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Simulation of Cotton Stalks for Syngas Generation Using CO_2 and Air as Gasifying Agents

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ABSTRACT

Gasification of coal and biomass using CO_2 and air mixture as a carrier gas offers an encouraging way to eliminate the shortage of energy and reduce carbon dioxide emissions. In the present study, the Eulerian-Lagrangian approach was applied to understand the thermochemical conversion behavior of feedstock in entrained flow gasifier. Commercial CFD (Computational Fluid Dynamics) code ANSYS FLUENT®14 was used for the simulation purpose. It was observed that with variation in the CO_2 in the air and the CO_2 to cotton stalk ratio had a meaningful effect on gasification performance. The different ratios of air and CO_2 in varying percentages such as 20% CO_2, 30% CO_2, 40% CO_2, 50% CO_2, 60% CO_2, 70% CO_2 and remaining percentages of air were introduced in entrained flow gasifier. With the increase in CO_2 to cotton stalk ratio, the concentration of H_2 and CO_2 decreased whereas as the concentration of CO improved. It is revealed that mole fraction of CO and CH_4 attained maximum when CO_2% in the air was 50% and H_2 mole fraction was observed maximum at a CO_2% in the air was 30%. At 50% CO_2 mixture in air, the maximum lower heating value and cold gas efficiency were observed. Therefore, the optimum situation might be 50% percentage CO_2 in the gasifying agent for this entrained flow gasifier. Hence an increase in CO and H_2, the cold gas efficiency and lower heating value reached the maximum. However, this study provides an appropriate route for energy production using cotton stalks as raw material and will help in designing and operation of the entrained flow reactor. The simulations indicate the thermodynamic limits of gasification and allow for the formulation of the general principles ruling this process. Moreover, no literature is available for the parametric investigations of Pakistani biomass gasification using entrained-flow gasifier. So this is a novel work for Pakistan and will be treated as foundation work for biomass gasification in the country.

Key Words: Cotton Stalks, CO_2, Renewable Energy, Computational Fluid Dynamics, Simulation, Syngas

1. INTRODUCTION

The conversion of biomass into biofuel is considered as a sustainable way to manage with the fossil fuels exhaustion and to meet environmental wellbeing [1]. Biofuels production from biomass sources will help in mitigating the greenhouse gas emissions particularly carbon dioxide that results in increasing level of CO_2 in the environment and subsequently causing a rise in global temperature [1-2]. The possible ways to reduce CO_2 emissions have remained a burning issue for the last few decades. Efforts are done throughout the world to minimize CO_2 emissions due to their continuous increase in the atmosphere. As consumption of fossil fuels at a larger scale cause numerous environmental issues. Therefore, different

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techniques and procedures are considered and used to obtain energy from renewable sources including biomass [3]. The energy from biomass may be recovered through combustion, biochemical and thermochemical conversion processes. Thermochemical processes include combustion, pyrolysis, liquefaction, and gasification. The gasification of feedstock occurs in two different stages. At first stage pyrolysis of feedstock takes place and at second stage char is converted into gas. During pyrolysis of feedstock, it is decomposed and converted into gaseous liquid and solid products including tars and chars [4]. The product obtained through biomass pyrolysis depends on the characteristics of biomass namely physical and chemical composition. Besides the composition of feedstock, gasifier selection and operational parameters of the gasification plant including temperature, pressure, and heating rate are vital parameters considered during selection of gasification technology [5]. The solid product obtained through pyrolysis of biomass is char [6]. Chars mainly contain the major part of carbon atoms and a different fraction of oxygen, hydrogen, nitrogen, and minerals. The chars formed react with gasifying medium CO_2, H_2, O_2 and some mixtures resulting in various gases particularly CO, CO_2 and H_2, the amount of additional gases produced heavily relies on the composition of gasifying agent used [7]. The most common gasifying agents used during pyrogasification of biomass include air and steam for syngas production. The pyrogasification of biomass can also be performed using CO_2 as a gasifying medium. Numerous studies have been conducted on thermochemical conversion of biomass using CO_2 as a carrier gas [8]. Gasification of biomass with steam and CO_2 as a carrier gas produce increased amounts of CO in the product gas [9]. CO_2 potentially reacts with hydrocarbons in the gas phase by a dry reforming reaction such as methane

