with air reduces the O_2 fraction, leading to reduction in bed temperatures and thus the reaction rates. Boudouard reaction is endothermic in nature and conversion of CO_2 to CO requires high bed temperature to be maintained in reduction zone. Mixing CO_2 with air reduces the volume fraction of O_2 which leads to reduced reaction rates and subsequently lower conversion rates of biomass/char.

A gas evolution plot showing the distribution of the three gases (CO, CO_2 and H_2) that were monitored while conducting experiments. The gas output with 15% CO_2 is shown in the figure below. Changes in CO and CO_2 fractions occur when CO_2 and O_2 mixture is injected

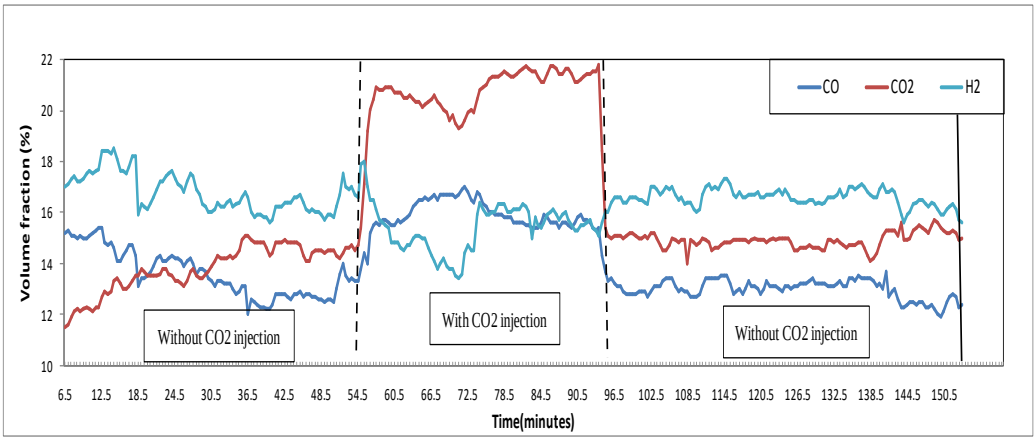

Figure 4.7 Gas composition of producer gas with and without injection of CO_2

We were observed that, on mixing 10% CO_2, O_2 fraction reduces to 19%. Hence, O_2 was mixed along with CO_2 to maintain O_2 fraction as that in air (21%). Figure 1 shows the equilibrium results for varying CO_2 input fractions. The results suggest that reduction in percent of CO_2 conversion with increase in input CO_2 fraction.

