

GASIFICATION OF LOW ASH PARTIALLY COMPOSTED DAIRY BIOMASS  
WITH ENRICHED AIR MIXTURE

A Thesis

by

SIVA SANKAR THANAPAL

Submitted to the Office of Graduate Studies of  
Texas A&M University  
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

December 2010

Major Subject: Mechanical Engineering

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Approved by:

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## ABSTRACT

Gasification of Low Ash Partially Composted Dairy Biomass  
with Enriched Air Mixture. (December 2010)

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Chair of Advisory Committee: Dr. Kalyan Annamalai

Biomass is one of the renewable and non-conventional energy sources and it includes municipal solid wastes and animal wastes in addition to agricultural residue. Concentrated animal feeding operations produce large quantities of cattle biomass which might result in land and water pollution if left untreated. Different methods are employed to extract the available energy from the cattle biomass (CB) which includes co-firing and gasification. There are two types of CB: Feedlot biomass (FB), animal waste from feedlots and dairy biomass (DB), animal waste from dairy farms. Experiments were performed in the part on gasification of both FB and DB. Earlier studies on gasification of DB with different steam-fuel ratios resulted in increased production of hydrogen. In the present study, dairy biomass was gasified in a medium with enriched oxygen percentage varying from 24% to 28%. The effect of enriched air mixture, equivalence ratio and steam-fuel ratio on the performance of gasifier was studied. Limited studies were done using a mixture of carbon dioxide and oxygen as the gasification medium and also a methodology was developed to determine the gasification efficiency based on mass and heat contents of gas.

The results show that the peak temperature within the bed increases with increase in oxygen concentration in the gasification medium. Also carbon dioxide concentration in the mixture increases with corresponding decrease in carbon monoxide with increase in oxygen concentration of the incoming gasification medium. The peak temperature increased from  $988^{\circ}\text{C}$  to  $1192^{\circ}\text{C}$  as the oxygen concentration increased from 21% to 28% at  $\text{ER}=2.1$ . The upper limit on oxygen concentration is limited to 28% due to high peak temperature and resulting ash agglomeration. Higher heating value (HHV) of the gases decreases with increase in equivalence ratio. The gases produced using carbon dioxide and oxygen mixture had a higher HHV when compared to that of air and enriched air gasification. Typically the HHV of the gases increased from  $2219 \text{ kJ/m}^3$  to  $3479 \text{ kJ/m}^3$  when carbon dioxide and oxygen mixture is used for gasification instead of air at  $\text{ER}=4.2$  in the absence of steam.

## DEDICATION

I dedicate this work to my parents, Mr. Thanapal and Mrs. Manimoli, and my brother, Dr. Sivakumar Thanapal. Everything which I have accomplished is because of their constant support and encouragement.

## ACKNOWLEDGEMENTS

I would like to thank my advisor and committee chair, Dr. Kalyan Annamalai, for admitting me into his research group and for his time and guidance which enabled me to understand and perform this research work. I thank my committee members, Dr. Eric Petersen and Dr. Sergio Capareda, for their support throughout this study. I thank all the professors and staff at the Department of Mechanical Engineering, Texas A&M University for providing an excellent environment for learning. I also thank my professors at the College of Engineering Guindy, Anna University who gave me a strong basic foundation and much needed exposure in the field of Mechanical Engineering.

Special mention goes to all the students in the Coal and Biomass Energy Laboratory (CABEL), Texas A&M University – Ben Lawrence, Dr. Hyukjin Oh, Dr. Gerardo Gordillo, Bjorn Altenburg, Wei Chen, Dustin Eseltine, Timothy Attaway, Aubrey Spear and Harikrishna. It was a whole new experience working with them and I thank everyone for their help. Finally, I thank all my friends for their help in getting me acquainted with a new environment and for their company in making these two years a memorable one after I landed in the United States in search of knowledge.

I would also like to acknowledge the financial support from the U.S. Department of Energy (DOE).

## NOMENCLATURE

$A_0$	Initial ash fraction, dry basis
A	Fraction of ash in dry sample after gasification
$(A:F)_{\text{stoich}}$	Stoichiometric air fuel ratio
$(A:F)_{\text{act}}$	Actual air fuel ratio
Ar	Argon
AR	As received
B	B number
C	Carbon
CAFO	Concentrated animal feeding operation
CABEL	Coal and biomass energy laboratory
CB	Cattle biomass
$\text{CH}_4$	Methane
$\text{C}_2\text{H}_6$	Ethane
CO	Carbon monoxide
$\text{CO}_2$	Carbon dioxide
$c_p$	Specific heat capacity at constant pressure
DAF	Dry ash free
DB	Dairy biomass
ER	Equivalence ratio
FB	Feedlot biomass



$f_g$	Gasified fraction
g	gram
H <sub>2</sub>	Hydrogen
H <sub>2</sub> O	Water
H <sub>2</sub> S	Hydrogen sulphide
H/C	Hydrogen to carbon ratio
HCN	Hydrogen cyanide
$h_c$	Enthalpy of reaction
He	Helium
HHV	Higher heating value
HHV <sub>ARfuel</sub>	Higher heating value of as received fuel
HHV <sub>gas mix</sub>	Higher heating value of gas mixture
kg	Kilogram
kJ	Kilojoule
LAPCDB	Low ash partially composted dairy biomass
MEET	Multi stage enthalpy extraction
$m_f$	Mass of fuel
$m_g$	Mass of gas mixture
MJ	Megajoule
MS	Mass spectrometer
N <sub>2</sub>	Nitrogen
N/C	Nitrogen to carbon ratio

$N_{\text{air}}$	Number of moles of air
$N_{\text{O}_2}$	Number of moles of oxygen
$N_{\text{O}_2,\text{total}}$	Total number of moles of oxygen
$\text{NO}_2$	Nitrogen dioxide
$\text{NO}_x$	Nitrogen oxides
$\text{NH}_3$	Ammonia
$\text{O}_2$	Oxygen
O/C	Oxygen to carbon ratio
O:F	Oxygen to fuel ratio
Sep-sol	Separated solid
S:F	Steam fuel ratio
SCFH	Standard cubic feet per hour
SMD	Sauter mean diameter
$T_{\text{peak}}$	Peak temperature
$T_s$	Char surface temperature
$x_{\text{O}_2}$	Mole fraction of oxygen
$y_{\text{O}_2}$	Mass fraction of oxygen
$\eta_{\text{gas}}$	Gasification efficiency based on heating value
$v_{\text{O}_2}$	Stoichiometric coefficient of oxygen

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## 1. INTRODUCTION

With the world energy consumption projected to increase (Fig. 1) in the upcoming years and concerns about fossil fuel depletion led to the need for renewable and non conventional energy sources. It has been observed that the developing countries consume and need more energy.

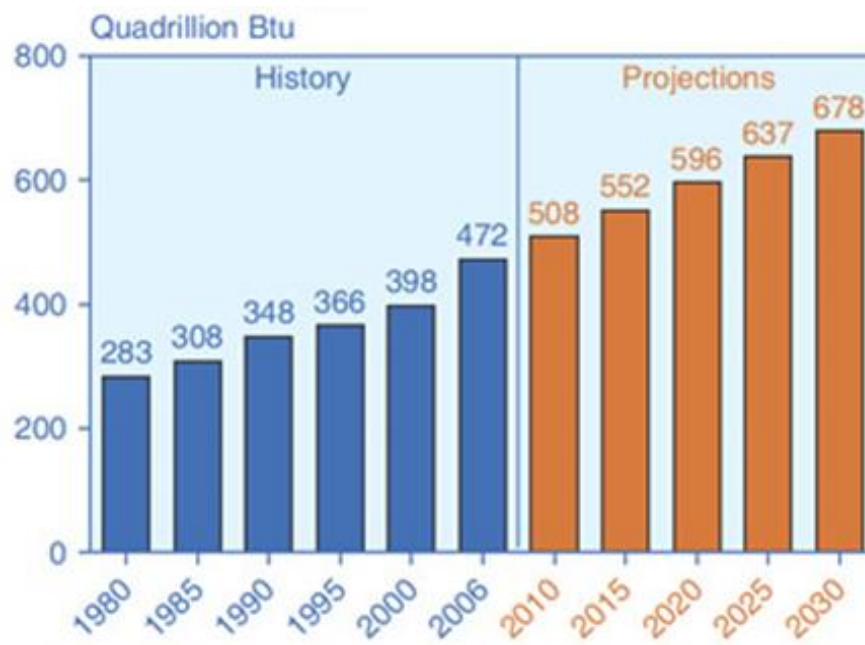


Fig. 1. Global energy consumption, adapted from [1].

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This thesis follows the style of Fuel.



Considering these factors efforts are being directed to identify potential alternate energy sources and the ways to improve the efficiency of conventional energy generation techniques. Different alternate energy sources identified and employed for power generation include geothermal, wind, hydropower, solar, tidal, fuel cells and biomass. Of these sources, biomass is available in plenty for potential energy extraction. The word biomass not only includes wood, but also municipal solid wastes and animal wastes. Large concentrated animal feeding operations (CAFO) in USA results in production of huge amount of dairy and feedlot biomass. Proper storage and disposal of this biomass is necessary or otherwise it will result in land and water pollution. Various methods of utilizing this biomass as fuel for energy generation have been studied extensively by the people in Coal and Biomass Energy Lab (CABEL) [2][3][4]. Co firing the dairy biomass with coal and gasification studies has been conducted.

Methods available for energy extraction from biomass include direct burning, thermo-chemical and bio-chemical methods. In the case of direct burning since the biomass does not have very high heating value when compared with fossil energy fuels like coal, co-firing them along with coal is one of the better options and it has been tested at CABEL, Texas A&M University. Bio-chemical methods include anaerobic digestion resulting in the production of bio gas which can then be used for heating applications. Thermo-chemical methods include torrefaction, pyrolysis and gasification. Torrefaction is carried out in the absence of air and at a temperature range between  $200^{\circ}\text{C}$  to  $300^{\circ}\text{C}$ . It results in the reduction of moisture and retains about 80% to 90% heat content of fuel. Pyrolysis is similar to torrefaction in terms of the environment used

but the temperature employed is much higher and it takes place above  $300^{\circ}\text{C}$ . Pyrolysis results in the production of gases, liquid and solids (char) all of which can be utilized to recover energy [5][6]. However gasification mainly produces gases.

Different gasifier configurations available are updraft, downdraft, crossdraft and fluidized bed gasifiers. Some of the gasifier configurations are in Fig. 2.

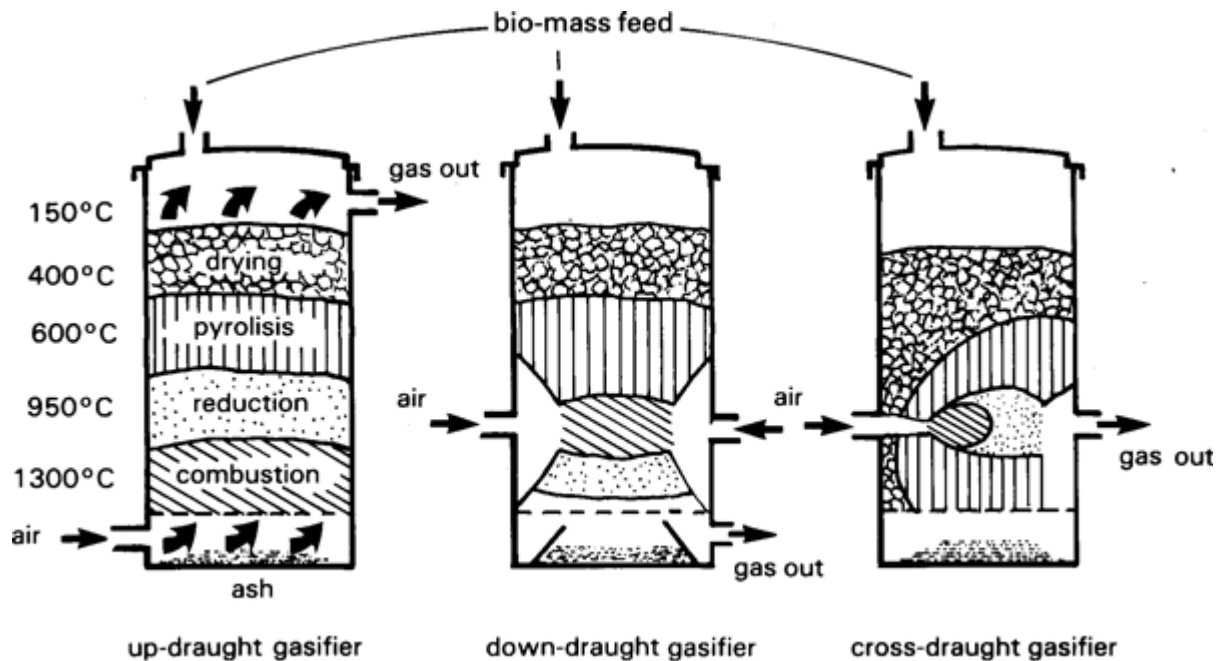


Fig. 2. Types of gasifiers, adapted from [7].

It can be seen from Fig. 2 that the different gasifiers are named according to the direction of movement of fuel and air within the gasifier. A fixed bed counter current facility is used for the current gasification study.

Counter current fixed bed gasifier has a higher thermal efficiency [8] because the hot gases produced in the reduction and oxidation zone move up along the pyrolysis and drying zone in turn heating the fuel in these upper zones and hence the exit gas has lower temperature. They have a simple, robust construction and high carbon conversion. The major drawback of this construction is the gases coming out have a significant proportion of tar which has to be removed before combustion in an internal combustion engine or gas turbines.

A simple schematic of updraft gasifier with different reaction zones and movement of the gasification medium within the reactor is shown below in Fig. 3.

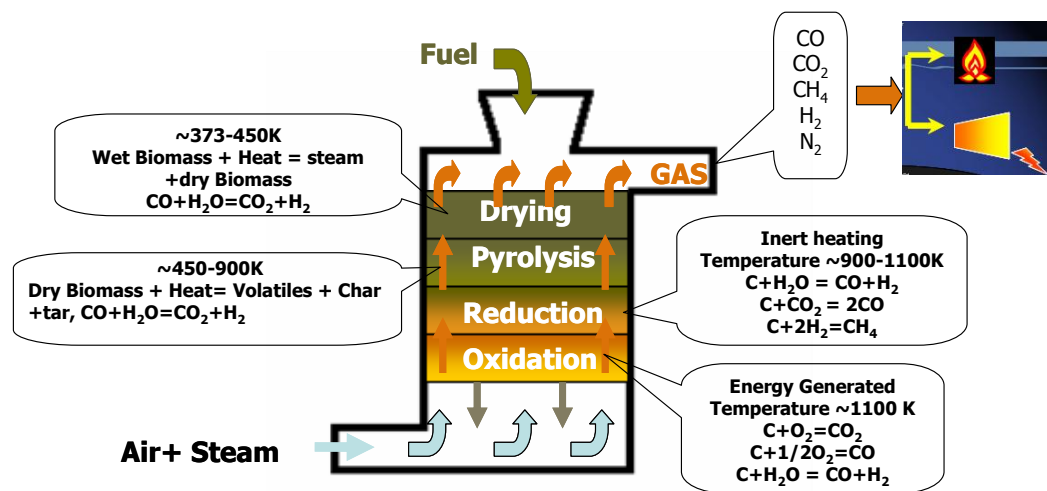


Fig. 3. Schematic of updraft gasifier, adapted from [9].

In the present study, counter current fixed bed gasification facility in CABEL was used to study for the effect of enriched air on the temperature profile and gas quality while gasifying dairy biomass. Enriched air mixture has higher oxygen concentration compared to that of air. In air gasification, it was found that nitrogen in air acted as a diluting agent for the heating value of the gases produced during gasification and hence enriched air was used to study for any increase in heating value of the produced gases. Also limited studies were done using carbon dioxide-oxygen mixtures as the gasifying medium since carbon dioxide can be easily sequestered from the flue gas compared to nitrogen, and hence heat value can be enhanced.

## 2. LITERATURE REVIEW

A number of studies have been carried out on the field of biomass gasification. A brief overview of some of the works is presented below.

### 2.1 Gasification of different biomass

Di Blasi et al. [10] studied the effect of different gasification conditions on the heating value of gases produced during gasification of several biomasses which includes beechwood, nutshells, olive husks and grape residues. A counter current gasification set up was used, and it was observed that the gas heating value varies from 4.6 to 5.5 MJ/Nm<sup>3</sup> with the air to fuel ratio and gasification of agricultural residues is more difficult when compared to that of wood.

Young et al. [11] investigated the gasification of dairy wastes in a multistage enthalpy extraction technology (MEET) gasifier. It uses a high temperature preheated air in a reactor vessel to gasify the biomass into synthetic gas. Two different gasifier configurations are used in the study carried out by Young et al. The first one being a slagging type and the other being a non slagging configuration. The different temperature ranges used are 1400<sup>0</sup>C for the slagging mode and around 900<sup>0</sup>C for the non slagging operation. It was observed that the calorific value of the gases produced increased while using high temperature air as the gasifying medium. Also both the gross and net gasification conversion efficiencies increased with increasing air preheat temperatures.

Zainal et al. [12] studied the gasification of furniture wood and wood chips in a downdraft biomass gasifier. The experimental system consists of a blow type downdraft gasifier with a cone structure, feeding system and an air supply system. Effect of equivalence ratio on the gas composition, calorific value and gas production rate are studied. From the study, it was concluded that the calorific value of the gases produced increases with the equivalence ratio, attains a peak and then starts decreasing with increase in equivalence ratio.

Raman et al. [13] studied the gasification of feedlot manure in a fluidized bed gasifier using the gas produced by the combustion of propane and air as the gas for fluidization and silica sand as the bed material. The effect of reactor operating temperature on the product gas yields, composition and the higher heating value was studied and it was observed that the gas yields (CO, H<sub>2</sub>, CH<sub>4</sub>) and the heating value increased with increase in the operating temperature.

Cao et al. [14] used a fluidized bed gasifier to study for complete tar elimination during gasification of sawdust under autothermic conditions. The effect of introducing the primary air and fuel at different ends was studied with the fuel entering the reactor from the top of the fluidized bed gasifier. It was observed that carbon conversion efficiency of 87.1% was obtained while the gases produced had a heating value of 5000 kJ/Nm<sup>3</sup> with reduced amount of tar.