$$CO_2 + CH_4 \rightarrow 2H_2 + 2CO \quad \text{(R1)}$$

In the water gas shift reaction, CO_2 reacts with hydrogen molecules

$$CO_2 + H_2 \rightarrow H_2O + CO \quad \text{(R2)}$$

CO_2 also reacts with carbon available in char

$$C + CO_2 \rightarrow 2CO \quad \text{(R3)}$$

Several researchers have done char gasification reactions using both CO_2 and H_2O as gasifying agents. Results gathered vary from study to study whether CO_2 hinders the H_2O char gasification reaction, increases reaction rates or two reactants function independently on char surfaces [10]. Thermochemical conversion of carbonaceous feedstocks performed by Renganathan *et. al.* [11], using different carrier gases. The research carried out by [11] concluded that the application of CO_2 substantially enhanced the energy conversion efficiency and reduced tar concentration in the syngas. Biomass gasification with CO_2 resulted in highest cold gas efficiency. Another study was done by [12], on rice straw gasification under varying gasification atmospheres such as CO_2, O_2, N_2, and H_2O. They concluded that the application of CO_2 as a gasifying agent increased the performance of the gasifier. Many researchers have experimented on char gasification reaction aiming to understand the kinetic behavior of the CO_2 char gasification reactions [13]. Biomass gasification with CO_2 as a gasifying medium influenced the syngas composition and production besides that it influenced the char properties and yield [14]. The modeling studies mostly present in previous work done by different authors on biomass thermochemical conversion focus only on pyrolysis steps or with sole char gasification steps [15]. This study is different from other studies as it focuses on the simulation of cotton stalks under varying CO_2 concentrations as a carrier gas with air and their impact on the production quality of syngas. The proximate and ultimate analysis results of cotton stalk samples obtained in this study through the use of thermogravimetric analysis techniques were used for the simulation work. The thermogravimetric analysis results of cotton stalks are shown in Table 1.

TABLE 1. CHARACTERISTICS OF THE COTTON STALKS OF PAKISTAN

Proximate Analysis				
Moisture	Volatile Matter (VM)	Fixed Carbon (FC)	Ash	LHV ($MJkg^{-1}$)
5.58	69.98	16.31	8.13	16.90
Ultimate Analysis				
Carbon	Oxygen	Hydrogen	Nitrogen	Sulphur
47.73	46.05	5.82	0.1	0.3

2. MODEL DEVELOPMENT AND COMPUTATIONAL DOMAIN

Cotton stalks gasification was performed through entrained flow gasifier using CO_2 and air in varying percentages as a gasifying agent. The geometry of entrained flow gasifier and its mesh is shown in Fig. 1(a-b) respectively. Ansys Design Modeler®14 was used for geometry development. Ansys Meshing®14 version was used for mesh generation. Cotton stalks, CO_2 and air mixture as a gasifying agent in different percentages were feed from the top of the gasifier as shown in Fig. 1(a). The density of the developed mesh was 77410 cells. Various cold flow simulations were performed on different meshes and this grid was found independent. After the development of geometry of gasifier, the governing equations were selected for predicting the behavior of gasification within the reactor. Synergistically combining of endothermic reactions and exothermic oxidation reactions of cotton stalks, varying percentages of CO_2 and air as gasifying agent were used. Feeding rate of cotton stalks in gasifier was maintained at 61kg/hr throughout the CFD simulation study, while the CO_2 % in the air was varied from 20-70%.

2.1 Assumptions in Simulation

Mass transfer, heat transfer and various other chemical and physical processes are involved during gasification operations. For tracking physical and chemical processes inside the reactor some assumptions were made. The assumptions made in this research include (a) steady state, axisymmetric, incompressible turbulent flow behavior was supposed. (b) Air pollutants formed during gasification such as hydrogen sulfide, ammonia, hydrogen cyanide, carbon disulfide, carbonyl sulfide were not taken into consideration. (c) Thermal radiation and flow forces inside gasifier were ignored and (d) The walls of the reactor were considered as adiabatic.

3. RESULTS AND DISCUSSION

3.1 Influence of CO_2-to- Cotton Stalks Mass Ratio

At fixed CO_2 percentage, it was noticed that with increasing CO_2/cotton stalks ratio intended that additional CO_2 was introduced to the entrained flow reactor, and the air introduced to the entrained flow reactor was similarly enhanced, at the same time supply of oxygen increased because of its fixed % in air.