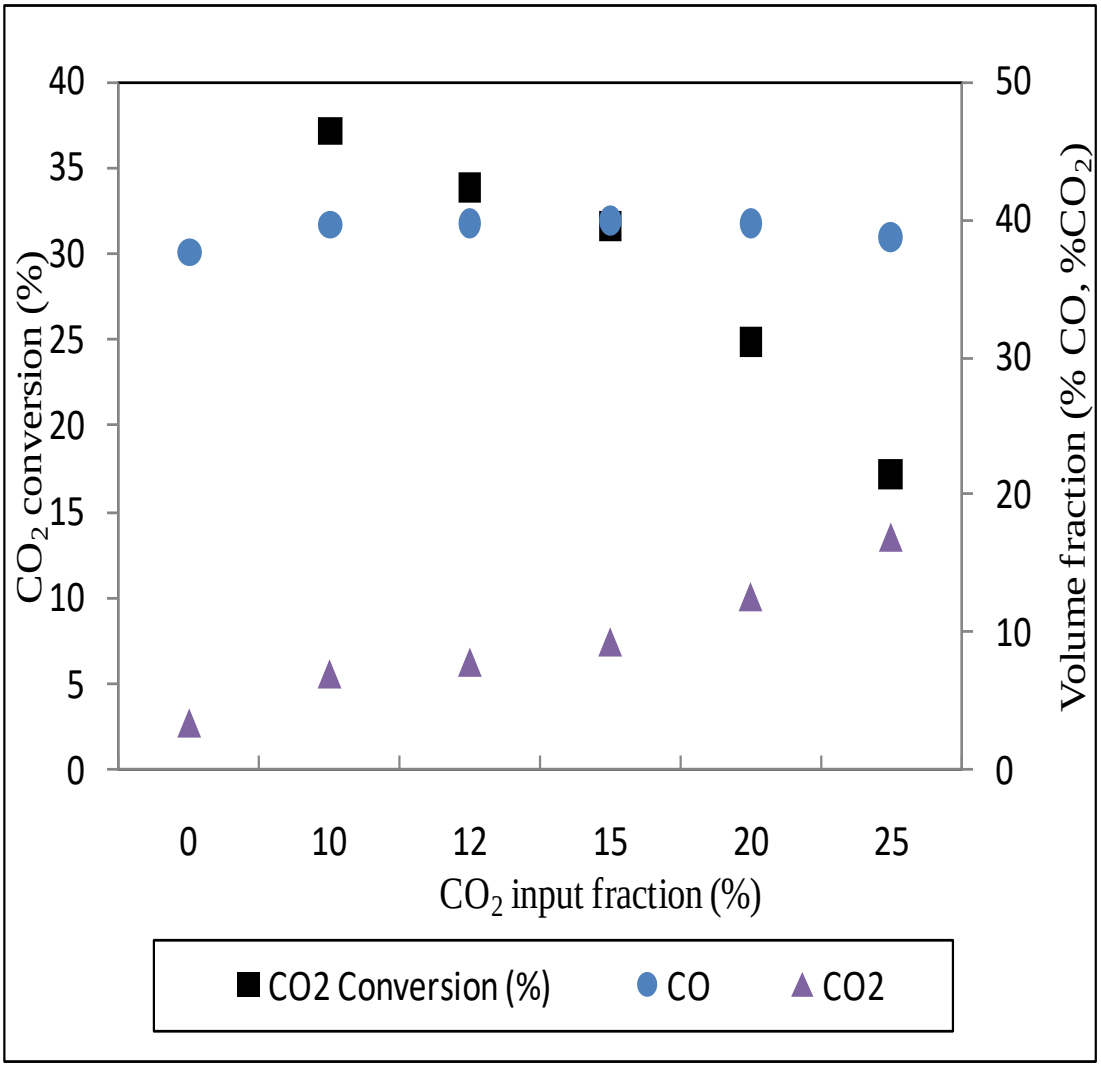

Figure 4.8 CO_2 conversion, CO_2 and CO output with varying CO_2 input fraction

A gas evolution plot showing the distribution of the three gases (CO, CO_2, H_2) that were monitored while conducting experiments with 15% CO_2 input (by volume fraction) is shown in figure. It represents the air gasification composition with and without CO_2 injection. Changes in CO and CO_2 fractions occur when CO_2 and O_2 mixture is injected. After steady operation, CO_2 and O_2 injection is stopped and volume fraction of CO & CO_2 return to its original fractions.