Priyadarshan et al. [15] used a counter current fixed bed gasification facility to study for the effect of particle size on the gasification of litter biomass and high ash feedlot biomass. It was observed that the particle size did not have much effect on the

gas composition and hence the heating value. However high alkaline content in litter biomass resulted in agglomeration in the bed causing a reduction in peak temperature. During these experiments the ash produced during gasification was not removed continuously from the reactor.

Gerardo et al. [16] [17] studied the gasification of dairy biomass and a mixture of dairy biomass with coal. Experiments were carried out for different equivalence ratios and steam-fuel ratios. From the experiments, it was observed that under fuel rich conditions the production of hydrogen was low while mixtures rich with steam produced more hydrogen resulting in increased heating value.

Luo et al. [18] studied the gasification of pine saw dust using steam as the gasification medium and dolomite as the catalyst. Effect of particle size at different bed temperatures on the gasification performance was examined in a fixed bed gasifier. It was determined that both the gas yield and carbon conversion efficiency increases with increase in temperature and hydrogen and carbon dioxide content in the produced gas increase with decreasing particle size.

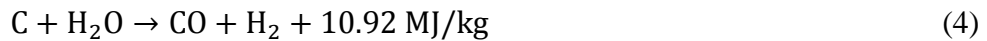
Zhang et al. [19] observed an increase in the heating value of the gases obtained by the gasification of loose biomass with oxygen enriched air in a fluidized bed gasifier. Gasification tests were carried out in a fluidized bed reactor using rice straw, rice husk, wheat straw, saw dust and combustible components in municipal wastes.

Considering all the previous work it was observed that studies have not been done for the gasification of cattle manure with enriched air mixture having higher

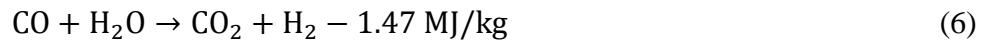
oxygen concentration as well as using carbon dioxide oxygen mixture as the gasification medium.

## 2.2 Gasification reactions

Various reactions which take place during gasification are listed below. [9][15]



Of these reactions, reaction (Eq.1) and (Eq.2) are found to be much faster than reaction (Eq. 3), (Eq. 4) and (Eq. 5). Apart from these reactions the water gas shift reaction (Eq. 6) also occurs in the presence of steam.



Gerardo et al observed increased production of hydrogen with increase in steam fuel ratio. Eq. 6 was used to validate the results obtained during experiments which employed the usage of steam. Further, due to the endothermic nature of the steam reforming reaction (Eq. 4) the temperature within the reactor also came down during



experimentation. In the present study, steam gasification was also studied in the presence of enriched oxygen.

### 3. OBJECTIVE AND TASKS

The overall objective of the gasification studies was to produce combustible gases using low ash partially composted dairy biomass (LAPCDB) as a fuel using air and steam as the gasifying medium. The specific objective of the current study was to use enriched air and steam as the gasifying medium and study their effects on temperature profile ( $T(x)$ ) in the bed, composition of gases produced and quality of gases produced. Following tasks were completed in order to achieve the current objective:

1. Modify the gasifier facility in order to provide enriched air.
  - i. Set up separate lines with rotameters for supplying pure oxygen and air.
2. Conduct gasification experiments and obtain results for temperature of bed, composition and heat value of gases.
3. Determine the effect of following operating parameters.
  - i. Oxygen level in the enriched air.
  - ii. Equivalence ratio.
  - iii. Inert gases  $\text{CO}_2$  and  $\text{N}_2$  in the enriched air.

## 4. EXPERIMENTAL SET UP AND PROCEDURE

### 4.1 Experimental facility

A 10 kW fixed bed gasification facility in Coal and Biomass Energy Laboratory, Texas A&M University was used for the current study. A schematic of the facility is shown in Fig. 4. It was constructed using a castable alumina refractory tube with an inner diameter of 13.9 cm (6 inches) and outer diameter of 24.5 cm (10 inches). The refractory tube is surrounded by an insulating blanket (9) of size 4.45 cm (1.75 inches) to minimize the heat losses. This entire set up is enclosed within a steel tube of inner diameter 34.3 cm (13.5 inches). The total height of the gasifier is 72 cm. [9]. The facility has a continuous fuel feeding facility (11), well insulated reactor to prevent any major heat loss (9), perfectly sealed to prevent air leak in order to maintain fuel rich condition within the reactor, air flow meters (2) to measure the amount of air being sent in to the reactor, a steam generator to produce steam to study gasification in the presence of steam (1), a set of electrical heaters (8) to maintain a uniform temperature, a grate with ¼” holes coupled with a pneumatic vibrator to remove the ash continuously during experimentation (5), suction pump (19) with gas filtration system to clean the gas produced during gasification, Thermo scientific Prolab mass spectrometer (16) along with computer (17) to analyze the clean gases coming out from the reactor followed by condensers (14) and filters (15), a suction fan (18) to drive out the gases produced and to maintain a slightly negative pressure within the reactor, K type thermocouples (6) present along the axis of the gasifier to measure the temperature, a Omega 8800

temperature recording system (7) which collects the data from the thermocouples and free board (10) above bed. Gerardo et al. [9] checked for the adiabaticity of the reactor.

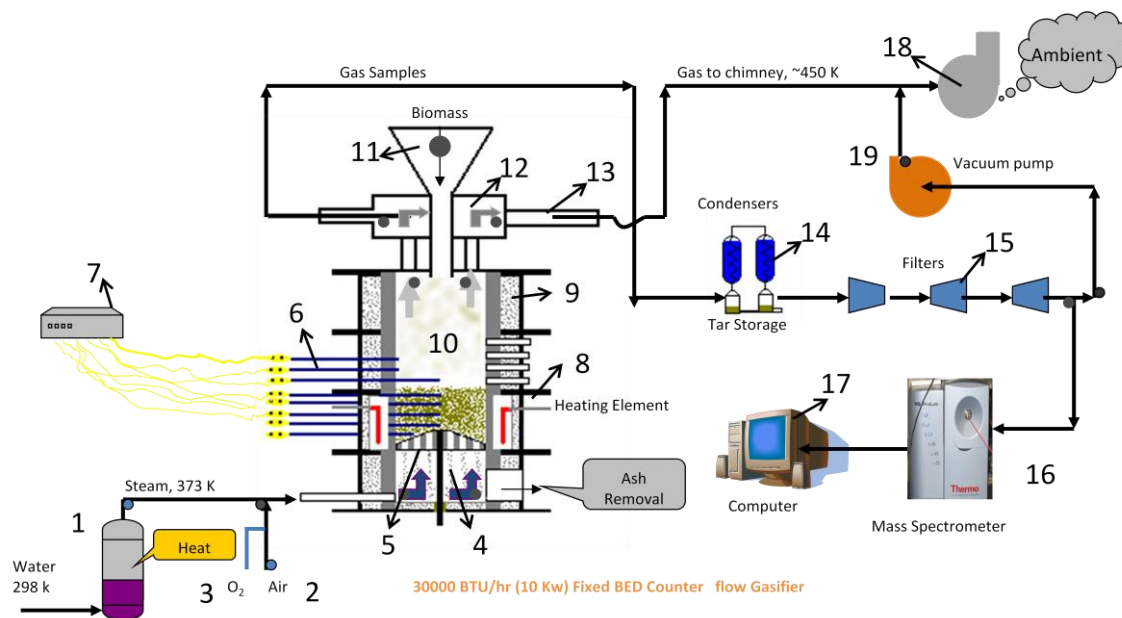


Fig. 4. Schematic of countercurrent fixed bed gasification facility.

Apart from these a new set of rotameters were installed to enable a specific amount of oxygen to be sent in along (3) with air so that gasification experiments can be carried out in enriched oxygen medium. In order to get a better understanding of the location of thermocouples within the bed, a zoomed in version of the reactor with the thermocouples is shown in Fig. 5. Eight K-type thermocouples were used for temperature measurement within the reactor and the location of each thermocouple is with respect to the top surface of the grate. They are located at 2 cm, 4 cm, 7 cm, 10 cm,

13 cm, 20 cm, 24 cm and 28 cm from the top of the grate and measure the temperature along the vertical axis of the gasifier.

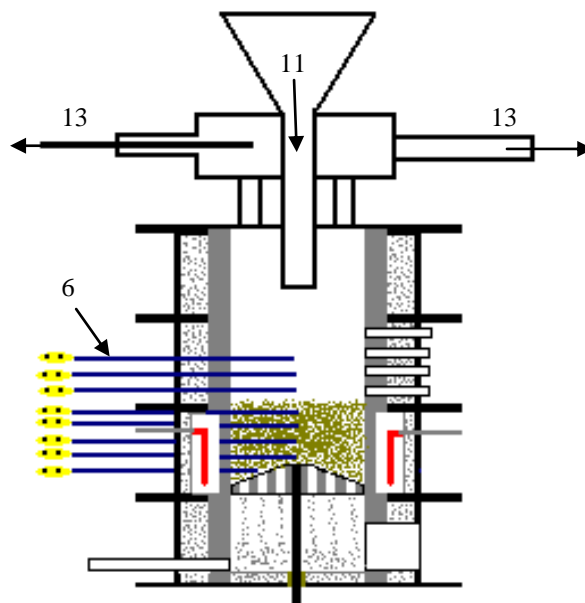


Fig. 5. Location of thermocouples within the reactor.

A picture of the facility is shown in Fig. 6. Due to the complaints received from the adjacent buildings about the odor of the gases produced during gasification of LAPCDB which were let out into the environment, a water quenching system and a vertical stack of height 10 ft were installed to clean the gases and let the gases out into the environment at an elevated height.

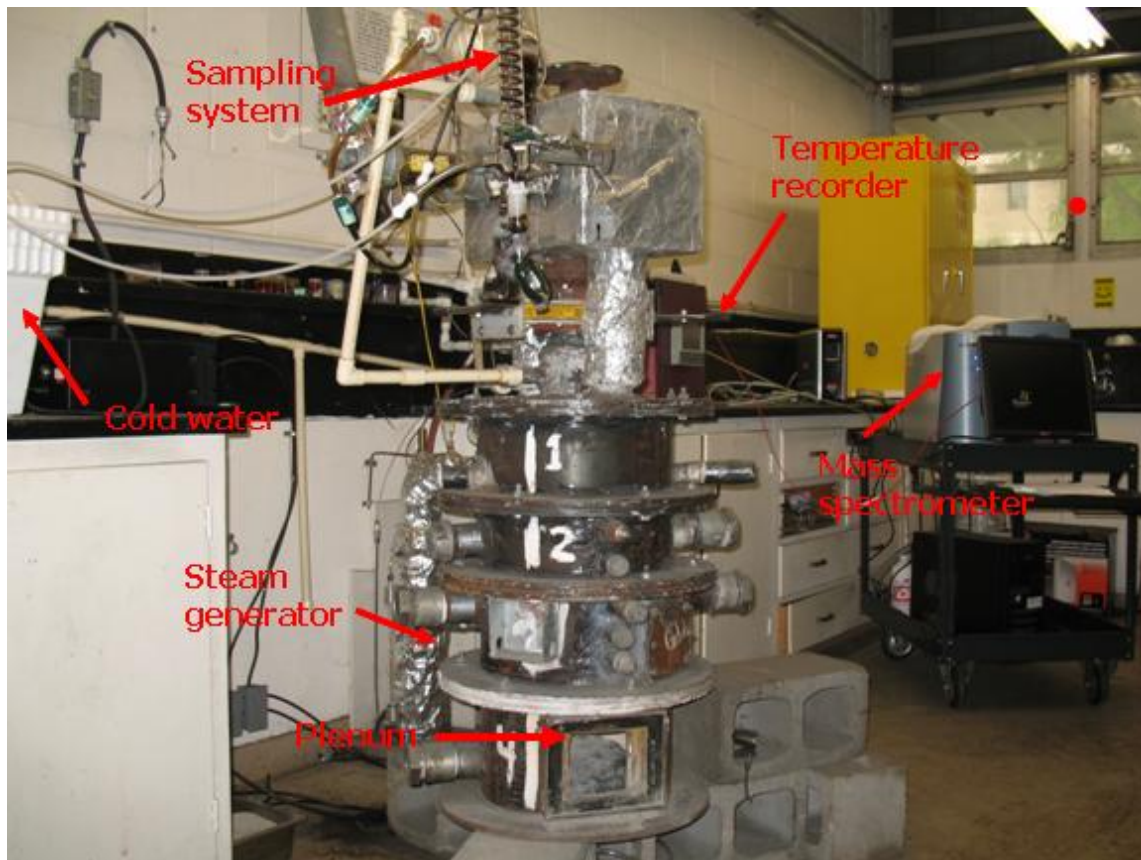


Fig. 6. CABEL gasification facility, adapted from [9].

#### 4.2 Steam generator calibration

Gerardo et al. [9] calibrated the steam generator to determine the amount of steam coming out for the known amount of power supplied to the heaters heating the steam generator. It is shown in Fig. 7. The steam flow produced is calculated according to the amount of water sent into the steam generator to maintain the water level within the generator which can be seen through the sight glass.

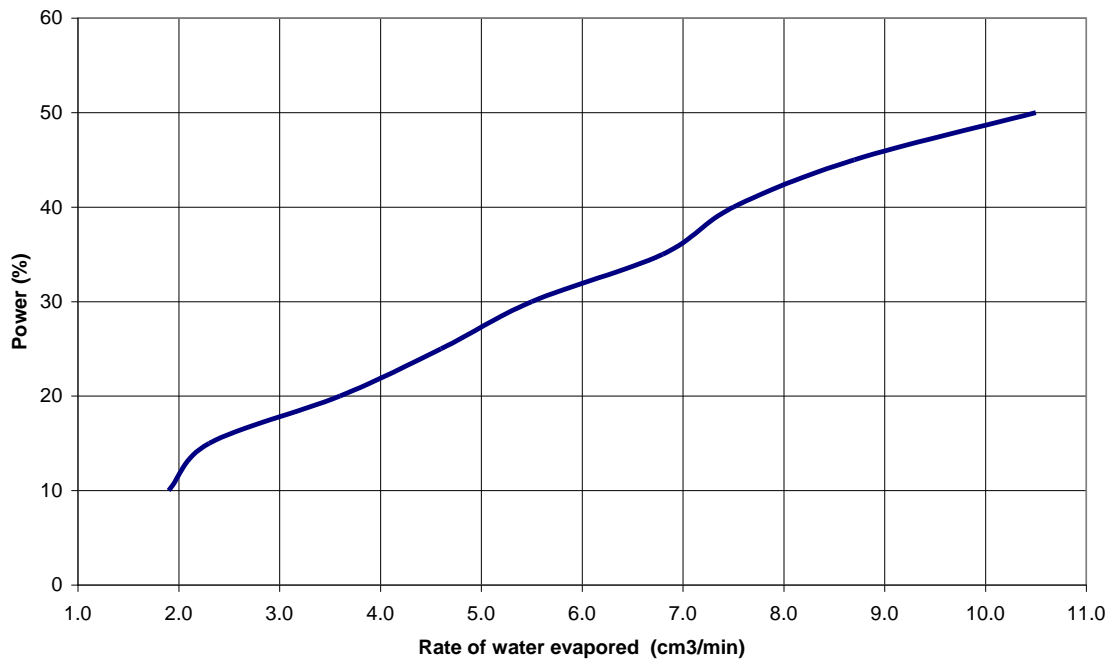


Fig. 7. Power supplied vs rater of water evaporated, adapted from [9].

#### 4.3 Experimental procedure

The gasifier was initially preheated using a propane torch until the temperature at a height of 2 cm from the grate reached a steady temperature of 800<sup>0</sup>C. Once the desired temperature was reached the torch was removed and the gasifier was sealed perfectly thereby preventing any air leak into the reactor. The pressure inside the reactor was maintained slightly below the atmospheric pressure using a suction fan. The fuel was added into the gasifier gradually until the bed height reached seven inches. The fuel got gasified and the ash produced was discharged. The bed height tends to decrease. The bed was maintained at a constant height by adding fuel at regular time intervals. Air mixtures

having higher percentage of oxygen were supplied to the reactor through the plenum (4). The temperature profile within the bed was monitored continuously using thermocouples located at different heights along the axis of the gasifier. The ash produced as a result of gasification was removed using a pneumatic vibrator coupled to the grate (5). Once the temperature profile reached a steady state, the gases were analyzed for their composition using a mass spectrometer (MS). A fraction of the gases produced during gasification was passed through a condensing system (14) which condensed out the condensables and then through a set of filters (15) to remove the particulates so that clean gas entered the MS without contaminating the MS. The same procedure was repeated for different equivalence ratio (ER) and steam fuel ratios (S:F).

Dwyer analog flow meters were used to control the flow of oxygen and air into the reactor. Different flow rates and equivalence ratios which were used are shown below in Table 1. Since minimum amount of oxygen which can be sent in through the analog flow meter is 2 SCFH (standard cubic feet per hour), higher equivalence ratios cannot be obtained when enriched air mixtures having higher oxygen percentages were used.



Table 1  
 Air and oxygen flows in SCFH (ft<sup>3</sup>/hr).

21%			24%			26%			28%		
Air (SCFH)	O <sub>2</sub> (SCFH)	ER	Air (SCFH)	O <sub>2</sub> (SCFH)	ER	Air (SCFH)	O <sub>2</sub> (SCFH)	ER	Air (SCFH)	O <sub>2</sub> (SCFH)	ER
60.00	0	2.11	50.67	2	2.10	44.40	3	2.15	41.14	4	2.10
40.00	0	3.16	-	-	-	29.60	2	3.23	30.86	3	2.80
30.00	0	4.21	-	-	-	-	-	-	20.57	2	4.20

#### 4.4 Parameters studied

A set of parameters which were used for the experiments are shown below.