3.2 Distribution of Temperature, Gas Composition and Velocity in the Gasifier

Fig. 2(a-b) signifies about the contours of the temperature of char and gas reactions within the entrained flow gasifier at 70% CO_2 in the air and at CO_2/cotton stalks ratio 1.826. At the lower part of the entrained flow gasifier, the temperature within the gasifier was uniformly distributed because of the exothermic solid phase oxidations reactions, however at the upper area of the reactor, the decrease in temperature of gas was noticed due to the endothermic char gasification reactions with H_2O and CO_2 primarily happened in the upper area of gasifier resulting decrease in temperature.

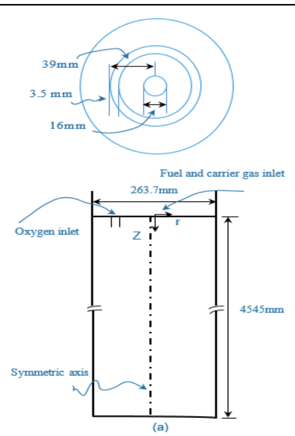

FIG. 1(A). GEOMETRY OF CONCENTRIC TUBE ENTRAINED FLOW GASIFIER

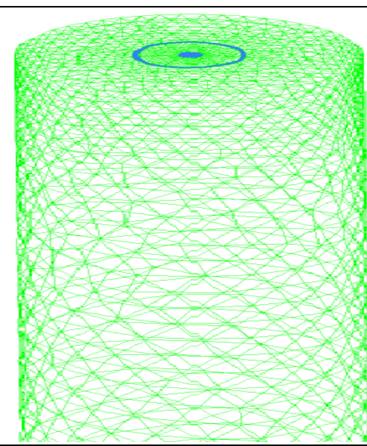

FIG. 1(B). MESH OF COMPUTATIONAL DOMAIN OF GASIFIER

The operating temperature at different CO_2 air ratios varied between 790K- 1100K.

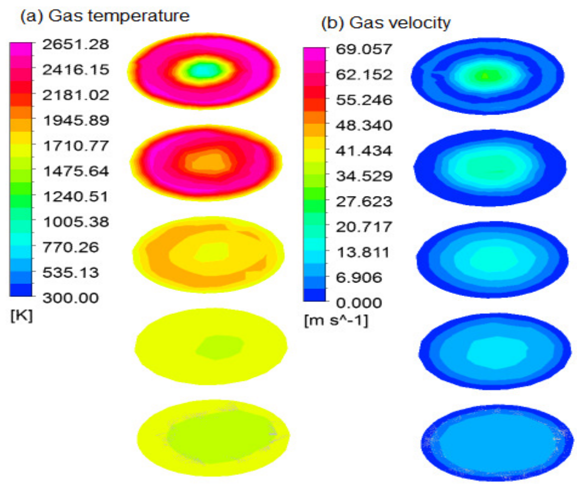

FIG. 2. TEMPERATURE AND VELOCITY CONTOURS AT DIFFERENT PLANES IN THE GASIFIER

The higher gas velocity was noticed within the gasifier near the feeding point of cotton stalks as shown in Fig. 2. The higher velocity at the inlet of cotton stalks was due to rapid devolatilization of cotton stalks and at this stage, the solid cotton stalks were transformed to gases. Under varying CO_2 % with air and the influence of CO_2-to-cotton stalks on syngas temperature is presented in Fig. 3. The temperature of syngas enlarged with growing CO_2/cotton stalk ratio for entire CO_2% in air. When CO_2% was increased in the air, less oxygen was present within the entrained flow gasifier for exothermic oxidation reactions to happen rapidly that lowered the temperature of syngas.