Effect of varying input CO_2% fraction on CO_2 conversion

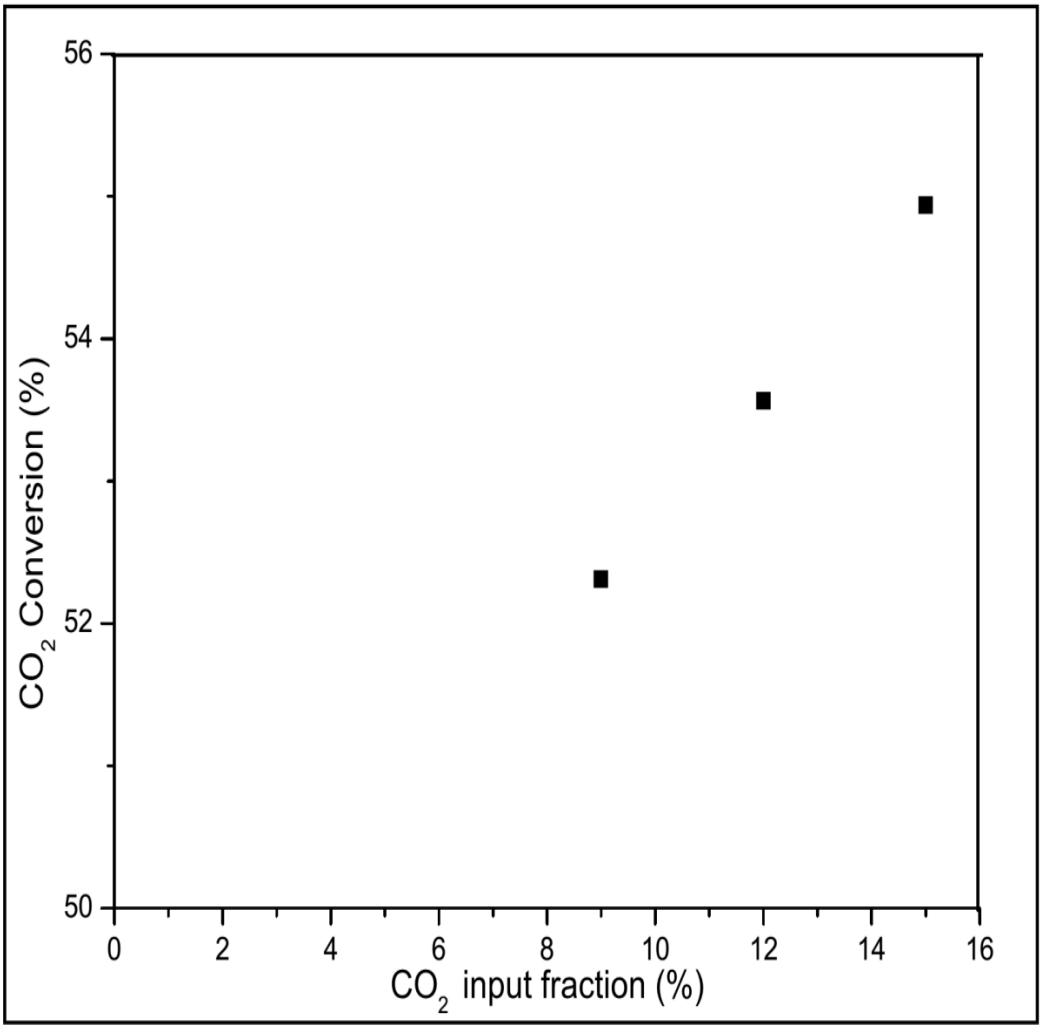

Figure 4.9 CO_2 conversion with varying CO_2 input fraction

It is evident from the figure that, CO_2 conversion of 53%-56% was observed while varying the CO_2 input fraction from 9 to 15%. CO_2 conversions rates calculations was based on the measured output gas flow rate, input air flow rate and char left in the gasification process.

Effect of varying input CO_2% on CO yield and H_2 yield

It was observed that effect of varying input CO_2% on CO yield and H_2 yield. The enhanced CO fraction which was the outcome of Boudouard and water shift reactions where as there was no appreciable change in H_2 fraction in the output gas. It enhanced relative cold gas efficiency of system by up to 30%.