- Enriched air (24%, 26%, 28% O<sub>2</sub>)
- Equivalence ratio (ER)(2.1 to 4.2)
- Steam fuel ratio (S:F) (0 and 0.33) (S:F=kg of steam/kg of AR fuel)
- CO<sub>2</sub> instead of N<sub>2</sub> (21% O<sub>2</sub> + 79% CO<sub>2</sub> and 28% O<sub>2</sub> + 72% CO<sub>2</sub>)

## 5. RESULTS AND DISCUSSION

### 5.1 Fuel properties

Low ash partially composted dairy biomass was used as the fuel for the present study. The ultimate and proximate analysis of LAPCDB is shown in Table 2. The fuel was obtained from the facility in Amarillo, Texas. Since the fuel was stored in the fuel storage room for the past 3 years, change in proximate analysis (ash and moisture percentage) was observed. However the H/C, O/C and N/C typically remain constant. Sweeten et al [20] [21] observed an increase in ash percentage and a corresponding decrease in combustibles on a dry basis with increase in composting time. The same trend was observed in the present study. Proximate analysis on the fuel was performed using Thermolyne benchtop muffle furnace in CABEL and the results are shown in Table 3. The standards used for the proximate analysis are ASTM D3173 to determine the moisture content, ASTM E3175 to determine the volatile matter and ASTM E1755 to determine the ash content in the biomass.

Thought the amount of ash in LAPCDB is very high when compared to woody biomass which has only 0.2 to 5 % of its weight as ash, LAPCDB has comparatively lower ash (14.9%) than the other dairy biomass which is high ash dairy biomass (59.9%) [4].

Table 2  
Fuel properties adapted from [9].

Dry loss %	25.26
Ash %	14.95
VM %	46.84
FC %	12.95
C %	35.27
H %	3.1
N %	1.9
O %	19.1
S %	0.42
HHV (kJ/kg)	12844
DAF HHV(kJ/kg)	21482
Dry HHV (kJ/kg)	17185
Empirical Formulae	$CH_{1.06}N_{0.047}O_{0.405}S_{0.0045}$
ER at which FC $\rightarrow$ CO	5.8
Air:fuel ratio FC $\rightarrow$ CO	0.87

From Table 3, we can see that the amount of combustibles has decreased from 80% to 76% on a dry basis. The reason can be attributed to partial composting of the biomass during the time period it was left unused.

Table 3  
Proximate analysis.

Composition	Percentage
Dry loss %	13.23
Ash %	20.28
FC and VM %	66.49

## 5.2 Biomass preparation

Properties of dairy biomass also depend on the surface from which the manure is collected. Biomass collected from concrete floor has lower ash content when compared to the one collected from soil surface because of collection technique disturbing the soil surface. The manure collected in concrete floors is first flushed out using a stream of water and the resulting fluid is then passed through a mechanical separator to remove the solids from the liquid. The liquid is then circulated to be used as lagoon water. LAPCDB separated solids are obtained using this collection technique [4].

For the current study, coarse ground samples of LAPCDB sep sol were obtained from Amarillo, Texas, since samples having lower particle size resulted in fuel entrainment and packed beds causing poor distribution of gasification medium within the reactor.

### 5.3 Size distribution

Size distribution studies were done on LAPCDB according to ASTM D4749, and the Rosin Rammler plot and histogram for the fuel size distribution is shown below in Fig. 8 and Fig. 9 respectively. Since coarse ground samples are used, size analysis showed 79% of the sample has a size greater than 300 micron.

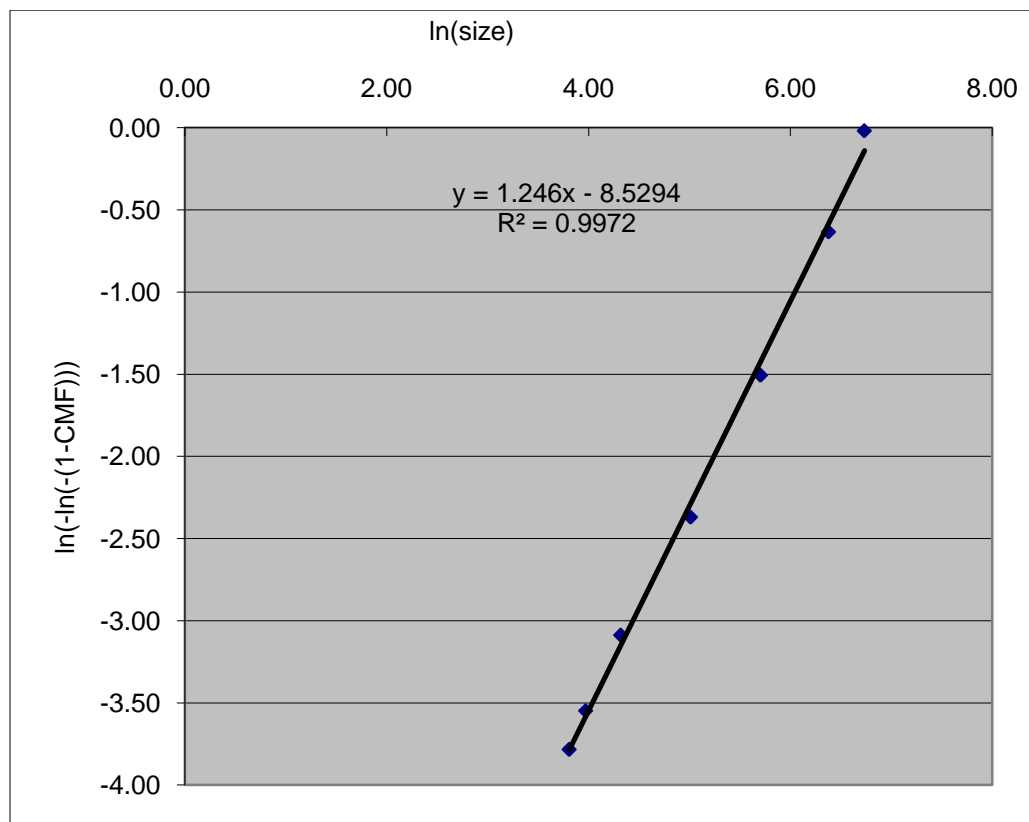


Fig. 8. Rosin-Rammler plot for LAPCDB.

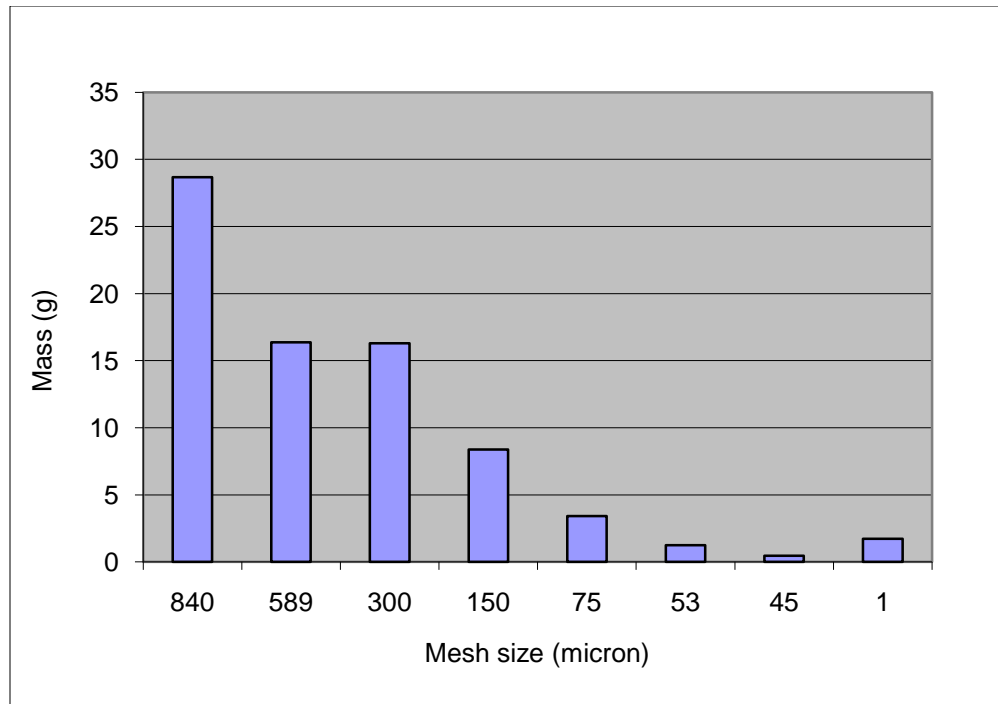
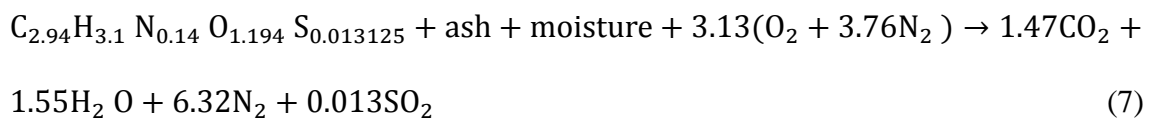


Fig. 9. Histogram for LAPCDB size distribution.

#### 5.4 Theoretical model for peak temperature

Using ultimate analysis of fuel one can derive an empirical formula of fuel using standard combustion literature [22]. The amount of stoichiometric air needed for complete combustion of LAPCDB is calculated as below.



From the above equation, stoichiometric air fuel ratio can be calculated and it is determined to be,  $(A:F)_{\text{stoich}} = 7.17$  kg/kg of dry ash free fuel = 4.3 kg of air/kg of as received fuel. Equivalence ratio (ER) is calculated using the following formula

$$ER = \frac{(A:F)_{\text{stoich}}}{(A:F)_{\text{actual}}} \quad (8)$$

However when enriched air with higher oxygen percentages is used, the equivalence ratio is calculated as below. Detailed calculations are shown in Appendix C.

$$ER = \frac{(O:F)_{\text{stoich}}}{(O:F)_{\text{actual}}} \quad (9)$$

When steam is used along with air, steam fuel ratios (S:F) are calculated according to the amount of steam sent in to the amount of fuel and is expressed as below.

$$S:F = \frac{\text{kg of steam}}{\text{kg of fuel sent in}} \quad (10)$$

Assuming all carbon in the fuel gets converted to CO or CO<sub>2</sub>, char surface temperature under diffusion controlled combustion can be estimated using Eq. 11 and Eq. 12 below [22]:

$$\frac{c_p(T_s - T_\infty)}{h_c} = B \quad (11)$$



$$B = \frac{Y_{O_2,\infty}}{v_{O_2}} \quad (12)$$

where  $T_s$  is the surface temperature of the particle (K),  $c_p$  is the specific heat of the mixture,  $Y_{O_2}$  is the mass fraction of the oxidizer,  $v_{O_2}=1.33$  for CO production, 2.667 for  $CO_2$  production and  $h_c$  is the reaction enthalpy for the carbon to carbon monoxide reaction (9204 kJ/kg). It should be noted that  $c_p$  represents the value for a mixture of gases,  $N_2$ ,  $O_2$ ,  $H_2O$  etc. B number Eq. 11 and Eq. 12 are used to determine the maximum theoretical temperature which can be obtained when using enriched-air mixtures as the gasification medium. Theoretical estimates for the peak temperature for an equivalence ratio of 2.1 are shown in Table 4.

Table 4  
Theoretical peak temperatures.

$O_2$ %	$T_{peak}$ ( $^{\circ}C$ )
21	950
24	1082
26	1170
28	1258

## 5.5 Experimental results

Initially experiments were carried out using finely ground LAPCDB. Very small particle size yielded poor temperature profiles and gas composition which is explained in detail in Appendix A. The finely ground samples were replaced with LAPCDB sep-sol fuel samples in order to get better results. The modifications performed on the mass spectrometer in order to get accurate measurements on gas composition are detailed in Appendix B.

### 5.5.1 Temperature profile

Experiments were carried out for different ER and S:F using enriched-air mixtures having 24%, 26% and 28% oxygen and the remaining being nitrogen.

#### 5.5.1.1 Temperature profile variation with time

Variations in temperature profiles with time are shown in Fig. 10 for gasification of LAPCDB sep-sol with air having 21% oxygen at two different ER. Fig. 11(b) shows the effect of S:F on temperature profile. From the graph, the following can be observed. The peak temperature decreases with increase in ER due to the decrease in the amount of oxygen supplied to the reactor during gasification. At ER=2.1 and S:F=0, there is a wide variation in the temperature profile with time. The peak temperature was moving between 2cm and 7 cm before finally reaching a steady state with peak temperature at 4 cm from the grate (Fig. 10).

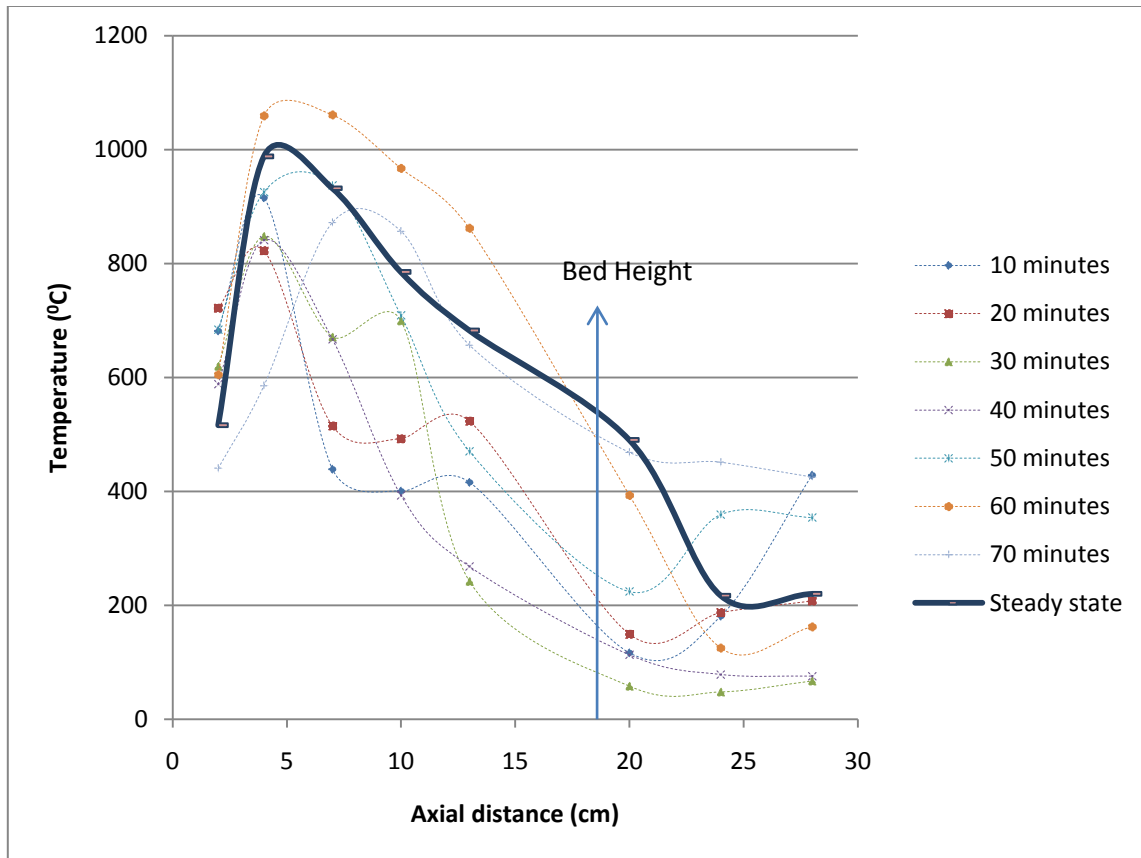


Fig. 10. Temperature profile variation, 21% oxygen, ER=2.1, S:F=0.

The temperature was expected to decrease when steam was introduced into the reactor. But for gasification with 21% oxygen at ER=4.2 and S:F=0.33, the peak temperature obtained was slightly higher than the peak temperature obtained for the case without steam. This may be due to (a) slight exothermic nature of the water gas shift reaction, (b) combustion of hydrogen within the oxidation and reduction zones, (c) cracking of steam into hydrogen and oxygen which in turn results in more oxygen

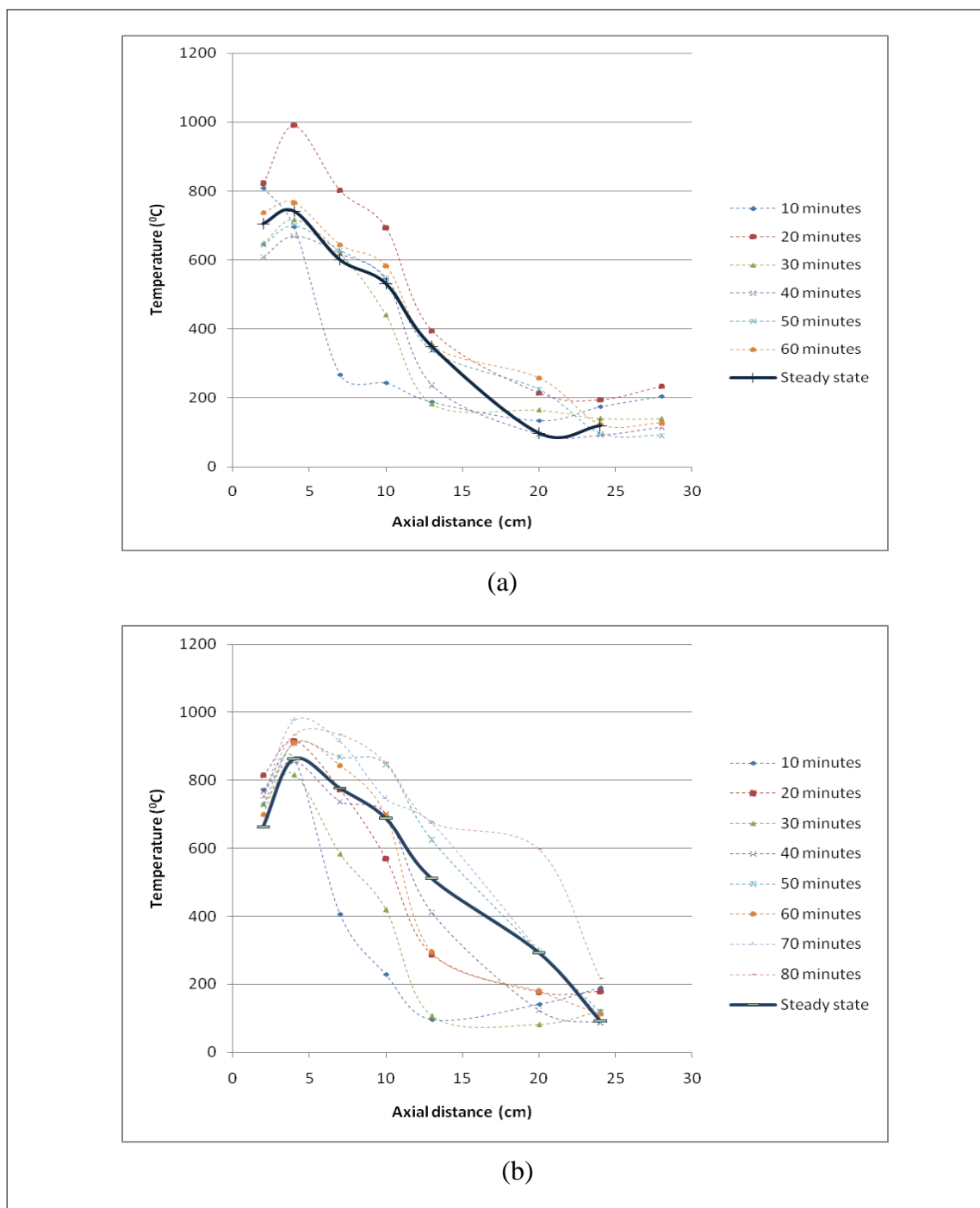


Fig. 11. (a) Temperature profile variation, 21% oxygen, ER=4.2, S:F=0, (b) Temperature profile variation, 21% oxygen, ER=4.2, S:F=0.33.

available for oxidation, (d) increased mass flow (air flow and steam flow) into the reactor which in turn results in better diffusion of air within the bed and in turn better oxidation and hence higher temperature. Variation of the temperature profile with time looks similar for the case of higher ER, i.e ER=4.2 with and without steam with respect to the location of peak temperature within the bed (Fig. 11 (a) and Fig. 11 (b)). The peak temperature was observed at 4 cm above the grate and it did not fluctuate once a steady temperature profile was obtained throughout the bed.