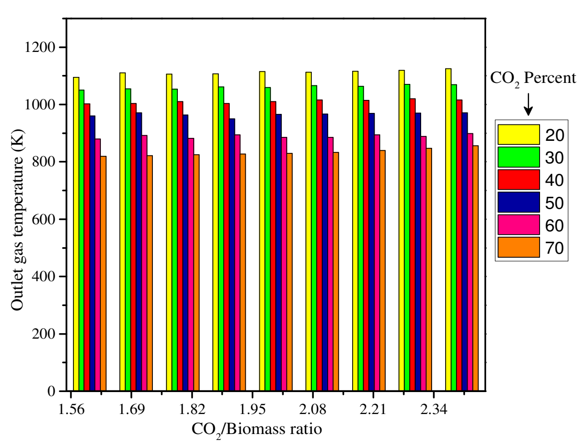

FIG. 3: EFRFECT ON THE TEMPERATURE AT THE DIFFERENT CO_2/BIOMASS RATIO

3.3 Distribution of Mole Fraction of Species

The composition of gas species at a different height within the entrained flow gasifier at 70% CO_2 in the air and at CO_2/cotton stalks ratio 1.826 it was noticed that at 2.183 m height within the gasifier O_2 was entirely used up. As oxidation reactions of volatiles and char produced heat. Near the cotton stalks inlet point, the highest mole fractions of CO_2 generation were observed due to the oxidation of CO. While CO_2 mole fractions after a height of 2.12 m dropped, and mole fractions CO improved as the char gasification with CO_2 and RWGSR (Reverse Water Gas Shift Reaction) were dominating. Whereas concentration of CH_4 in syngas was primarily influenced by pyrolysis of cotton stalks that mainly happened in a lower part of the reactor. However, mole fractions of H_2 increased slightly within the entrained flow gasifier after the height of 1.15m because of the char gasification with H_2O to generate CO and H_2. Nevertheless, the rate of RWGSR was larger than the rate of FWGSR. Because of the higher rate of RWGSR, part of the H_2 was used up with CO_2 to generate H_2O and CO.

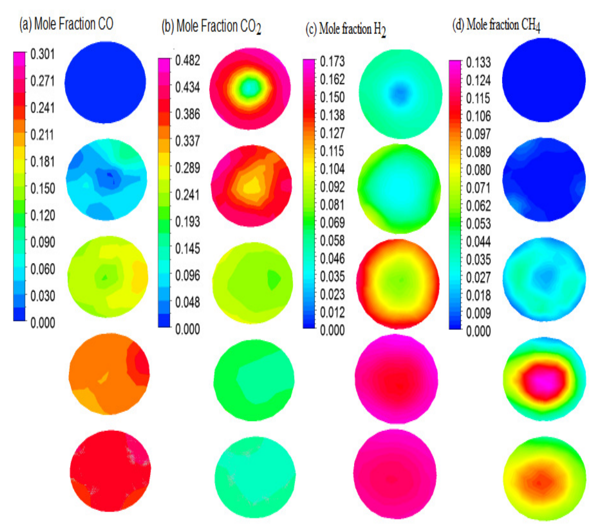

FIG. 4. CONTOURS OF GAS SPECIES AT GASIFIER PLANES

3.4 Mole fractions of producer gas

In **Fig. 5(a-d)**, the influence of CO_2/cotton stalks mass ratio when the percentage of CO_2 in the air was varied