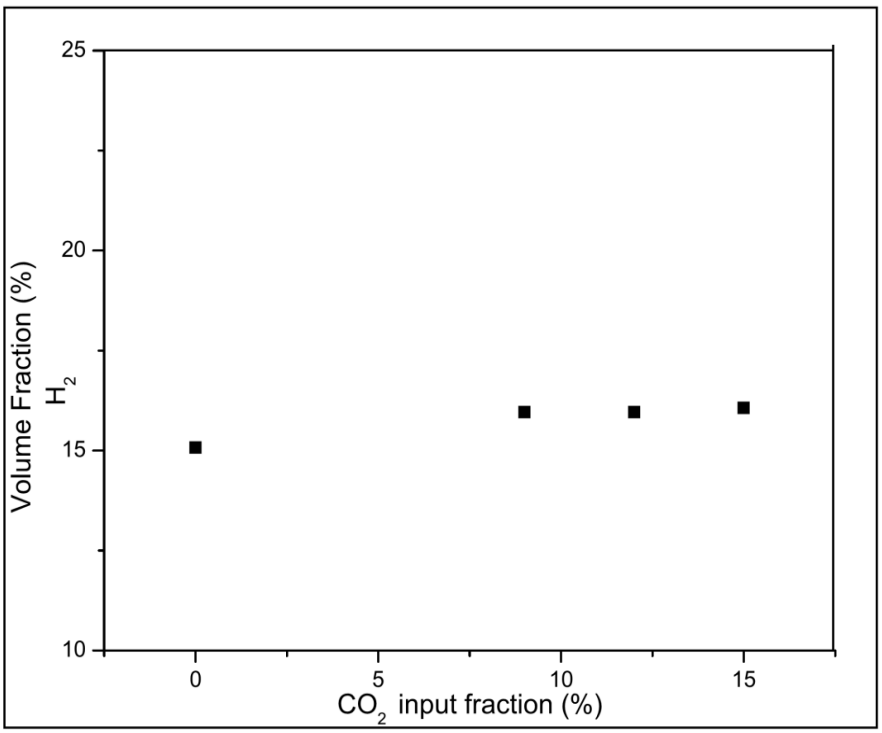

Figure 4.10 H_2 fraction with varying CO_2 input fraction

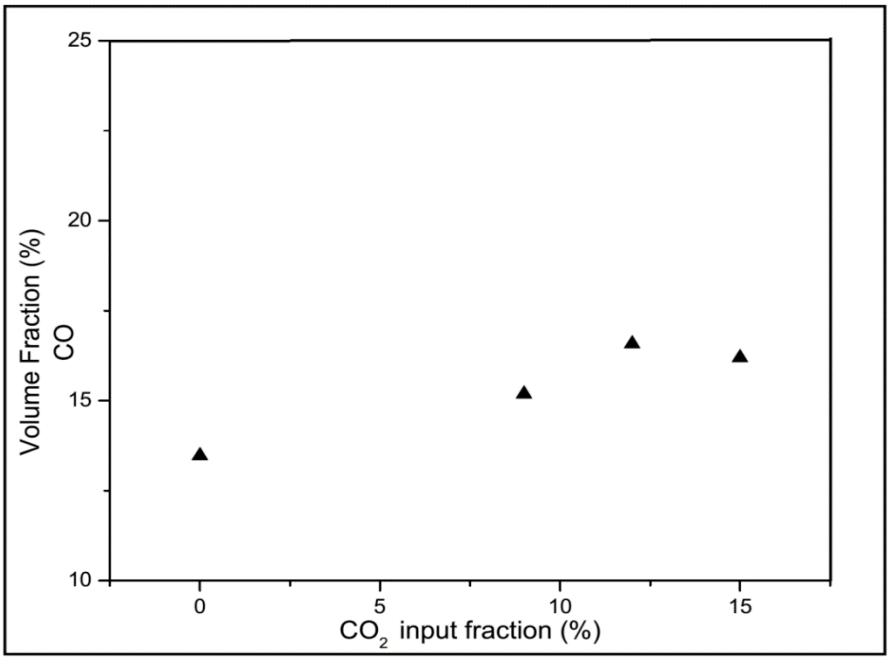

Figure 4.11 COfraction with varying CO_2 input fraction

Gas composition was measured on dry basis. To account for condensed H_2O during cleaning and cooling process, species balance of C, H and O was performed, based on exit gas

composition, which accounted for 10% H_2O in the producer gas. H_2O was accounted for all the calculations of mass balance to calculate total CO_2 fraction converted and captured in process. Table 4.1 shows carbon balance for all the sequestration experiments. Case 1 considers Carbon input into the system only in the form of biomass. Case 2, on the other hand, considers Carbon input into the system in the form of biomass as well as additional CO_2. The input and output mass flow matches quite reasonably. It indicates that the CO_2 measurements are well accounted, and proves validity of the CO_2 conversion levels. The results of varying CO_2 input fraction are tabulated in Table 4.1. The lower heating value of the gas varies from 3.8 to 4.3 MJ/Nm^3.