With enriched air of 28% oxygen, the variation of temperature profile with time is shown in Fig. 12. It can be observed from the graph that the peak temperature is higher when compared to that obtained when using air as the gasification medium. Also the variation in temperature was similar for both the cases with and without steam. The time taken to achieve steady state within the bed was less for the case using steam. In the case of enriched air, the total amount of oxygen supplied to the reactor is the same as the case of air gasification, but only the concentration of oxygen in the mixture differs, i.e the total mass flow of the gasifying medium which goes into the reactor decreases in order to maintain same ER. The amount of nitrogen supplied decreases when using the enriched-air mixture, and hence the amount of heat required to heat the nitrogen (specific heat of nitrogen varies between 1.146 kJ/kg K to 1.204 kJ/kg K for the temperature range of 900 K to 1200 K) to the bed temperature also decreases. This in turn results in higher bed temperature since there is less inert gas nitrogen.

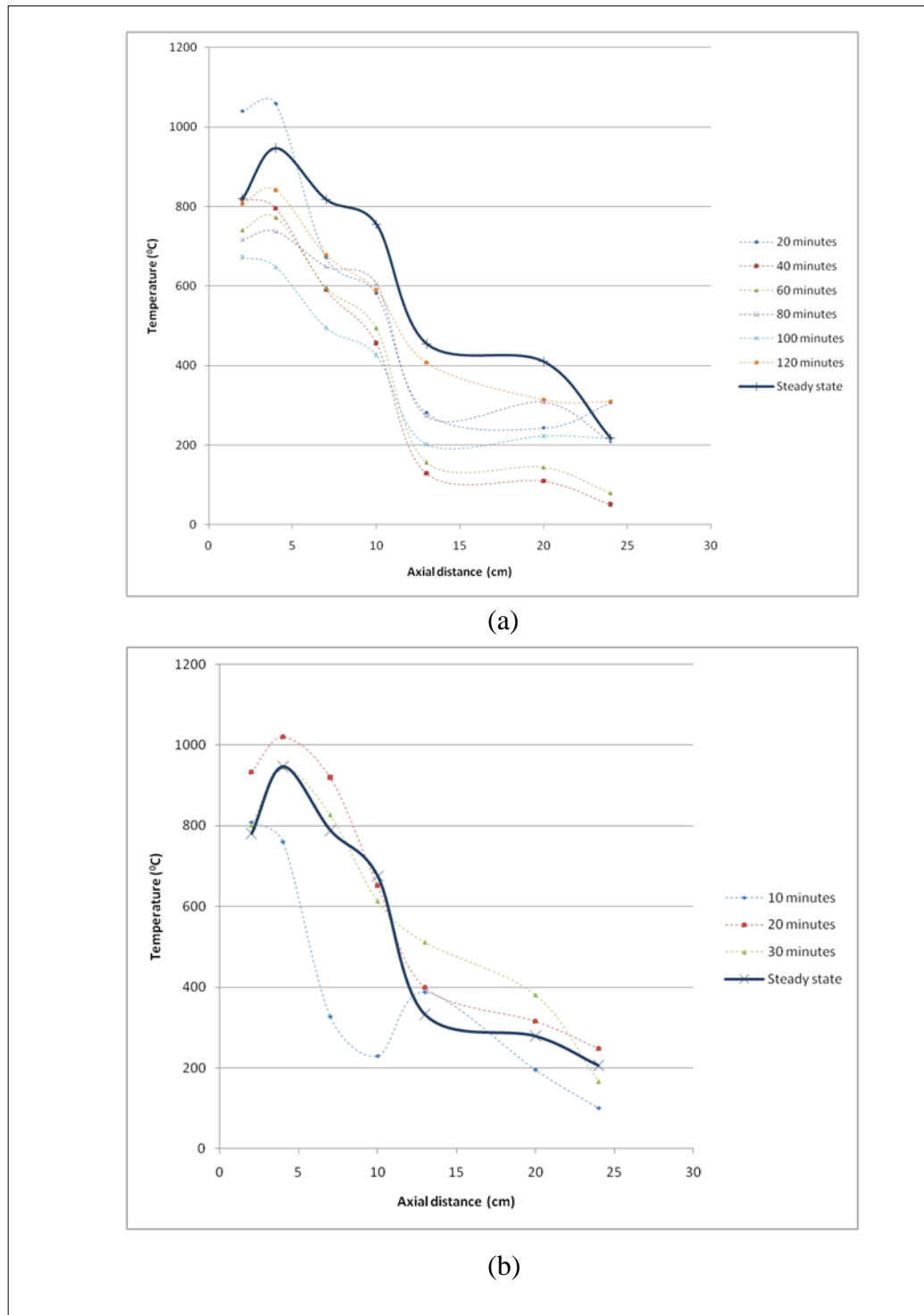


Fig. 12. (a) Temperature profile, 28% oxygen, ER=4.2, S:F=0, (b) Temperature profile, 28% oxygen, ER=4.2, S:F=0.33.

### 5.5.1.2 Effect of oxygen percentage

Once the steady state is reached, the effects of various parameters on peak temperature, temperature profiles and gas composition were studied. For the gasification experiments with higher oxygen percentages, at  $ER=2.1$  and  $S:F=0$ , the temperature profiles obtained are plotted in Fig. 13. The peak temperatures obtained can be compared to that of the theoretical values obtained using B number.

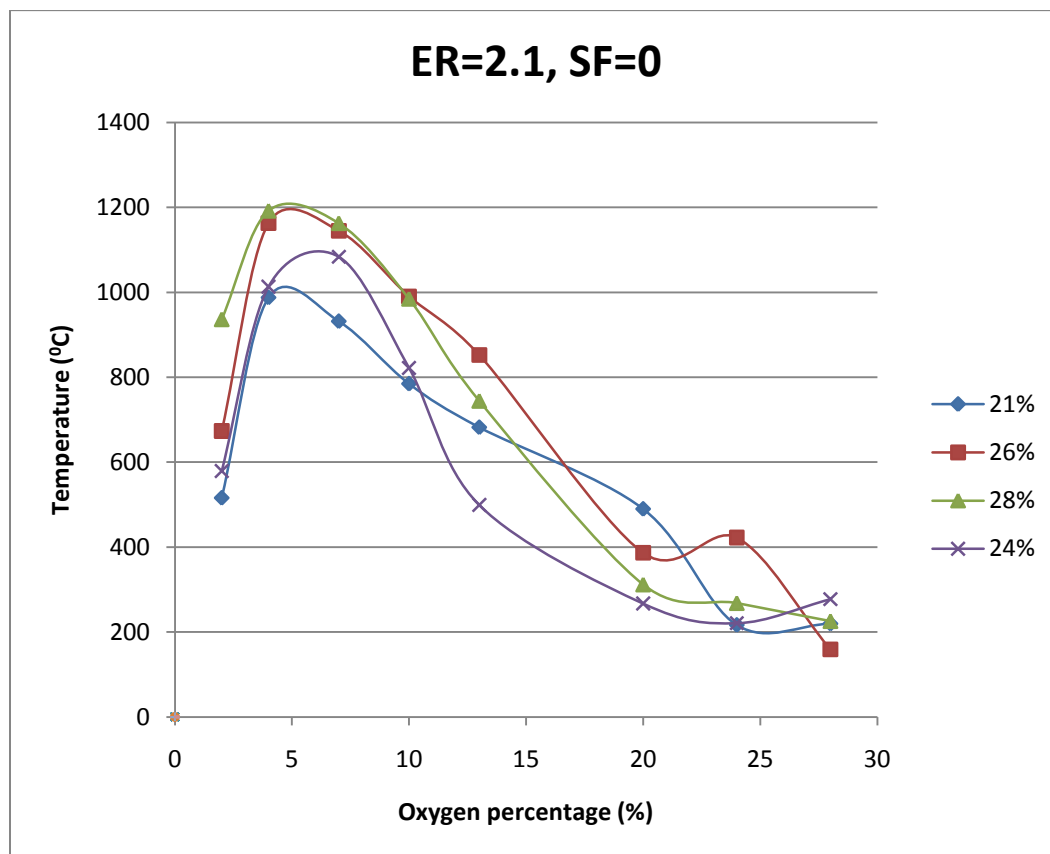


Fig. 13. Steady state temperature profile,  $ER=2.1$ ,  $S:F=0$ .

From Fig. 13 the peak temperature obtained when using enriched air mixtures is observed to increase with increased oxygen concentration. The numbers obtained experimentally were almost same as the values calculated theoretically using B number calculations. This can be seen in Fig. 14.

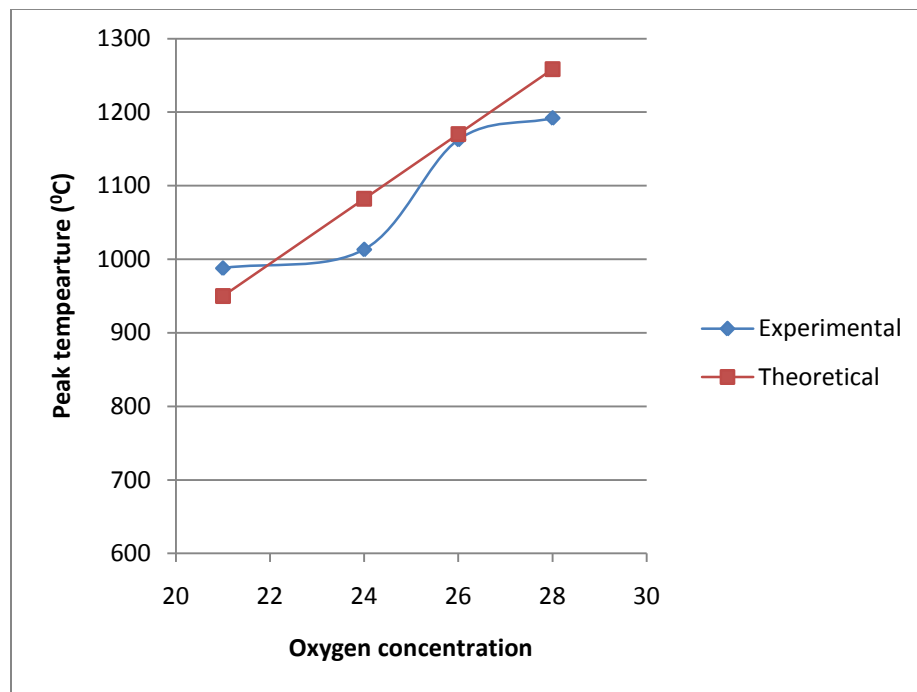


Fig. 14. Experimental peak temperature vs theoretical peak temperature.

### 5.5.1.3 Effect of ER and S:F

As the ER increases the peak temperature was observed to decrease. Fig. 15 shows the steady temperature profile with and without steam at ER=2.8. In the present study all the experiments involving steam are carried out for only one S:F which is 0.33 kg of steam per kg of as received fuel or 0.55 kg of steam per kg of dry ash free fuel.



The temperature profiles have different slopes because of the variation in thermal diffusion and convection of the gasification medium (air or enriched air or air steam mixture) and the pore spaces through which the hot gases travel up along the bed through the available voids within the bed. Fig. 16 shows the temperature profiles for gasification at ER=4.2 in the absence and presence of steam for two oxygen concentrations.

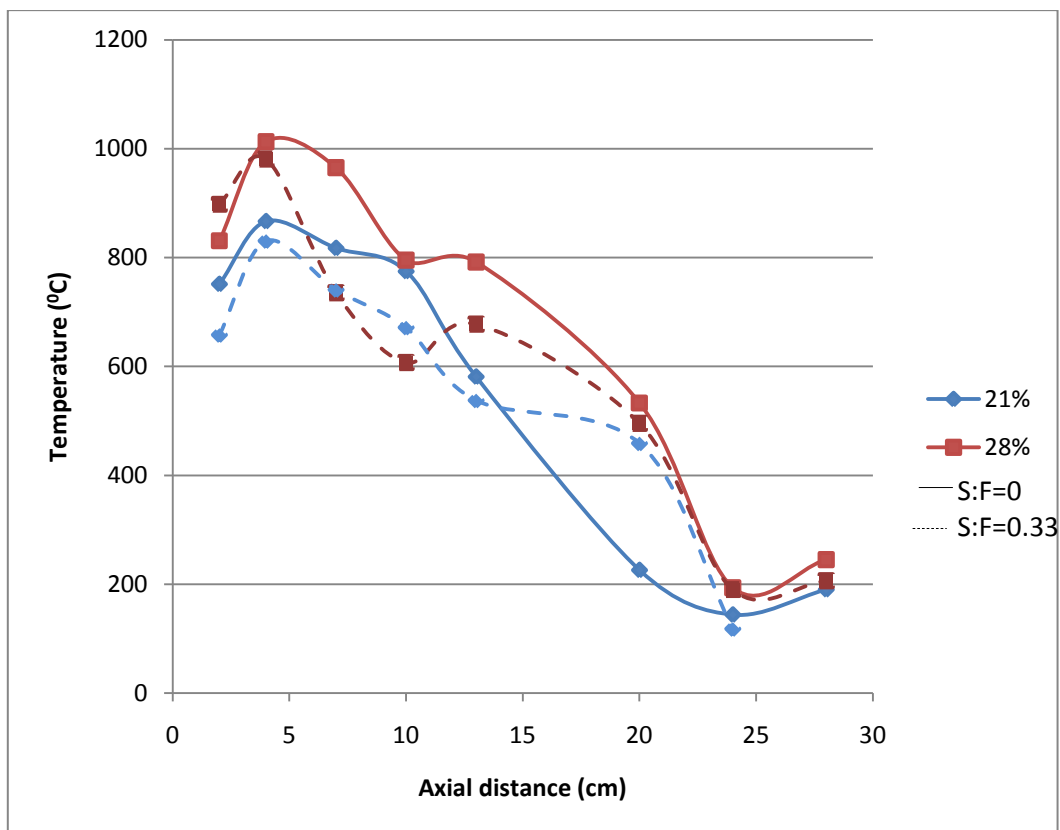


Fig. 15. Steady state temperature profile, ER=2.8.

Enriched-air mixtures having 24% and 26% oxygen were not used at ER=2.8 because of the limitations in the analog flow meters which cannot measure flows less

than 2 SCFH. Higher oxygen percentages result in higher peak temperature within the bed. In the presence of steam the temperature decreases in most cases but in some cases the temperature raises or remains the same. The reasons behind higher temperatures were mentioned earlier using Fig. 11 which shows the variation in temperature profiles with time.

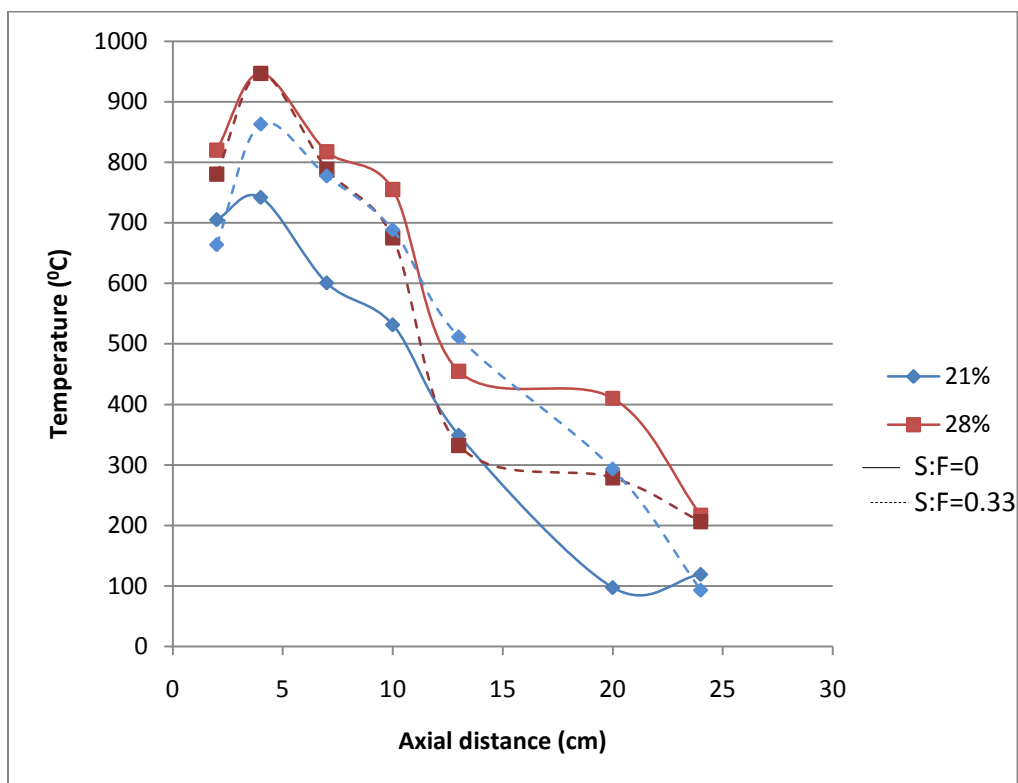


Fig. 16. Steady state temperature profile, ER=4.2.