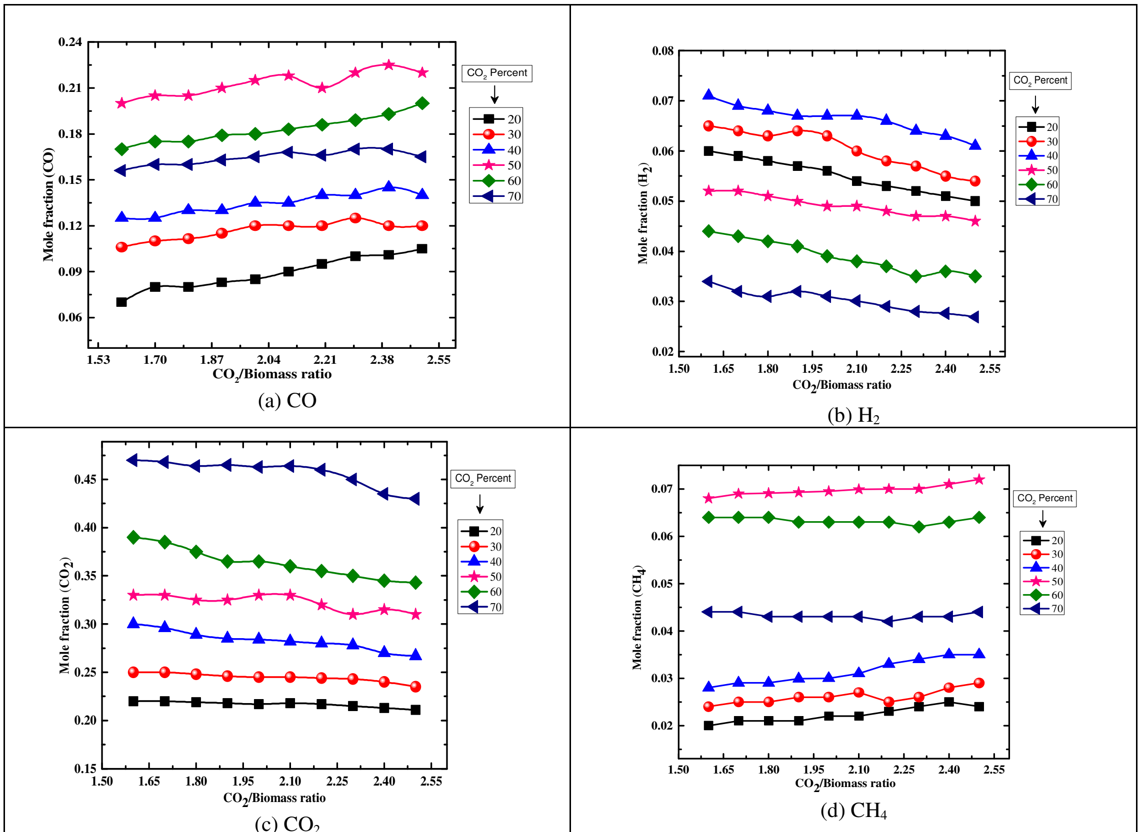

FIG. 5. UNDER DIFFERENT CO_2% IN AIR AND ITS EFFECT ON SYNGAS QUALITY

and its effect on the quality of syngas composition at the outlet of the entrained flow gasifier is shown. As mentioned earlier the cotton stalk feeding rate was maintained 61kg/hr, the increase in CO_2/cotton stalks ratio intended that additional CO_2 was introduced to the entrained flow reactor, increased percentage of air or oxygen, due to that temperature inside the reactor increased.

$$CO + 0.5O_2 \rightarrow CO_2 \quad (R4)$$
$$H_2 + 0.5O_2 \rightarrow H_2O \quad (R5)$$
$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 \quad (R6)$$
$$CO + H_2O \leftrightarrow H_2 + CO_2 \quad (R7)$$
$$C + CO_2 \rightarrow 2CO \quad (R8)$$
$$C + H_2O \rightarrow CO + H_2 \quad (R9)$$
$$C + 0.5\,O_2 \rightarrow CO \quad (R10)$$

With the increase in reactor temperature, the BR (Boudouard Reaction) became more activated [16]. As well as because of the high operating temperature of the reactor RWGSR also became more rigorous. RWGSR and BR both participated in CO_2 conversion to CO. Therefore, concentration of CO in syngas improved. However, because of the RWGSR, more H_2 and CO_2 were used up to generate CO and H_2O at greater CO_2/cotton stalks mass ratio; the decreasing trend in H_2 mole fractions was noticed.

The concentration of CH_4 was not affected significantly with change in CO to cotton stalk ratio due to the concentration of CH_4 were affected by the pyrolysis of cotton stalks when feeding of cotton stalks was maintained constant. Furthermore, the high concentrations of CO_2 shifted WGSR in the backward direction and produced increased mole fractions of CO. With the increase in CO_2% in air from 20% to 50% increased the mole fractions of the CO. However, a slight drop in CO mole fractions was observed when the CO_2 concentration in the gasifying agent was kept above 50-70%. This variation in mole fractions might be because of the too much CO_2, as compared to the quantity of air supplied within the entrained flow reactor being not sufficient in order to sustain the reactor at required high temperature. For endothermic BR, when the temperature of the reactor decreased, the higher CO_2% in reactor further lessened the CO production [17].

Lowering the CO_2 percentage in gasifying agent from 7-30%, the concentration of H_2 enhanced due to reduced percentage of CO_2% as compared to air decreased the rate of RWGSR, however when CO_2% was further lowered from 30% to 20% the concentration of H_2 reduced due to additional H_2 was used by the oxidation reactions. Increase in mole fractions of CH_4 was found from 20-60% CO_2 in air mixture because of reduced involvement of oxygen concerning oxidation of CH_4. The mole fractions of CH_4 decreased when CO_2% was further increased from 50-70% because of a reduction in operating temperature the rate cotton stalk pyrolysis reduced.

The concentration of CO_2 improved with growing CO_2% in the air because of more unreacted CO_2 at a given CO_2/ cotton stalks mass ratio. The results collected in this analysis revealed that mole fraction of CO and CH_4 were highest when CO_2% in the air was 50% and H_2 mole fraction was observed maximum at a CO_2% in the air was 30%. Therefore, the optimum situation might be 50% percentage CO_2 in the gasifying agent for this entrained flow gasifier.