Table 4.1 Mass balance for CO_2 conversion

CO_2 input fraction (%)		Input Carbon in kg/hr			Output Carbon in kg/hr				
		Biomass	CO_2	Total Input	CO	CO_2	CH_4	Char	Total Output
15.0	Case-1 (Air)	4.30	0	4.30	1.40	1.4	0.28	0.98	4.14
	Case-2(Air+ CO_2)	3.27	0.85	4.20	1.49	1.8	0.25	0.78	4.43
12.0	Case-1(Air)	3.68	0	3.69	1.45	1.29	0.2	0.90	3.82
	Case-2(Air+ CO_2)	3.71	0.69	4.40	1.70	1.69	0.2	0.89	4.46
9.0	Case-1(Air)	3.28	0	3.29	1.41	1.38	0.32	0.79	3.84
	Case-2(Air+ CO_2)	2.90	0.41	3.28	1.49	1.60	0.28	0.69	4.01

Chapter 5

Conclusions and Future scope

Present work focuses on CO_2 sequestration using effection and waste to energy conversion methodology. Various methadologies and technologies for CO_2 sequestration has been discussed. Biomass gasification has been identified as one of the promising technology for not only CO_2 sequestration, but also its conversion to fuel gas CO. Various gasifier design has been discussed and compared keeping in view of the current requirements. Downdraft gasifier configuration has been identified as best suited.

Experiments has been conducted in NIBE, Kapurthala. The CO_2 is premixed with air and required O_2 and injected into the system. The gas is analysed using continuous gas analyser.

The present work focuses on using CO_2, from the product of combustion of fuels in an engine or a combustion device, as a co-reactant along with other reacting media. Experiments were conducted with CO_2 volume fraction varied from 0 to 15% in a mixture of O_2 and N_2. CO_2 is associated with Bouduard reaction ($C+CO_2 \rightarrow 2\ CO$) which is endothermic in nature. Increase in CO_2 fraction resulted in decrease in bed temperature, primarily due to reduction in O_2 fraction, in the gasifying medium, and the endothermic reaction of char and CO_2. Low bed temperature was addressed by maintaining the O_2 volume fraction in the input at 21% by introducing additional oxygen. At 15% CO_2 injection, the CO fraction increased from 13.1% to 16.3% and over 55% of the input CO_2 conversion was noted. Recorded an increase in cold gas efficiency by 30% owing to higher conversion rate of char. Working with the engine exhaust also eliminates the cost incurred in separation of CO_2 and makes the system less complicated.

Further, thermodynamic equilibrium studies has been performed addressing the issue of lower bed temperature during experiments. with CO_2 as reactant. NASA SP 273 software has been employed to study the temperature variation under adiabatic and isothermal condition. Equilibrium analysis has provided an oppurtunity to identify the optimum O_2 fraction required to maintain the bed temperature with CO_2 as reactant similar to those of air gasification. The higher O_2 fraction with increased CO_2 in input has been identified and analysed. The system is found to shift from gasification to combustion regime with the increase in Equivalence Ratio (ER) as O_2 fraction increases with CO_2 fraction. The operation at higher ER is leading to slightly lower efiiciencies.

Present work recommends to operate at O_2 fraction of 21% when CO_2 fraction in reacting media is low but to operate at higher O_2 at higher CO_2 fractions. The experiments at higher O_2 fractions is suggested as future work.

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