While using steam, the peak temperature increases while it remained almost the same for enriched air having 28% oxygen. As the ER is varied between  $2.1 < ER < 4.2$ , we notice a drop in peak temperature with increase in ER. This can be seen from Fig. 17.

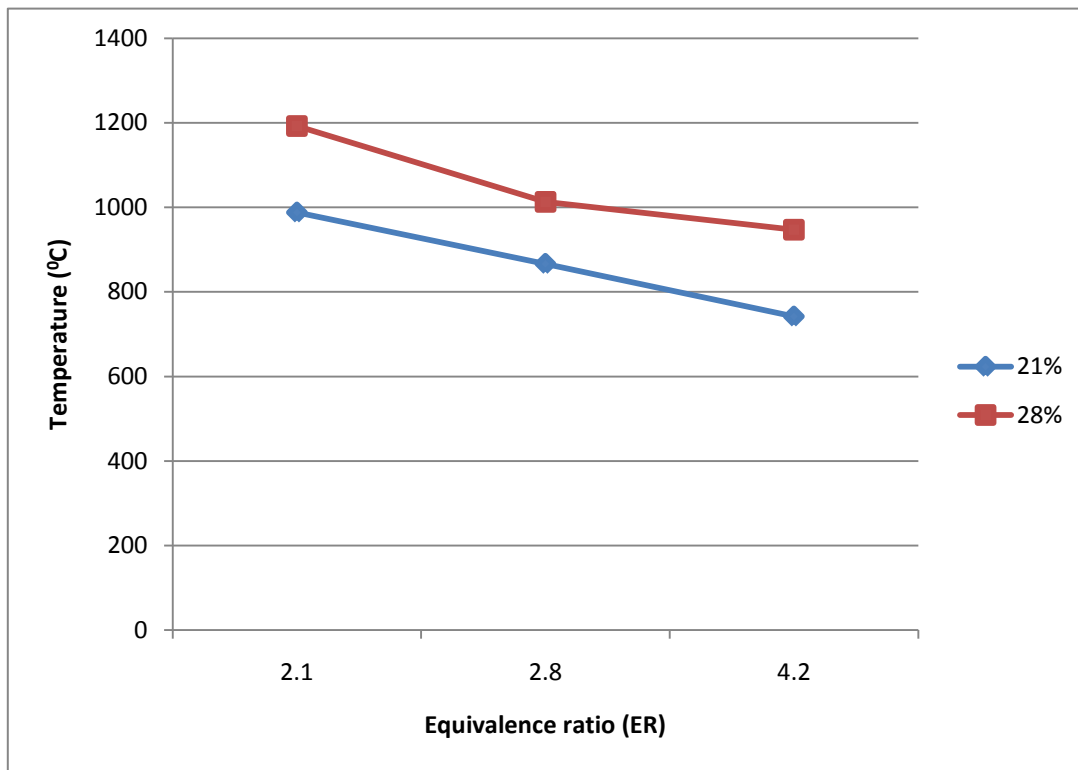


Fig. 17. Peak temperature vs equivalence ratio (ER); S:F=0.

When ER increases beyond upper limit, the gasification process is not self sustaining. Since higher ER results in lower oxygen supply to bed and hence less heat is available from char oxidation to sustain the pyrolysis and drying of the solid fuels. However lower equivalence ratios result in very high temperatures and for fuels like LAPCDB with high ash content, but it may cause ash slagging and result in formation of big lumps of ash over the grate as the reactor cools down. Young et al [11] observed dairy biomass ash softening at  $900^{\circ}\text{C}$  and melting at  $1350$  to  $1400^{\circ}\text{C}$ . Since the temperature obtained at  $\text{ER}=2.1$  was greater than  $900^{\circ}\text{C}$ , ash softening and

agglomeration took place at lower ER. The ash lumps formed during experiments at lower ER (ER=2.1) are shown in Fig. 18. This agglomerated ash hinders the diffusion of gasification medium (air and steam) within the bed and its removal from the reactor also was difficult. Because of these constraints experiments were not carried out with steam for ER=2.1. Hence an appropriate ER should be selected for proper gasification and for this study it was chosen to be  $2.8 < ER < 4.2$ .

From the ash composition of LAPCDB obtained by Gerardo et al [9], we can calculate the slagging and fouling potential using the method stated by Maglinao et al [23]. Slagging potential was calculated to be 0.35 which is low but the fouling potential was 1.67 which is a very high number and causes severe fouling. A sample calculation is shown in Appendix F.



Fig. 18. Agglomerated ash by slagging and the normal ash.

#### 5.5.1.4 Effect of CO<sub>2</sub>:O<sub>2</sub>

Enriched air results in the presence of nitrogen in syn gas which lowers the heat value of gases. CO<sub>2</sub> can be separated easily from products compared to N<sub>2</sub> in the event CO<sub>2</sub> sequestration is necessary to enhance the heat values. Hence, experiments were performed using carbon dioxide – oxygen mixture as the gasification medium instead of air. In this case, carbon dioxide is substituted for nitrogen in the air mixture. The same Dwyer mass flow meter was used to control the flow of carbon dioxide and oxygen so that a mixture having 21% oxygen and 79% carbon dioxide is obtained. Enriched oxygen mixtures were also used to study for the effect of higher oxygen concentration on gasification. Since the flow meters were specifically designed to measure air flow, necessary correction factors were used to determine carbon dioxide flow using the same Dwyer flow meter. The use of carbon dioxide as the gasifying medium helps to reduce the formation of NO<sub>x</sub> if any is produced during gasification reactions. Also the carbon dioxide produced as a result of gasification can be separated and circulated again into the reactor at high temperatures (e.g as cooling medium for gasifier) in order to increase the efficiency of the reactor and also to sustain the reaction within the gasifier. This will also increase the upper limit on ER. This in turn helps to reduce the amount of carbon dioxide released into the environment.

Carbon dioxide (CO<sub>2</sub>) has a slightly higher specific heat than nitrogen (N<sub>2</sub>) at higher temperatures. The difference in specific heat of CO<sub>2</sub> and N<sub>2</sub> is shown in Fig. 19.

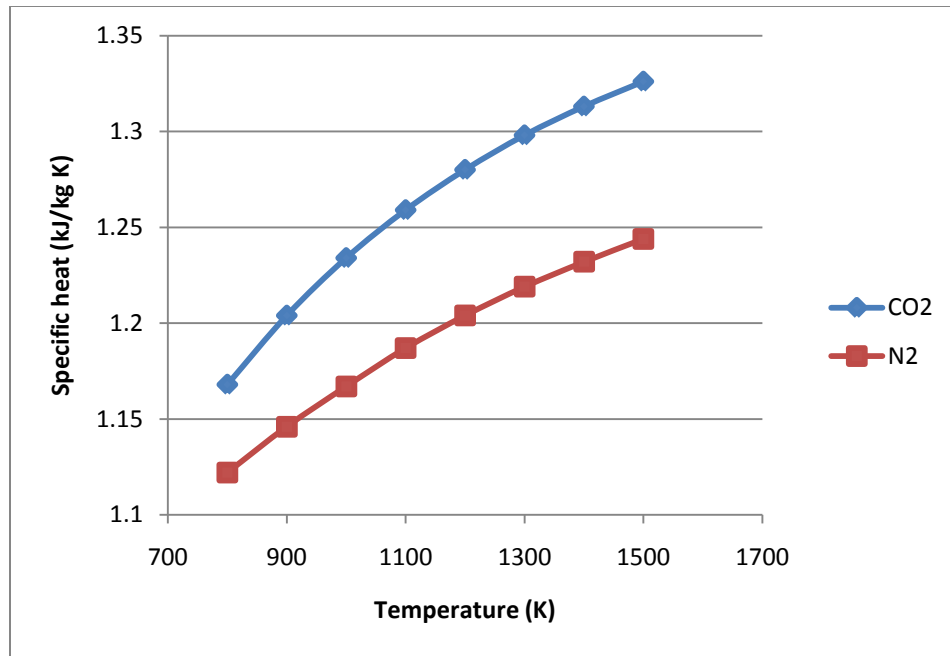


Fig. 19. Specific heat capacities of CO<sub>2</sub> and N<sub>2</sub>, adapted from [24].

Then  $c_p$  of the mixture of CO<sub>2</sub> and O<sub>2</sub> is higher than  $c_p$  of the mixture of N<sub>2</sub> and O<sub>2</sub>. Hence  $T_{\text{peak}}$  is expected to be low according to Eq. 11. The difference in peak temperatures can be observed in the temperature profiles (Fig. 20 and Fig. 21) obtained using carbon dioxide in the gasifying medium instead of nitrogen.

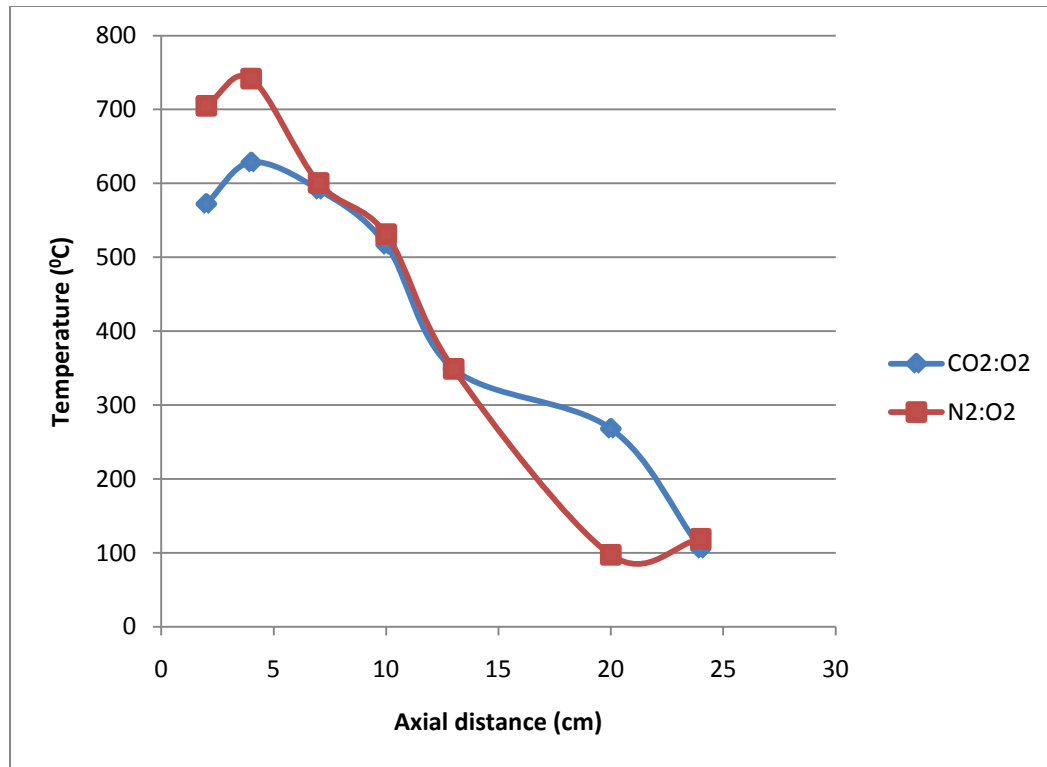


Fig. 20. Temperature profile, 21% oxygen, ER=4.2, S:F=0.

However at higher oxygen percentages, the peak temperature obtained using carbon dioxide was almost similar to that of air. This may be explained as follows; as  $O_2$  increases,  $T_{peak}$  is expected to go up which then drives the endothermic Boudouard reaction (Eq. (3)). Further studies have to be done to get a better understanding of the various mechanisms taking place within the gasifier during  $CO_2:O_2$  gasification.

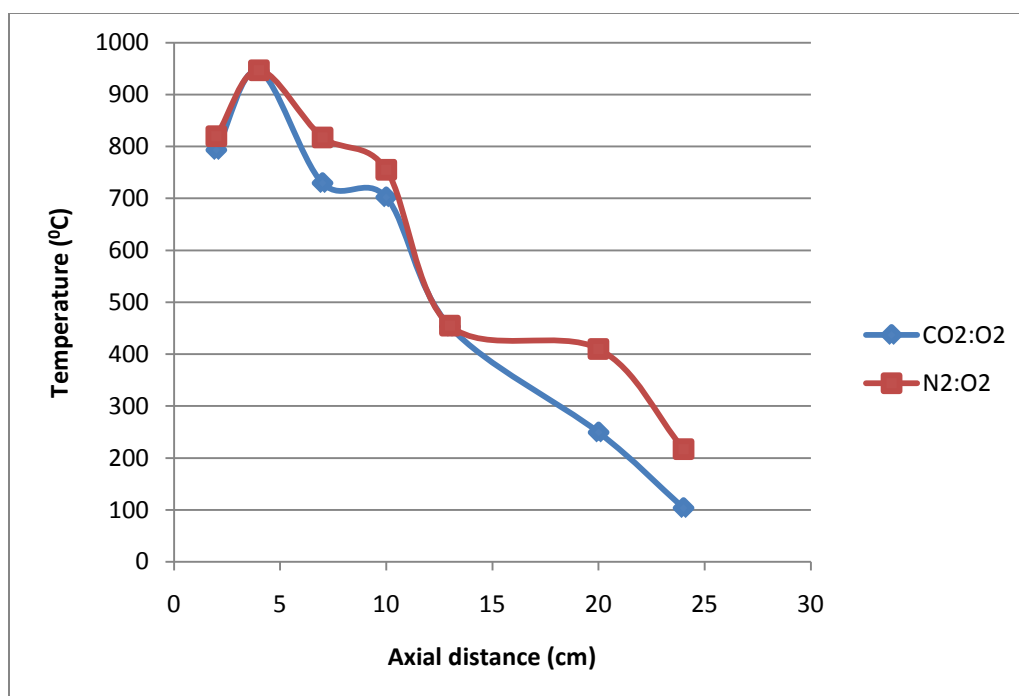


Fig. 21. Temperature profile, 28% oxygen, ER=4.2, S:F=0.

### 5.5.2 Gas composition

For all the experiments, the gas composition was measured using a Thermo scientific ProLab mass spectrometer. The mass spectrometer should be calibrated initially using gases with known composition. The procedures followed in order to ensure proper working of the mass spectrometer are outlined in Appendix B.

#### 5.5.2.1 Effect of oxygen percentage

Fig. 22 shows the gas composition obtained for enriched air gasification with ER=2.1. The percentage of carbon dioxide produced increased with increased oxygen percentage due to higher oxygen concentration in the incoming gasification medium. It



was accompanied by a decrease in carbon monoxide and an increased production of hydrogen.

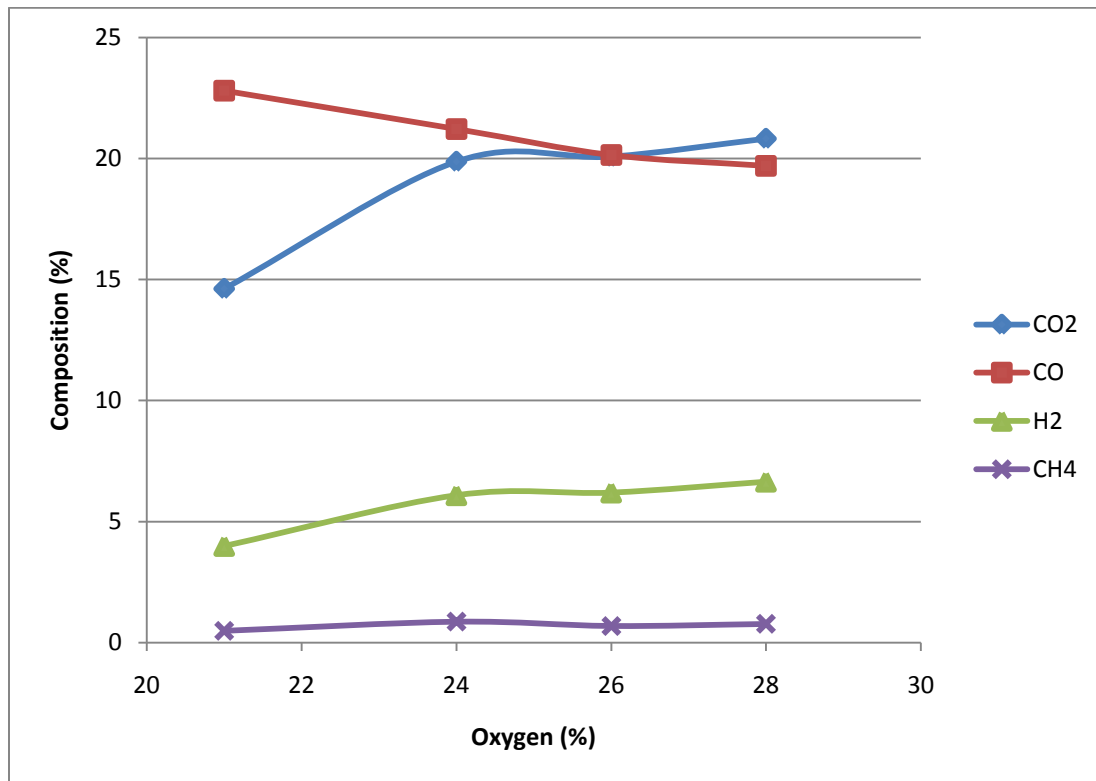


Fig. 22. Gas composition for enriched air gasification, ER=2.1, S:F=0.