3.5 Lower Heating Value (LHV)

When a particular amount of combusting material is fully burned and the quantity of heat released during combustion excluding the latent heat of water is known as lower heating value. For the estimation of the LHV of feedstock Equation (1) was used [18].

$$\mathrm{LHV_{fuel}} = 33.9\mathrm{Y_C} + 102.9\mathrm{Y_H} - 11.2Y_o 2.5\ \mathrm{Y_{H_2O}}\ \left[\frac{\mathrm{MJ}}{\mathrm{kg}}\right] \qquad (1)$$

Here $\mathrm{Y_H}$, $\mathrm{Y_O}$, $\mathrm{Y_C}$ and $\mathrm{Y_{H_2O}}$ show mass fractioons of hydrogen, oxygen, carbon and water in the feedstock. For calculation of LHV of syngas Equation (2) was used [18].

$$\mathrm{LHV_{gas}} = 10.8\mathrm{y_{H_2}} + 12.6\mathrm{y_{CO}} + 35.8\mathrm{y_{CH_4}}\ \left[\frac{\mathrm{MJ}}{\mathrm{m^3}}\right] \qquad (2)$$

where $\mathrm{y_{H_2}}$, $\mathrm{Y_{CH_4}}$ and $\mathrm{y_{CO}}$ represent the concentration of CO, H_2 and CH_4 in, syngas.

3.6 Cold Gas Efficiency (CGE)

It is the ratio between cooled syngas heating value and energy possessed by the feedstock used for gasification [19]. The sensible heat of syngas is not taken into consideration during the calculation of cold gas efficiency of producer gas. Equation (3) was used for the estimation of CGE.

$$\mathrm{CGE} = \frac{\mathrm{V_{gas}LHV_{gas}}}{\mathrm{m_{fuel}LHV_{fuel}}} \times 100\% \qquad (3)$$

Here V_{gas} is syngas flow rate in m^3/s, m_{fuel} is the feedstock flow in kg/s, LHV_{gas} represents the syngas LHV in MJ/m^3 and LHV_{fuel} shows the feedstock LHV in MJ/kg.

The influence of the gasifying agent flow rate on LHV_{gas} and cold gas efficiency is shown in **Figs. 6-7**, under diverse percentages of CO_2 in the air. It was observed that the simulated LHV_{gas} improved with growing CO_2-to-cotton stalks mass ratio for all percentages of CO_2 in the air. For the calculation of LHV mole fractions of H_2, CO and CH_4 in syngas were used [18]. Due to the achievement of the higher operating temperature of entrained flow gasifier with higher CO_2-to cotton stalks ratio, more noncombustible gases CO_2 and H_2O were changed into combustible gases such as CO and H_2, it was noted that with an increase in CO_2-to-cotton stalks ratio LHV of syngas increased [18]. As per Equation (3) the cold gas efficiency was proportional to the product of LHV_{gas} and syngas flow rate because syngas flowrate and LHV_{gas} enhanced with CO_2-to-cotton stalks ratio. The significant rise in CGE was more prominent with CO_2-to-cotton stalks ratio as compared to that of LHVgas. From 20% to 50% CO_2/cotton stalk ratio in the gasifying agent, LHV_{gas} and cold gas efficiency of syngas increased and then dropped when CO_2 percentage in air further enhanced to 70%. Therefore 50% CO_2 in the air was the optimal percentage of CO_2 where cold gas efficiency and LHV of syngas was highest.

3.7 Conversion of CO_2

The transformation of the proportion of CO_2 meant that the proportion of CO_2 converted during the operation of a reactor to the proportion of CO_2 contained in a feedstock and introduced into the reactor [19-20]. The conversion ratio of available CO_2 in the feedstock and the CO_2 in the product gas collected at the out of entrained flow gasifier was calculated using the following formulae.

$$X_{CO_2} = \frac{\text{moles of} CO_2 \text{ in gasifiying agent} - \text{moles of } CO_2 \text{ in producer gas}}{\text{moles of } CO_2 \text{ in gasifying agent}} \quad (4)$$

$$X_{CO_2} = \frac{\text{moles of} CO_2 \text{ in gasifying agent} - \text{moles of producer gas} \times \text{mole fraction of } CO_2}{\text{moles of } CO_2 \text{ in gasifying agent}} \quad (5)$$