A small amount of hydrocarbons (methane and ethane) were also produced. The rest is nitrogen from the air. Though experiments on LAPCDB sep sol were performed using air as gasification medium by Gerardo et al. [9], some experiments were performed using the same conditions for the same biomass sample since proximate analysis appear to be different due to the aging effect on the fuel. The difference in results obtained is shown below in Fig. 23. The major difference is in the amount of hydrogen produced. This may be due to the amount of moisture in the LAPCDB which was more in the fuel used by Dr Gerardo (Table 2) while aged biomass had low moisture and higher ash percentage (Table 3). Though some amount of moisture might evaporate while passing through the drying zone, moisture trapped within the fuel may react with carbon monoxide to form hydrogen and carbon dioxide according to water gas shift reaction (Eq. 6).

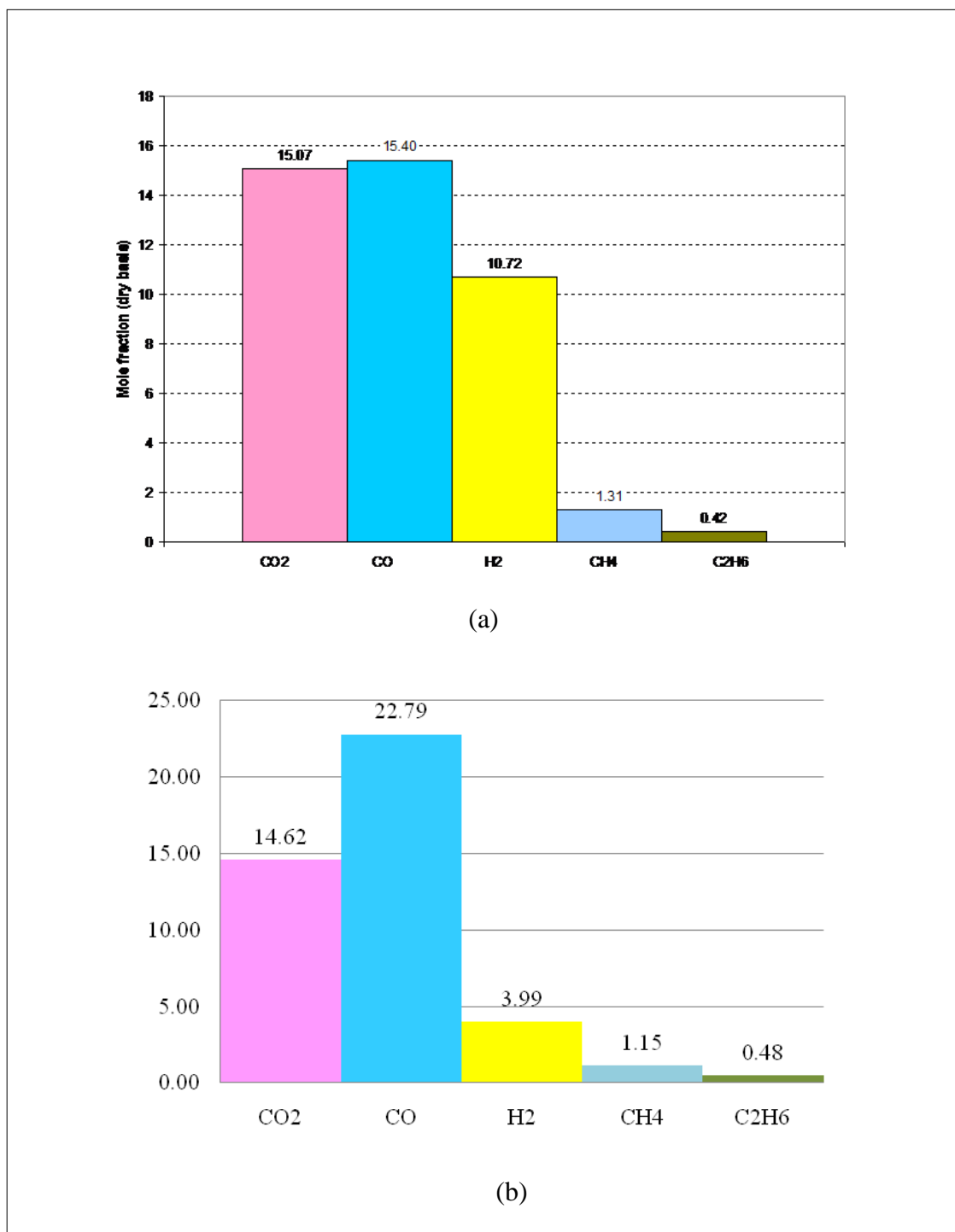


Fig. 23. (a) Gas composition for experiments at ER=2.1, adapted from [9], (b)

Gas composition for composted LAPCDB, ER=2.1, S:F=0.

### 5.5.2.2 Effect of ER and S:F

Fig. 24 shows the variation in gas composition for different equivalence ratios when using air as the gasifying medium with and without steam. The amount of hydrogen produced increases with introduction of steam into the gasification reactor. Also the presence of moisture in fuel can increase  $H_2$  production as mentioned earlier. The trend observed was an increase in carbon dioxide and decrease in carbon monoxide with increased ER. The results obtained while using steam can be validated using water gas shift equation (Eq. 6).

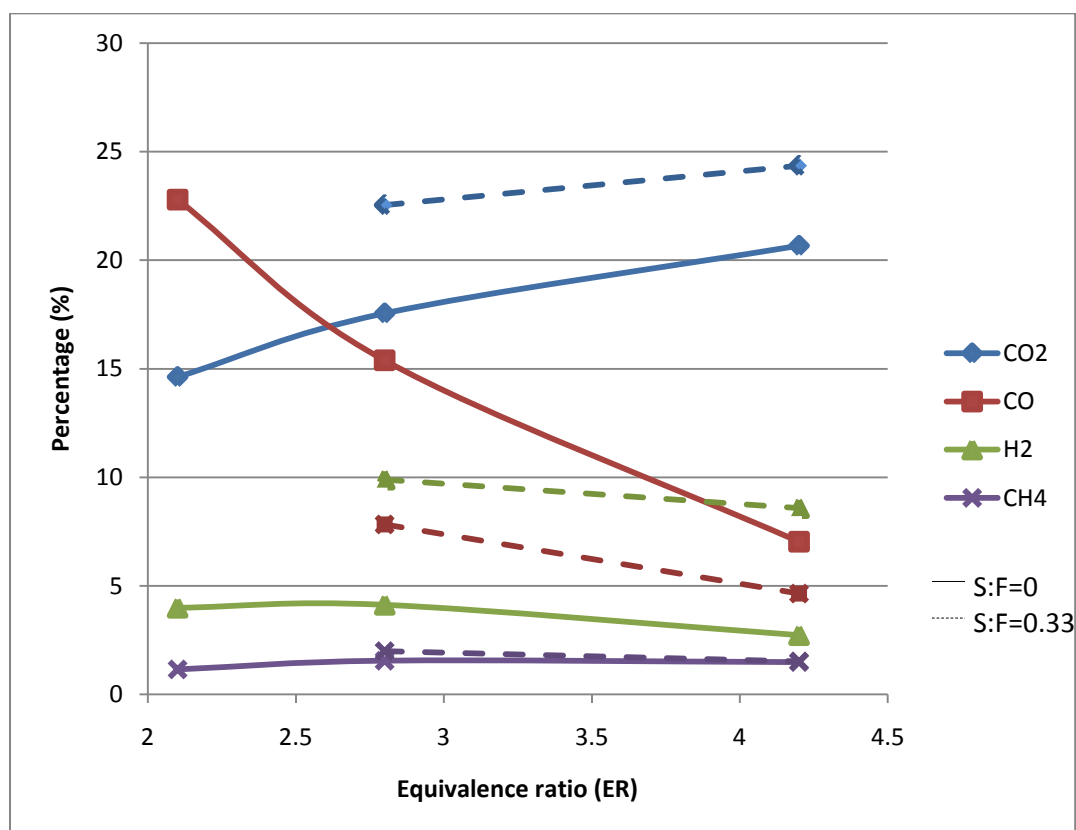


Fig. 24. Gas composition results with and without steam, 21% oxygen.

The gas composition obtained for experiments with 28% oxygen is shown in Fig. 25. From the gas composition obtained it can be seen that CO production is enhanced at lower ER in the absence of steam due to higher  $T_{\text{peak}}$  at lower ER. However with increase in ER, i.e. at ER=4.2, the amount of carbon monoxide is lesser possibly due to the water gas shift reaction.

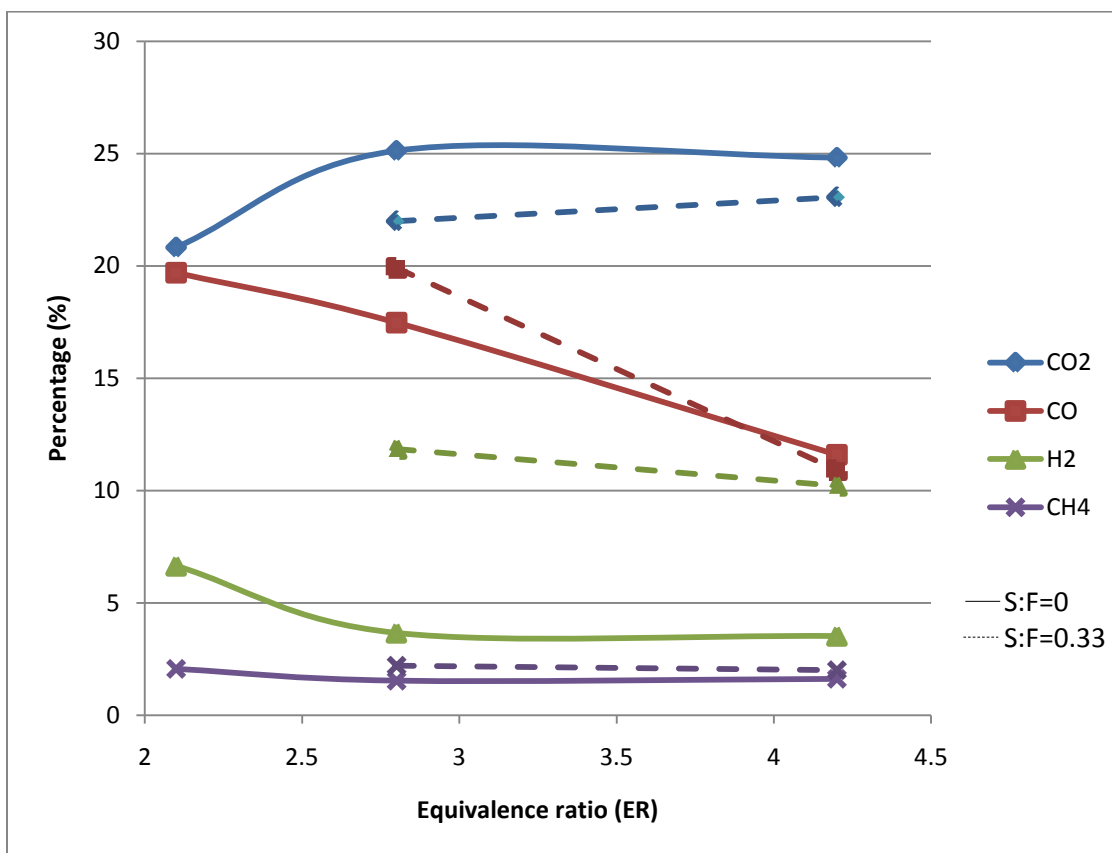


Fig. 25. Gas composition results with and without steam, 28% oxygen.

### 5.5.2.3 Effect of CO<sub>2</sub>:O<sub>2</sub>

The composition of the gases obtained for the gasification with carbon dioxide was also measured using the Thermo ProLab mass spectrometer. Fig. 26 and Fig. 27 show the comparison between the gas composition at 21% O<sub>2</sub> obtained for the gasification with air and carbon dioxide at ER=4.2. Since carbon dioxide replaces nitrogen in the air the gases produced during gasification has a higher percentage of carbon dioxide which possibly includes carbon dioxide produced during gasification as well as the carbon dioxide coming in as the gasifying medium. Also, the heating value of the gases produced using carbon dioxide as the gasifying medium was higher when compared to that of air gasification having nitrogen.

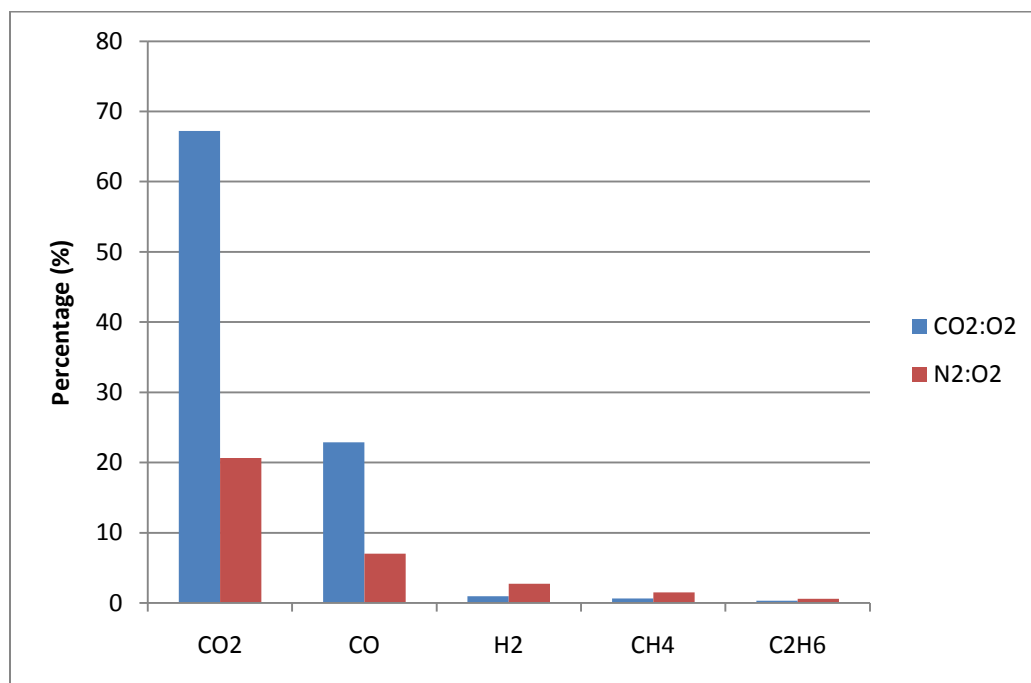


Fig. 26. Gas composition, 21% oxygen, ER=4.2, S:F=0.

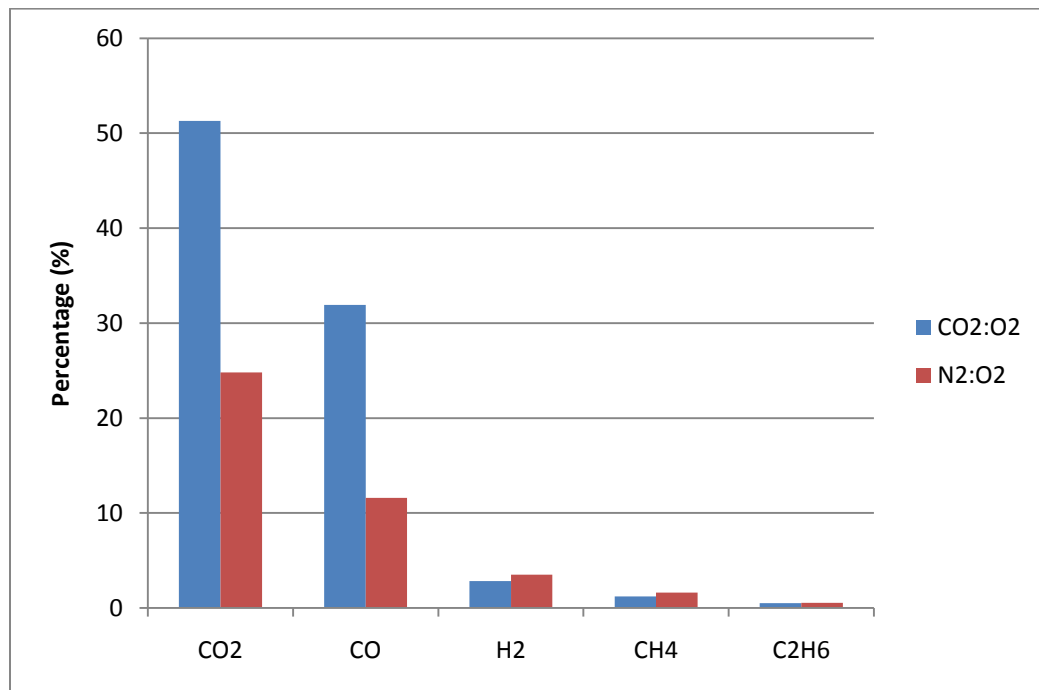


Fig. 27. Gas composition, 28% oxygen, ER=4.2, S:F=0.

This is due to higher CO. Even enriched oxygen gasification with carbon dioxide yielded gases with higher HHV than enriched air gasification having nitrogen.

Use of carbon dioxide has resulted in a higher yield of carbon monoxide. This may be partly due to the reactions as in reaction Eq. (1) and reaction Eq. (3). However Eq. (3) is endothermic. But in the presence of enriched oxygen, higher oxygen concentration may result in the formation of a higher amount of carbon monoxide and carbon dioxide according to Eq. (1) and Eq. (2).

### 5.5.3 Heating value of syngas

The most important factor which needs to be studied is the heating value of the resulting gas mixture.

#### 5.5.3.1 Effect of oxygen percentage

Fig. 28 shows the heating value for the gases produced using enriched air mixtures at ER=2.1 in the absence of steam. The higher heating value (HHV) for this case is calculated on mass basis. It can be observed that the HHV increases with increase in oxygen concentration in the incoming gasification medium within the reactor. The heating value of the nitrogen free gas is much higher when compared to the gas mixture having nitrogen.

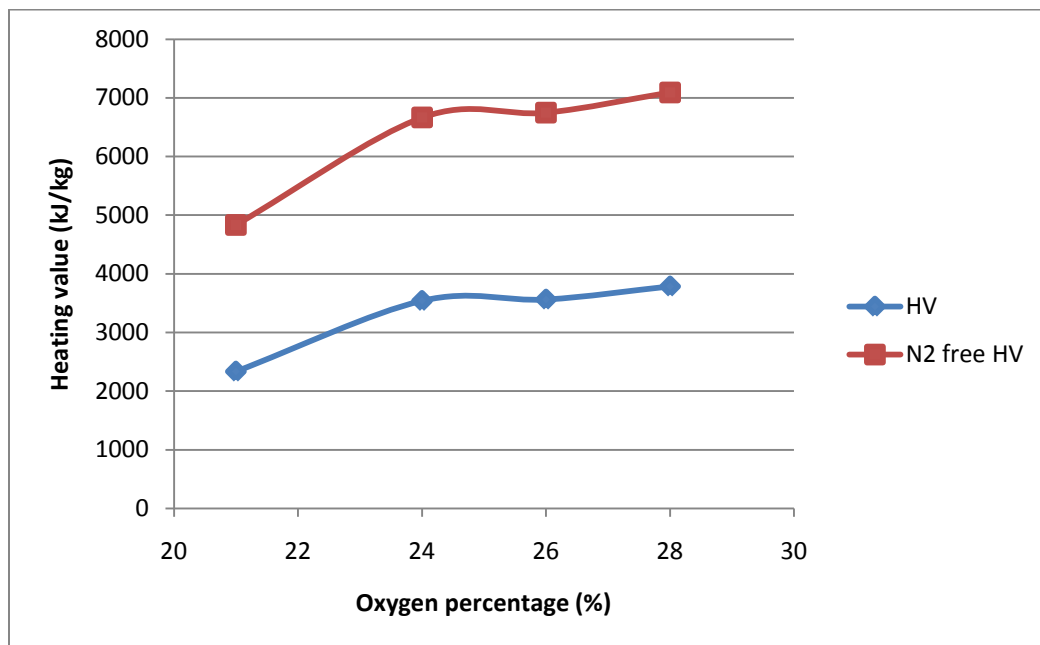


Fig. 28. Heating value of the gas mixture, ER=2.1, S:F=0.



### 5.5.3.2 Effect of ER and S:F

Variation of HHV with ER with and without the presence of steam for the case of air and enriched air mixtures is shown below in Fig. 29. From the figure it is evident that the enriched-air medium results in gas with higher HHV. Since, the amount of hydrogen produced increases in the presence of steam, but the HHV based on mass is less even with  $H_2$  due to lower molecular weight of  $H_2$ . This can be seen in Fig. 30 where the HHV is on mass basis. For both air gasification and enriched-air gasification, we observe a decrease in HHV with ER. Limited ER were studied because of time constraints.

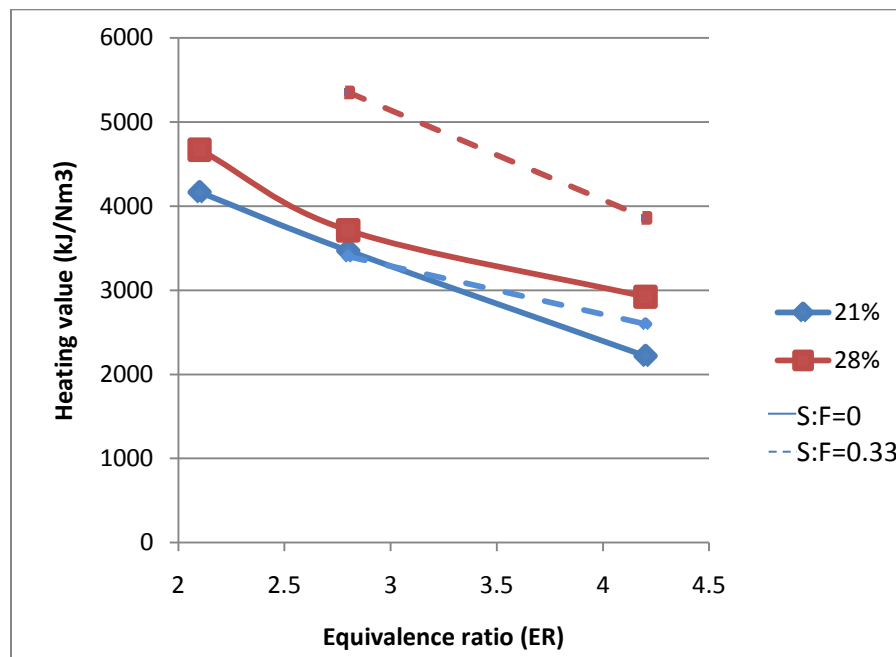


Fig. 29. Heating value vs equivalence ratio (volume basis).

We can see that HHV on a volume basis for enriched air gasification with steam is higher than that of air gasification. From Fig. 30, we can observe that the HHV decreases with increasing ER for enriched air gasification. The same trend was observed for experiments involving steam.

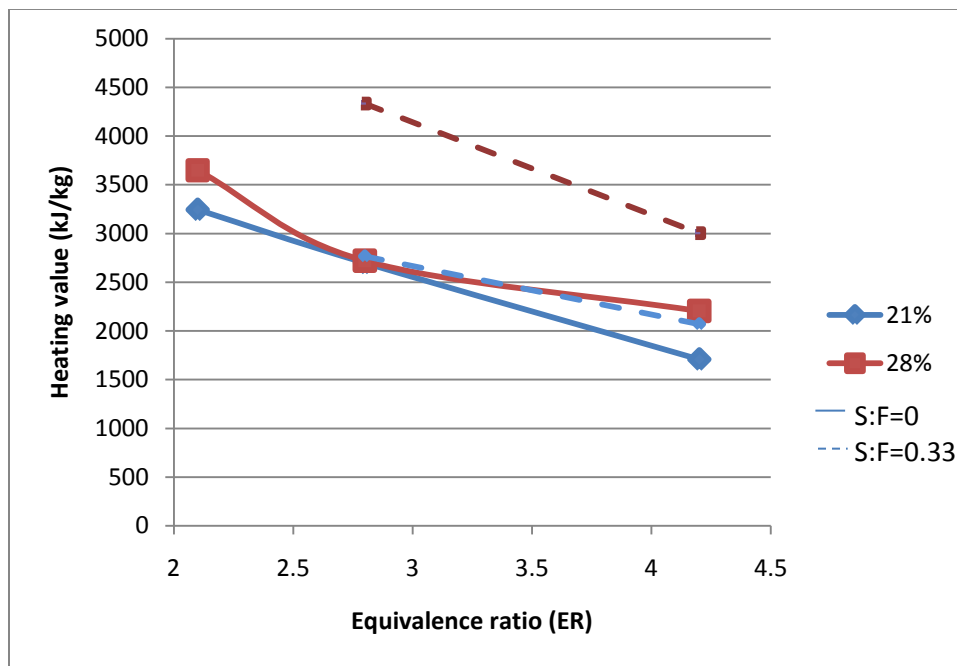


Fig. 30. Heating value vs equivalence ratio (mass basis).

Though the heating value was expected to increase with increase in ER, a decreasing trend was observed for both enriched and air gasification. However Gerardo et al. [9] observed a slight increase in heating value with increase in ER for his experiments with LAPCDB using air and steam as the gasification medium. Though the same fuel was used in this study, the only reason which can be attributed for this

decreasing trend is higher amount of tar having heavier hydrocarbons will be collected at higher ER. Hence the gases have lower HHV.

### 5.5.3.3 Effect of CO<sub>2</sub>:O<sub>2</sub>

The gases produced while using carbon dioxide-oxygen mixture as the gasification medium had higher percentage of carbon monoxide. Higher production of carbon monoxide may be due to higher concentration of carbon dioxide available for reaction by the Boudouard reaction (Eq. (3)). Hence the heating value of the resulting gas mixture is higher than those obtained using air as gasification medium (Fig. 31).

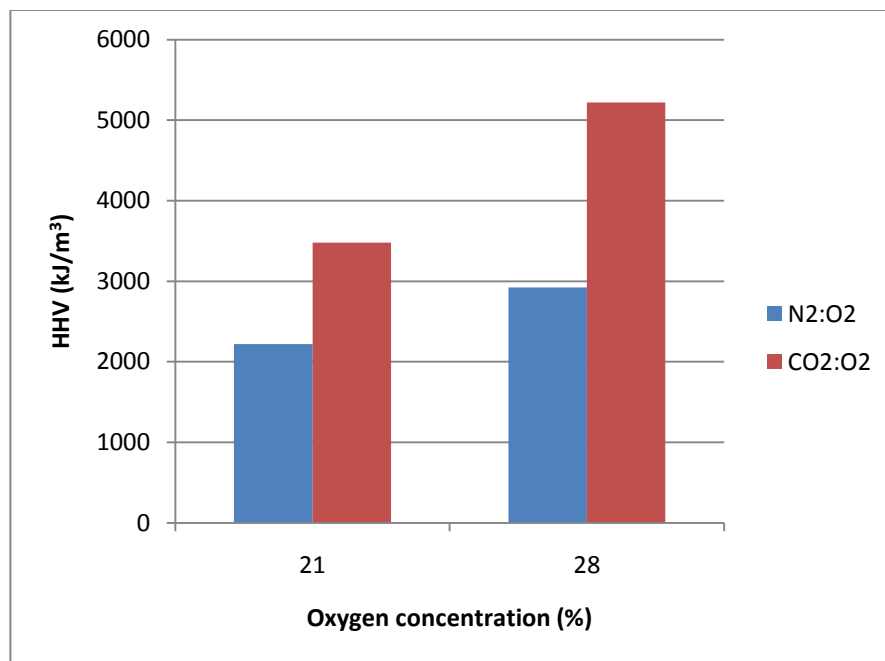


Fig. 31. Heating value of the gases obtained using CO<sub>2</sub>:O<sub>2</sub>.

## 5.6 Char conversion with enriched air

In order to determine the char conversion efficiency while using enriched air, the ash produced during the experiments were collected and were analyzed. Thermolyne benchtop muffle furnace was used to measure the percentage of combustibles left over in the ash removed during gasification. Ash samples which were used for the tests were removed from the bottom of the gasifier during the experiments. From the tests, it was observed that the percentage of combustibles left over in the ash was higher for the experiments using air having 21% oxygen as the gasifying medium. It can be seen from Table 5 that when enriched air having higher oxygen percentages was used, the percentage of combustibles left over in the ash came down by half.

Table 5  
Ash test to determine the combustibles.

<b>Experimental Condition used</b>	<b>Percentage of combustibles (%)</b>
ER=4.2, SF=0, air having 21% oxygen	8.43
ER=4.2, SF=0, air having 28% oxygen	4.64

From these tests it was determined that enriched air mixtures result in better char conversion to gases.

## 5.7 Ash tracer method

From the amount of combustibles left over in the ash, we can calculate the fuel gasified fraction using Ash tracer method [1]:

$$\text{Gasified fraction, } f_g = \frac{\left(\frac{1}{A_0}\right) - \frac{1}{A}}{\frac{1}{A_0} - 1} = \frac{A - A_0}{\{A(1 - A_0)\}} \quad (13)$$

where, A is the fraction of ash in a dry sample after gasification and  $A_0$  is the initial fraction of ash on dry basis. Using this, the amount of combustibles gasified for the case of 21% oxygen at ER=4.2 is 97.19% and 98.52% for enriched air gasification having 28% oxygen at ER=4.2 in the absence of steam.

### 5.8 Nitrogen tracer method

Nitrogen tracer method was developed to determine the heat based gasification efficiency from the percentage of nitrogen in the gases produced during gasification. The major assumption used in this method is that no nitrogen comes out from the fuel during gasification and all the nitrogen in the gas mixture comes from the nitrogen in air used as the gasification medium. It is also assumed that nitrogen in biomass is released as HCN and  $\text{NH}_3$ . From the concentration of nitrogen in the gases produced and the total amount of nitrogen entering the reactor along with air, the total dry moles of gas produced during gasification can be estimated using the following formula.

$$\text{N}_2(\text{Volume \%}) = \frac{\text{N}_2 \frac{\text{kmole}}{\text{hr}}}{\text{dry gas moles}} \quad (14)$$

From the dry gas moles, gasification efficiency based on heating value of gas can be obtained using the formula below.

$$\eta_{\text{gas}} = \frac{m_{\text{gas}} * \text{HHV}_{\text{gas mix}}}{m_f * \text{HHV}_{\text{ARfuel}}} \quad (15)$$

From the nitrogen tracer method, it was observed that the total mass of gases produced decreases with increase in ER because of decrease in the amount of gasification medium going into the reactor and due to higher tar production at higher ER. Heat based gasification efficiency ( $\eta_{\text{gas}}$ ) depends on the mass of gas produced,. Hence at higher ER,  $\eta_{\text{gas}}$  is low. From the calculations, it was obtained that  $\eta_{\text{gas}}$  at ER = 2.1 was 73% for air having 21% oxygen and it decreased to 17.33% at ER=4.2. For enriched air gasification having 28% oxygen,  $\eta_{\text{gas}}$  decreased from 66% at ER=2.1 to 18% for ER=4.2.

A sample calculation for determination of  $\eta_{\text{gas}}$  is presented in Appendix D.

## 6. SUMMARY AND CONCLUSION

Experimental studies have been performed on low-ash, partially composted dairy biomass in an adiabatic, fixed-bed gasifier using different gasifying mediums such as air, enriched air having higher oxygen percentage in the presence and absence of steam and also with carbon dioxide-oxygen mixture. From the current studies the following conclusions can be drawn:

- a. Lower ER and higher oxygen percentage in the gasifying medium results in higher peak temperature within the bed which can lead to ash melting and fouling. This hinders normal diffusion of the gasifying medium within the bed and in turn makes a steady temperature distribution impossible and hence there exists a lower limit on ER and upper limit on oxygen percentage (28%).
- b. Fuels with very low particle size of the order of 250 micron may not be suitable for gasification in a fixed-bed facility. Since they cause fuel entrainment within the reactor without undergoing gasification, they result in poor gasification and unsteady conditions within the bed.
- c. The peak temperature obtained for enriched-air gasification is higher when compared to that of air gasification, and the values obtained were much closer to the values predicted using B number calculations. (Eq. 11). When oxygen percentage increased from 21% to 28%, the peak temperature increased from  $988^{\circ}\text{C}$  to  $1192^{\circ}\text{C}$  at  $\text{ER}=2.1$  in the absence of steam.

- d. In the presence of steam, the peak temperature generally decreases as expected for most of the cases due to higher specific heat of steam (2 kJ/kg K for steam when compared to air which has a specific heat of 1.01 kJ/kg K) and endothermic steam reforming reaction. This is expected to control the bed temperature below the ash melting temperature. Also Gerardo et al [9] observed an increase in HHV of the gases produced with increase in steam-fuel ratio due to increased hydrogen production by the water gas shift reaction (HHV increased from 4115 to 4793 kJ/Nm<sup>3</sup> for increase in steam-fuel ratio at ER=3.18).
- e. The peak temperature values decreased from 988<sup>0</sup>C to 741<sup>0</sup>C with an increase in ER from 2.1 to 4.2 for the case of air gasification with 21% oxygen. The same trend was observed for enriched air gasification as well.
- f. There is more likelihood of formation of CO<sub>2</sub> at higher oxygen concentration.
- g. The heating value of the gases produced decreases with increase in ER for both air and enriched air gasification mostly due to higher tar production at higher ER. At a fixed ER=2.1, the HHV of the gases increased from 4.2 MJ/Nm<sup>3</sup> to 4.6 MJ/Nm<sup>3</sup> with increase in oxygen concentration (enriched air) from 21% to 28% in the gasification medium.
- h. Oxy fuel gasification in the presence of carbon dioxide instead of nitrogen can be used to get lower peak temperatures even with increased oxygen concentration within the reactor owing to the higher specific heat of carbon dioxide when compared to that of nitrogen. Also, the carbon dioxide produced during gasification can be separated and re-circulated thereby reducing the emission of



carbon dioxide into the environment. The CO<sub>2</sub> separation can lead to a higher heating value for the gases produced.

- i. The heating value of the gases produced while using a carbon dioxide-oxygen mixture as the gasifying medium is higher than the enriched-air gasification. Though DB is a low quality fuel which produces gas with lower HHV when compared to wood gasification, use of CO<sub>2</sub>:O<sub>2</sub> mixture with 28% oxygen results in production of gases with HHV (5.22 MJ/Nm<sup>3</sup>) comparable to wood gasification using air (5.56 MJ/Nm<sup>3</sup> [12]). Further studies should be carried out for oxy-fuel gasification at different ER using different oxygen concentrations for different fuels with lower ash percentage.
- j. The heating value of the gases also increases if carbon dioxide is sequestered from the gas mixture. The resulting gas mixture after CO<sub>2</sub> sequestration has a heating value which is 40% the heating value of natural gas in volume basis.
- k. The char conversion rate increases with an increase in oxygen percentage in the incoming gasifying medium.
- l. Heat-based gasification efficiency decreases with an increase in equivalence ratio because of the decrease in gas production. It decreased from 66% to 18% for an increase in ER from 2.1 to 4.2 for enriched oxygen gasification having 28% oxygen.

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## APPENDIX A

## GASIFICATION OF HAMMER MILLED LAPCDB

Gasification of hammer milled LAPCDB resulted in very poor temperature profiles and poor gas composition with higher percentages of oxygen. Very low particle size of SMD 0.2 mm makes the particle to be entrained within the reactor. This result in poor gasification and most of the smaller particles come out without undergoing any reactions and hence the gases analyzed has higher amount of oxygen. The variation of temperature profile with time is shown in Fig. 32.