The conversion of CO_2 at different proportions into different species and its ratio with cotton stalk is given in Fig. 8. When CO_2 percent was increased in air, it increased the operating temperature of the gasifier [21]. The operating temperature of the gasifier increased from 790-835K, when CO_2 concentration was enhanced in the air. The higher CO_2 ratio also favored reversed water gas shift reaction and BR [22]. However, at a set ratio of carbon dioxide to cotton stalks, the transformation ratio of CO_2 improved with rising CO_2 ratio in air. At CO_2/biomass ratio of 1.66, the CO_2 conversion was 0.59 mole fractions whereas as when CO_2/biomass ratio was raised from 1.65-2.55, it enhanced the conversion of CO_2 mole fractions from 0.59-0.65. The enhanced concentration of CO_2 favored WGSR and BR hence the application of carbon dioxide for char gasification is fairly higher [22].

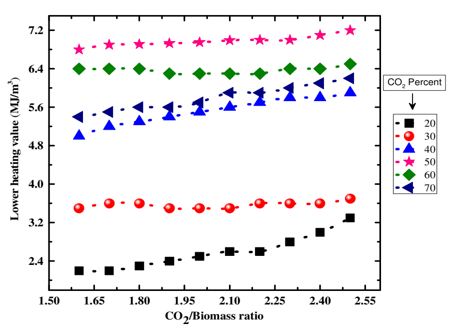

FIG. 6. LOWER HEATING VALUE UNDER VARYING CO_2/COTTON STALK RATIO

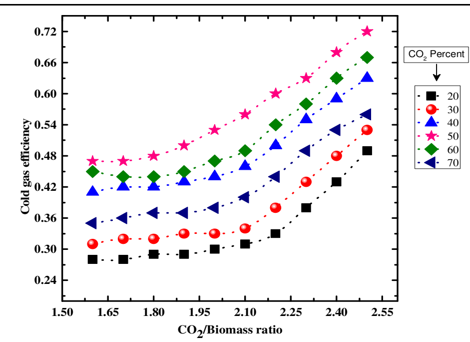

FIG. 7. BEHAVIOR OF CGE UNDER VARYING CO_2/COTTON STALK RATIO

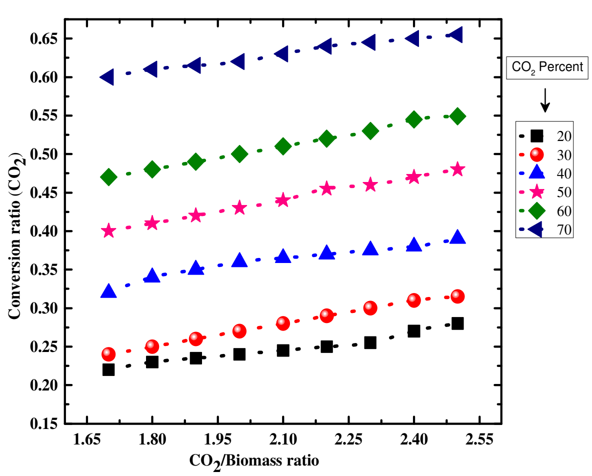

FIG. 8. CONVERSION OF CO_2 UNDER DIFFERENT CO_2 COTTON STALK RATIO

4. CONCLUSION

In this research, the Eulerian Langragian method was adopted to investigate the behavior of biomass gasification inside entrained flow gasifier using varying percentages of CO_2. The CO_2 was used with the air at varying percentages and their effect on the syngas quality, cold gas efficiency, carbon conversion efficiency, lower heating value of syngas was examined. Following findings were noticed during the gasification of biomass.

(i) When CO_2 to biomass ratio was increased, an excessive quantity of oxygen was available in gasifier for exothermic oxidation reactions. The excessive oxygen resulted in a rise in gasifier temperature and produced more concentrations of CO_2 in syngas composition. The more oxygen also lowered the mole fraction CO and H_2 in syngas composition.

(ii) The maximum mole fractions of CO production were found at 50 weight percent of CO_2 in the air. At 50 weight percent of CO_2, the LHV and cold gas efficiency of syngas were observed at maximum level. Therefore, the optimum CO_2% in air is 50% CO_2 as it resulted in enhanced mole fractions of CO in syngas and increased the CCE, CGE, and LHV of syngas.

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