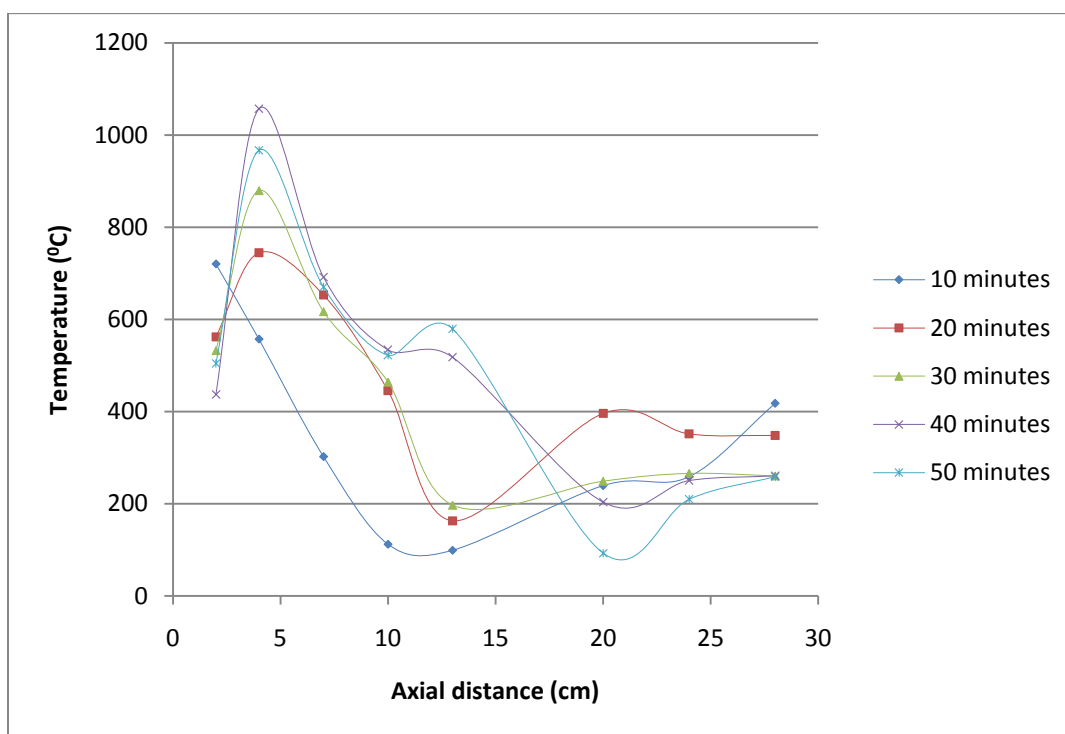


Fig. 32. Temperature profile variation, ER=1.3, 25% oxygen.

Variation of gas composition with time is shown in Fig. 33. Even when a steady temperature distribution is achieved within the bed, the gas composition was not steady and was varying with a standard deviation of around 5%.

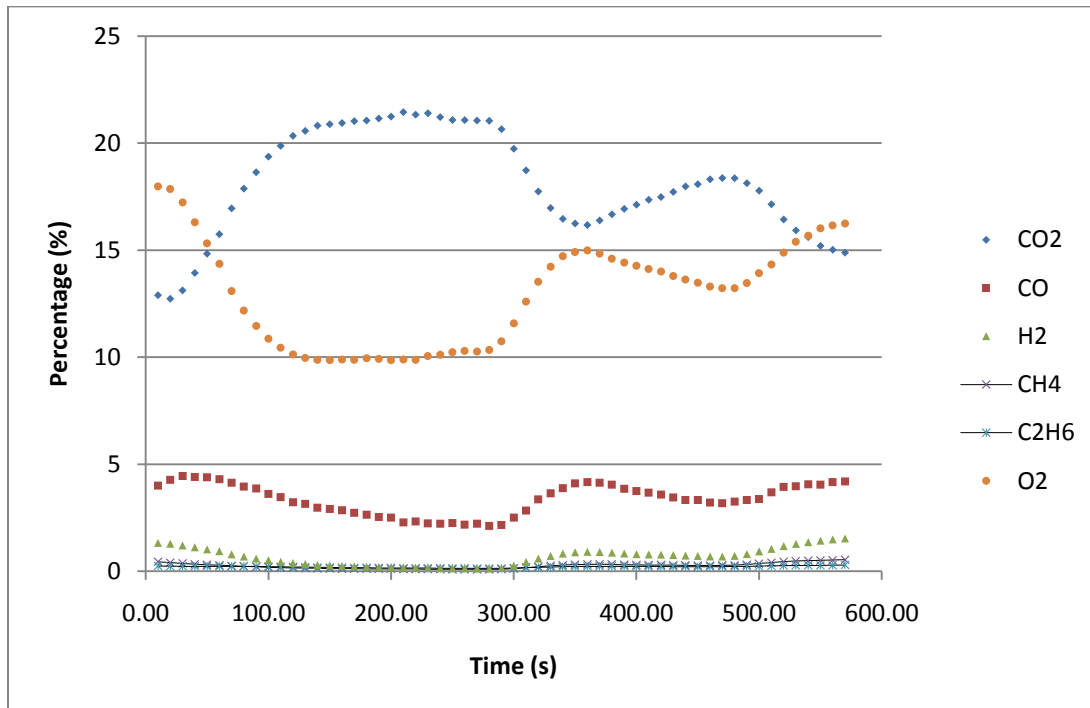


Fig. 33. Gas composition variation with time, ER=1.3, 25% oxygen.

Variation in the fuel color was also observed due to tar condensation at lower temperatures in the drying zone in reactor. It can be seen from Fig. 34 that the fuel gets darker and moister in the drying zone (left) than the raw fuel which is fed into the reactor (right).



Fig. 34. Fuel color variation as it enters the reactor.

Considering these reasons, hammer milled LAPCDB was replaced by sep-sol LAPCDB which has considerably larger particle size.

## APPENDIX B

## MASS SPECTROMETER CALIBRATION

Thermo scientific Prolab Mass Spectrometer was used to determine the composition of the gases produced during gasification. Before taking measurements using the mass spectrometer, it has to be calibrated using gases of known composition. Gas cylinders were acquired and the same calibration procedures used by Gerardo et al. [9] was followed with some minor modifications. Details on the gas cylinders used for calibration is shown below in Table 6. The major problem which has been identified with the mass spectrometer is the filaments which provide the necessary charge to ionize the atoms. A filament set has twin filaments in which we can utilize the other filament once one filament goes off. They should be replaced once in every 4 months.

Table 6  
Calibration mixtures used for MS, adapted from [9].

Gas	Calibration Mixtures								
	1	2	3	4	5	6	7	8	9
CO	15% L			30% FS					
H <sub>2</sub>	15% L	20% S							
C <sub>2</sub> H <sub>6</sub>	5% L						1% FS		
CH <sub>4</sub>	5% L				1% FS				
CO <sub>2</sub>	15% L		0.04%					20% FS	
NO <sub>2</sub>	5% L					5% FS			
N <sub>2</sub>	40% L		78.08% FS						
O <sub>2</sub>			20.95% FS						
He									100%
Ar		Balance	0.93%	Balance	Balance	Balance	Balance	Balance	



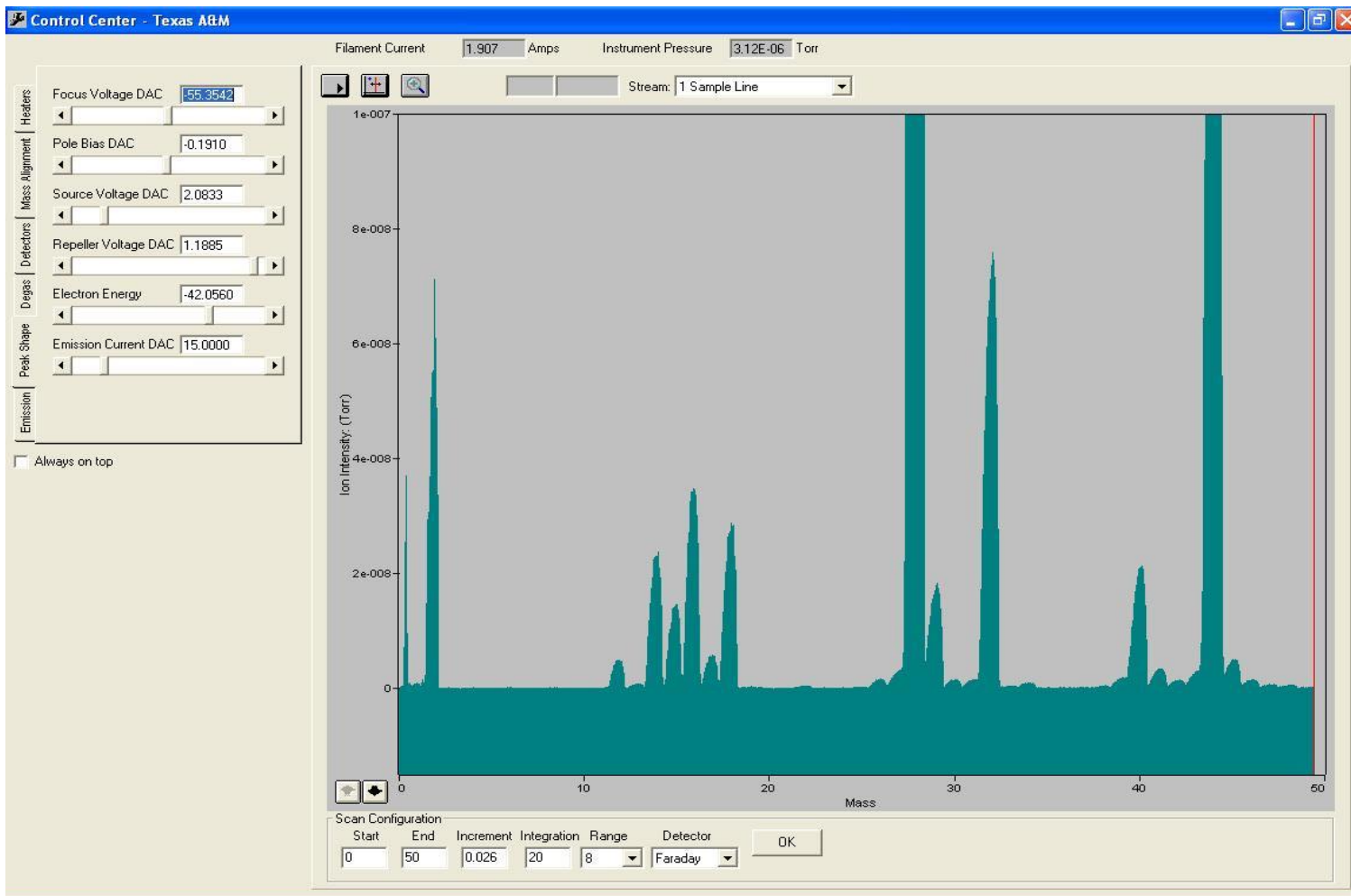


Fig. 35. Manual scan using MS, 21% oxygen, ER=4.2, S:F=0.33.

Since it has been more than 3 years after the purchase of mass spectrometer, a complete check was performed and filaments, lubricant reservoir for the turbomolecular pump and the oil for the turbo pump were replaced. The MS was calibrated and used for measuring the gas composition. Manual scans were performed on the gas samples to determine the different gases produced by identifying the peaks. These scans were useful to determine the amount of ammonia and hydrogen cyanide produced during gasification and pyrolysis of biomass and one of such scans is shown in Fig. 35. We can see peaks at molecular weight 17 which is ammonia and molecular weight 27 which is hydrogen cyanide. From the peak heights, we can determine the ion intensity.

It was observed that for the pyrolysis of coal 60% of nitrogen in the fuel becomes HCN, 30% becomes  $\text{NH}_3$  and the rest leaves as nitrogen. However for the pyrolysis of biomass, 60% of nitrogen in the fuel becomes  $\text{NH}_3$ , 30% becomes HCN and the rest leaves as nitrogen. From Fig. 35, we can observe higher peak for  $\text{NH}_3$  indicating that higher amount of ammonia is produced when compared to that of HCN.

We can also observe a small peak at amu 34 indicating the presence of hydrogen sulphide,  $\text{H}_2\text{S}$ . Though LAPCDB has a very low percentage of sulphur, the sulphur gets converted to  $\text{H}_2\text{S}$ .

## APPENDIX C

## ER CALCULATIONS FOR ENRICHED AIR

Equivalence ratio for the gasification experiments are calculated using Eq. 9. For the same ER enriched air mixtures have a lower mass flow because of higher oxygen concentration and lower nitrogen from air. The amount of air flow and oxygen flow are calculated according to the following equations.

$$x_{O_2} = \left( \frac{N_{O_2} + N_{air} * 0.21}{N_{O_2} + N_{air}} \right) \quad (16)$$

$$N_{O_2} = N_{O_2, total} - N_{air} * 0.21 \quad (17)$$

$$x_{O_2} (N_{O_2, total} + N_{air} * 0.79) = N_{O_2, total} \quad (18)$$

$$N_{air} = \left\{ \frac{N_{O_2, total} (1 - x_{O_2})}{0.79 * x_{O_2}} \right\} \quad (19)$$

If any two of the variables is known, we can calculate the value of the remaining variable using one of the above equations. The values are calculated in volume basis. For complete combustion of LAPCDB, the stoichiometric air fuel ratio is calculated to be 126 standard cubic feet per hour per kg of as received fuel. Using this value in Eq. 9, the ER values are calculated for different oxygen and air flows for enriched air gasification experiments. The different flows of oxygen and air calculated are shown in Table 1.

APPENDIX D  
NITROGEN TRACER METHOD

A sample calculation for determining the heat based gasification efficiency using the nitrogen concentration in the gas mixture is presented here. For ER=2.1, 21% oxygen, S:F=0, 60 SCFH of air (47.4 SCFH of nitrogen and the remaining being oxygen) was used for gasifying 1kg of fuel. From the experiments it was observed that the gas produced during gasification had 55.54% nitrogen in dry mole basis. Using Eq. (14), the dry moles of total gas produced can be estimated.

$$\begin{aligned} \text{dry gas moles} &= \frac{N_2 \frac{\text{kmole}}{\text{hr}}}{N_2(\text{Volume } \%)} \\ &= \frac{0.0599}{0.55} \\ &= 0.1078 \text{ kmol/hr} . \end{aligned}$$

Molecular weight of the gas mixture can be calculated using the mole fraction of different gases in the mixture. For this case the molecular weight of the gas mixture was 28.78 kg/kmol and the heating value of the mixture was 3245.08 kJ/kg. The heating value of the as received (AR) LAPCDB sep sol was 13698.1 kJ/kg. So, the heat based gasification efficiency is calculated using Eq. (15)

$$\begin{aligned} \eta_{\text{gas}} &= \frac{m_{\text{gas}} \cdot \text{HHV}_{\text{gas mix}}}{m_f \cdot \text{HHV}_{\text{ARfuel}}} \\ &= \frac{3.103 \cdot 3245.08}{1 \cdot 13698.1} \\ &= 73.53\% \end{aligned}$$

Mass balance can also be done using the nitrogen tracer method. Considering 1 kg/hr of AR LAPCDB sep-sol is used as the fuel at ER=4.2, 21% oxygen and S:F=0.

Amount of nitrogen from air = 23.7 SCFH = 0.8391 kg/hr

Amount of oxygen from air = 6.3 SCFH = 0.255 kg/hr

Amount of dry ash free fuel in =  $1 - 0.15(\text{moisture}) - 0.25(\text{ash}) = 0.6 \text{ kg/hr}$

Concentration of nitrogen in the gas produced = 62.73 %

From nitrogen tracer method, dry gas moles produced = 0.05 kmol = 1.389 kg/hr

(Molecular weight of the gas mixture produced by gasification = 29.1 kg/kmol)

By mass balance, the amount of tar produced can be estimated as = 0.305 kg/hr

This calculation does not include the moisture in the fuel. Hence nitrogen tracer method can also be used to do mass balance analysis for gasification.

## APPENDIX E

### UNCERTAINTY ANALYSIS

The data collected using mass spectrometer, the thermocouples and the air flow meter should be studied for its uncertainty. The mass spectrometer was calibrated once in 72 hours using gas cylinders of known composition for linearity, sensitivity and overlapping [9]. The calibration was checked by analyzing the gases from a cylinder having known compositions. However the gas composition measured has some uncertainty. Table 7 shows the gas composition uncertainty for gasification of LAPCDB. The uncertainty of each gas is calculated as the ratio of the standard deviation to the average value measured. From Table 7 it can be seen that the value fluctuates from 5% to 15% of the average value measured.

Table 7  
Gas data uncertainty (%).

Gases	Maximum	Minimum	Average
Carbon dioxide	16.78	2.10	9.44
Carbon monoxide	19.55	2.24	10.90
Hydrogen	22.28	2.20	12.24
Methane	22.27	1.16	11.72
Ethane	19.93	1.68	10.81
Nitrogen	7.40	1.51	4.46

Table 8 shows the uncertainty calculated for the temperature data collected at different heights along the axis of the gasifier. It can be observed that the uncertainties of the temperature data is much lower than that of the gas data. Apart from the temperature data uncertainty, the instrument uncertainty is  $\pm 1.5$  °C.

Table 8  
Temperature data uncertainty (%).

Distance (cm)	Maximum	Minimum	Average
2	0.144	0.140	0.142
4	0.129	0.144	0.137
7	0.149	0.180	0.165
10	0.209	0.150	0.180
13	0.078	0.397	0.238
20	1.159	0.912	1.036
24	0.930	0.696	0.813

The uncertainty in the equivalence ratio increases with decrease in the amount of gasification medium sent in using the Dwyer variable area RMB series mass flowmeter, which has an accuracy of  $\pm 3\%$ . From the uncertainty calculations, it was observed that the uncertainty in ER increase from 8.9% for ER=2.1 to 17.9% for ER=4.2, using the method by Kline and McClintock [25].

## APPENDIX F

## SLAGGING AND FOULING POTENTIAL

We can calculate the values for slagging and fouling potential using the formula from Maglinao et al [23]. The analysis of the LAPCDB ash is shown in Table 9.

Table 9  
DB ash composition, adapted from [9].

<b>Compound</b>	<b>Sep.DB Solid</b>
Silicon, SiO <sub>2</sub>	35.13
Aluminum, Al <sub>2</sub> O <sub>3</sub>	6.02
Titanium, TiO <sub>2</sub>	0.21
Iron, Fe <sub>2</sub> O <sub>3</sub>	2.67
Calcium, CaO	17.60
Magnesium, MgO	6.12
Sodium, Na <sub>2</sub> O	1.96
Potassium, K <sub>2</sub> O	6.85
Phosphorus, P <sub>2</sub> O <sub>5</sub>	7.21
Sulfur, SO <sub>3</sub>	2.55
Chlorine, Cl	0.32
Carbon dioxide, CO <sub>2</sub>	2.15
Total ash analysis	88.79

Basic constituents in ash: Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, Na<sub>2</sub>O, K<sub>2</sub>O

Acid constituents in ash: SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>

Slagging potential = (Base/acid) \* sulphur % = (35.2/41.36) \* 0.417 = 0.35

Fouling potential = (Base/acid) \* Na<sub>2</sub>O % = (35.2/41.36) \* 1.96 = 1.67



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